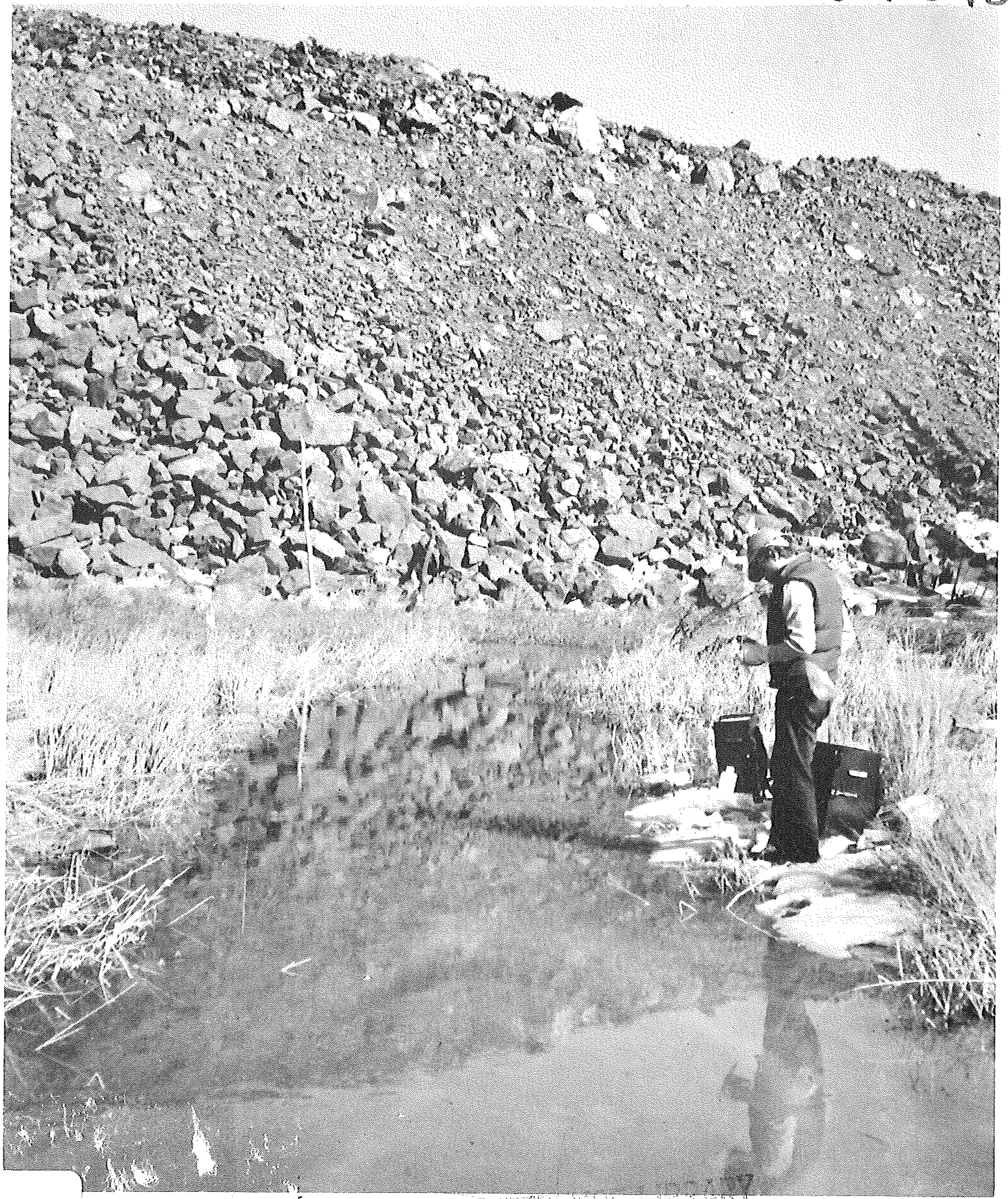
ENVIRONMENTAL LEACHING OF DULUTH GABBRO
RATORY AND FIELD CONDITIONS:
OXIDATIVE DISSOLUTION OF METAL SULFIDE AND SILICATE MINERALS



nnesota Department of Natural Resoures
Division of Minerals
1980

Environmental Leaching of Duluth Gabbro under Laboratory and Field Conditions:

Oxidative Dissolution of Metal Sulfide and Silicate Minerals

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Division of Minerals

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FOREWORD

This report is essentially in final form although certain typographical problems still exist. Rather than delay the release of this report any longer, it is being issued in its present form.

Addendum

In the process of compiling the references for this report three references were inadvertently omitted. A large portion of the material presented in this report has been taken from the thesis of Kim Lapakko, which is presently in the process of being completed. A report by Hoffmann et al., (1979) and a literature review by Eisenreich et al., (1976) were also omitted. The omissions are listed below:

Lapakko, K.A., M.S. Thesis, University of Minnesota Department of Civil and Mineral Engineering - In progress.

Hoffmann, M.R., Eisenreich, S.J., Lapakko, K. 1979. Kinetics and mechanisms of the oxidative dissolution of metal sulfide minerals found in Duluth gabbro ore. Report to Minnesota Environmental Quality Board Regional Copper-Nickel Study.

Eisenreich, S.J., Hoffmann, M.R., Iwasaki, I., Bydalek, T.J. 1976. Metal sulfide leaching potential in the Duluth gabbro complex. Report to the Minnesota Environmental Quality Board Regional Copper-Nickel Study.

Acknowledgments

The authors wish to thank all those who helped make this report a reality. Special thanks goes to the staff of the Regional Copper-Nickel Leaching/Pathways program:

Bruce Johnson, chemist in charge of field operations, Ely
Pete Otterson, hydrologist, St. Paul
Steve Lampman, laborer, Ely
Teddy Brox, work study student, Ely
Pete Dauer, work study student, Ely

Without their dedication much of the data presented in this report would not exist.

Additional support was obtained from the staff of the Regional Copper-Nickel study; the Minnesota Department of Natural Resources, Division of Minerals; the Environmental Engineering department at the University of Minnesota; the Minnesota Department of Health; Erie Mining Company; Amax Exploration Inc; the U.S. Forest Service and the U.S. Geological Survey. Michael Hoffmann and Steven Eisenreich of the University of Minnesota; Don Ericson, Bill Gothard and Jim Zerbel of the U.S.G.S. in Grand Rapids and Ed Marsolek and John Ramquist of the U.S.F.S. in Ely deserve special mention for their patience and willingness to assist us with our problems both with data collection and analysis.

Additional data analysis support was provided by Martha Hewett, a hydrologist who willfully joined us in mid-stream and our student workers Jean Liang, Gary Hohenstien, and Chris Adams.

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Abstract

Field and laboratory experiments were conducted to examine the leaching potential of Duluth gabbro. Four types of laboratory experiments were conducted to investigate the effect of several factors on the leaching reaction. These factors included particle size and surface area, solid composition, pH, dissolved oxygen, ionic strength, organic compounds and bacteria.

Field studies were conducted at four sites in the study area, to examine leaching under natural conditions. Field data were used to estimate the quality of leachate, such as stockpile runoff and pit water, generated by various components of mining operations.

Release rates for trace metals (copper, nickel, cobalt, zinc); sulfate and some major cations (e.g. calcium) under both laboratory and field conditions were computed and compared.

Acid production, although not prevalent, was observed under certain laboratory and field conditions. Net acid production is discussed in respect to these observations.

Additional information on trace metal transport and removal in natural systems will be presented in future reports.

Summary

I. Mechanism of Metal Sulfide Leaching

A. Leaching is a two step process involving:

1. The dissolution of the metal sulfide, and
2. The transport of the metal from the reaction site.

The net release of metals to the environment is determined by all the factors which affect not only dissolution but also transport.

B. Observations in the laboratory and the field, in conjuction with information from pertinent literature, indicate that three mechanisms appear to operate in the oxidative dissolution of metal sulfides (MeS):

$$MeS + 2O_2 = Me^{2+} + SO_4^{=} \quad (1)$$

$$MeS = Me^{2+} + S^{=} \quad (2)$$

$$MeS + 2H^+ = Me^{2+} + H_2S \quad (3)$$

C. The rate and dominant mechanism for metal sulfide dissolution is dependent upon the chemistry of the individual metal.

D. The reactions subsequent to the metal sulfide dissolution are dependent upon the chemistry of the individual metal.

1. If $Me^{2+} = Cu^{2+}$, the dominant reaction product
   a.) for $pH>6$, is $Cu_2(OH)_2(CO_3)$, and
   b.) for $pH<6$ is Cu^{2+}.

(The pH distinction is approximate.)

2. If $Me^{2+} = Ni^{2+}$, the dominant reaction product is Ni^{2+}
3. If $Me^{2+} = Fe^{2+}$, the major reaction product is apparently FeOOH:

$$Fe^{2+} + \frac{3}{2} H_2O + \tfrac{1}{4}O_2 = FeOOH(s) + 2H^+ \quad (4)$$

E. Information from relevant literature and observations in the laboratory and the field indicate that some trace metals are removed from solution by adsorption onto surfaces such as SiO_2, FeOOH, MnO_2, and TiO_2.

F. The variation in the rate of nickel leaching in batch reactor experiments was described as:

$$\frac{d\ (Ni^{2+})}{dt} = k_1\ A_s^{0.4}\ (H+)^{0.2}\ (O_2)^{0.8}\ (Cit)^{0.3} \qquad (5)$$

for $5 \leq pH \leq 8, 1 \leq O_2 \leq 9.3\ mgl_1$, $1.29 \times 10^{-4}\ \underline{M}$ and $1.29 \times 10^{-3}\ \underline{M}$ citrate, and where A_s is area/1 of solution.

G. The variation in the rate of copper leaching as a function of H^+ was

$$\frac{d\ (Cu^{2+})}{dt} = k_2(H^+)^{0.6} \qquad (6)$$

II. Laboratory Results

A. Batch reactor experiments indicated that trace metal leaching increased with decreasing pH, increasing concentration of complexing organics, increasing availability of oxygen at the metal sulfide surface and increasing surface area. The results are summarized in Table 1.1.

B. Results from the column experiments indicated that sulfate release increased as the sulfide composition of the rock increased. Nickel release increased with increasing nickel sulfide composition, but at a rate greater than that which the increasing composition would suggest. Copper release was controlled by the

Table 1.1 Batch reactor summary:

EXPERIMENT	ROCK TYPE	PARTICLE SIZE	pH EFFECT	SILICATE DISSOLUTION	SULFIDE DISSOLUTION	CU-NI MOBILITY
<u>Solid Phase</u>						
Mineralized rock(Min)$^+$ vs. Unmineralized (Unmin)$^+$	Both	d<0.074mm	Decrease w/ increased mineralization	Greater Ca,Mg release with unmin.	Increased mineralization increased SO_4 released	Drop in pH increases mobility
Loading	μnmin	d<0.074	Increased w/ loading	Increased with loading	Increased with loading	Decreased with loading
Size	Min	d<0.074 0.074<d<0.42 0.42 <d<0.84 0.84 <d<2.38	Decreased w/ size	Increased w/ decreasing size	Increased w/ decreasing size	Increased w/ decreasing size (pH effect)
<u>Aqueous phase</u>						
pH	Unmin Min	d<0.074mm d<0.074mm	------ ------	Increased w/ decreasing pH	Increased w/ decreasing pH	Increased w/ decreasing pH
Dissolved oxygen	Min	d<0.074mm	Decreasing w/ increasing D.O.	Increased w/ increasing D.O. (pH effect)	Increased w/ increasing D.O.	Increased w/ increasing D.O. (pH effect)
Ionic strength	Min	d<0.074mm	pH controlled	Increased w/ ionic strength	Slight increase w/ ionic strength	No effect detected
Organics citrate	Unmin	d<0.074mm	pH controlled	Increased w/ (Cit)	Increased at high (Cit)	Increased w/ increasing (Cit)
Phtallic acid	Min	d<0.074mm	pH controlled	Slight increase w/ (PHTH)	Decreased w/ increasing (PHTH)	No effect detected
Bog water	Min	d<0.074mm	pH approx. 8	Little effect	Little effect	Enhanced mobility
Groundwater	Min	d<0.074mm	pH approx. 8	Little effect	Little effect	Enhanced mobility

+Composition of Mineralized and Unmineralized samples is given in Table <u>2.6</u> T=17° C D.O. Approx. 9.3 mg/l unless noted.

solution composition and not the composition of the solid phase. Results are summarized in Table 1.2.

C. Results from the environmental leaching test indicated that under acid conditions, the release to solution was related to the solid phase compostion. Release from tailings under neutral pH conditions was small.

D. Preliminary experiments indicated that the presence of sulfide-oxidizing bacteria produced no increase in trace metal leaching.

III. FIELD RESULTS

A. Field leachates were generally characterized by a neutral to slightly basic pH, moderate to high levels of alkalinity and organic carbon, and high concentrations of dissolved solids, sulfate and trace metals.

B. Acid conditions were observed at the U.S. Steel bulk sample site and at one of the six AMAX test piles.

C. Nickel is leached more readily than copper. Nickel: copper ratios in leachate range from 3:1 to 60:1.

D. Trace metal concentrations in leachate collected at the field sites have ranged from 10 - 10,000 times the background concentration found in the streams of the area.

E. Trace metal leaching increased with decreasing pH at stockpiles in the field.

F. Trace metal leaching at stockpiles in the field increased with the amount of water contacting stockpiled material.

Table 1.2 Column experiment summary:

VARIABLE	pH EFFECT	SULFATE LEACHED (sulfide dissolution)	COPPER LEACHED	NICKEL LEACHED	COBALT LEACHED
Composition: Min vs Unmin	None	Greater leaching with mineralized	little effect	significantly greater with mineralized	
Water: rain, surface, and groundwater (RW, SW, GW)	None	GW>RW>SW	SW>GW >RW	GW > SW > RW	GW > SW > RW

GW = synthetic ground water

SW = synthetic surface water

RW = distilled water was used to represent rainwater

Min = Mineralized rock sample
Cu = 1.4%, Ni = .36%, S = 3.92%

Umnin = Unmineralized rock sample
Cu = .24%, Ni = .095% S=1.1%

Particle size; $0.25<d<0.62$ cm

G. Bioassay tests performed on field leachates indicated that under certain conditions the leachate was toxic.

H. Field results are summarized on Table 1.3.

IV. Rates of Release

Release rates calculated from both field and laboratory results span a wide but similar range, due to variable reaction conditions.

V. Acid Generation

A. Acid conditions can result from leaching of Duluth gabbro. Acid conditions were observed in batch reactors, the AMAX FL-5 test stockpile and the U.S. Steel pit.

1. Most acid production is the result of iron sulfide dissolution:

$$\mathrm{FeS} + \frac{5}{2}\mathrm{O_2} + \mathrm{H_2O} = \mathrm{FeOOH} + \mathrm{SO_4^{=}} + 2\mathrm{H^+}$$

2. Most acid consumption results from silicate mineral dissolution:

$$\mathrm{Me^{2+}}\ \text{(silicate)} + z\mathrm{H^+} = \mathrm{Me^{2+}} + \mathrm{H_z^+}\ \text{(silicate)}\ \text{(solid)}$$

B. The potential for acid production increases as the iron sulfide content increases and/or the silicate mineral composition decreases. Preliminary data suggest that acid conditions can occur when the fraction of FeS is greater than 1.6%(0.8% S)

VI. "Model" Waters

Estimates of leachate quality for future mining operations indicate that stockpile runoff and pit water may pose the most significant environmental problems. Release of trace metals from tailings appears to be a secondary concern.

Table 1.3

OBSERVED CONCENTRATIONS; FIELD SITES

CONCENTRATION RANGE IN MG/L

	pH	Cu	Ni	Zn	Co	$SO_4^=$	Cl^-	Flow[a] (cfs)
Erie Waste Rock[1] Stockpile EM-8	6.4-7.7	0.010-0.18	0.386-7.50	0.007-0.17	0.010-0.3	281-2130	21-66	0-5.3
Erie Waste Rock[1] Stockpile, Seep-1	6.3-7.5	0.003-0.329	0.053-12.5	0.037-2.4	0.110-1.0	149-5636	10.2-121.4	0-0.15
Erie Lean Ore[1] Stockpile, Seep-3	6.4-7.9	0.037-1.71	0.42-39.8	<0.05-0.65	0.12-2.40	297-2750	10-70.4	0-0.60
AMAX Stockpiles[2] FL 1-4	6.8-8.1	*0.007-0.200	*0.030-0.700	*0-0.174	*0.001-0.090	85-1700	1-1020	0-0.0036
AMAX Stockpile[3] FL-5	3.5-7.6	*0.020-10.30	*0.445-83.00	*0.036-2.46	*0.045-7.76	700-2000	8-313	0-0.0028
AMAX Stockpile[4] FL-6	7.1-8.1	*0.06-0.29	*0.54-2.42	*0.003-0.120	*0.030-0.39	950-2400	150-607	0-0.0031
U.S. Steel Bulk[5] Sample Site	4.46-6.36	8.7-22.6	11.8-37.4	0.14-0.37	0.710-1.900	99-515	0.90-2.35	Not applicable
Inco Bulk[6] Sample Site	6.42-7.42	0.01-0.888	0.09-11.00	0-0.22	0.016-0.870	350-520	No data	Trickle

1 June 1976 to November 1978
2 April 1977 to November 1978
3 September 1977 to November 1978
4 April 1978 to November 1978
5 March 1977 to August 1977
6 April 1976 to August 1977

All metal values are total unless denoted by * in which case they are filtered

[a] Erie flows are based on instantaneous readings whereas AMAX flows are based on daily volumetric measurements.

INTRODUCTION

Historically, the major water quality problem associated with mining heavy metal sulfides has been the production and release of highly contaminated leachate (Hawley 1972). In general, this leachate tends to be acidic and contains high levels of toxic trace metals. Some examples are shown in Table 2.1. Leaching occurs in tailings basins, stockpiles, and in the mine itself. There is potential for leachate production wherever there is a source of water, oxygen and metal sulfides.

This report summarizes the major results of the leaching studies (both field and laboratory studies) conducted by the Regional Copper Nickel Study during the period July 1, 1976 to September 1977.

Background on the study can be found in the Minnesota Naturalist (Autumn/ Winter, 1976). Detailed information on the copper-nickel resource is available in a report by Listerud and Meineke (1979), while information on the geology and mineralogy of the Duluth gabbro complex can be found in publications by Sims and Morey and Weiblen and Cooper (1977). A review of the literature pertaining to the leaching of metal sulfides was conducted by Eisenreich et al, in 1976, and detailed reports on the laboratory study have also been completed (Eisenreich et al, (1976) (1977), Hoffmann et al, (1978).

Although the Duluth gabbro contains low percentages of sulfides, initial water samples collected near stockpiled gabbro indicated a potential for significant water quality deterioration. The leaching study was a

Table 2.1. (from Eisenreich et al, 1976)

Chemical Characteristics of mine water from proper reference

Characteristic	*New Brunswick from MECo (1972)*		*Ontario-from Hawley (1972a)*			*N.W.T.-from Falk et al (1973)*		
	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 2.1 (cont)

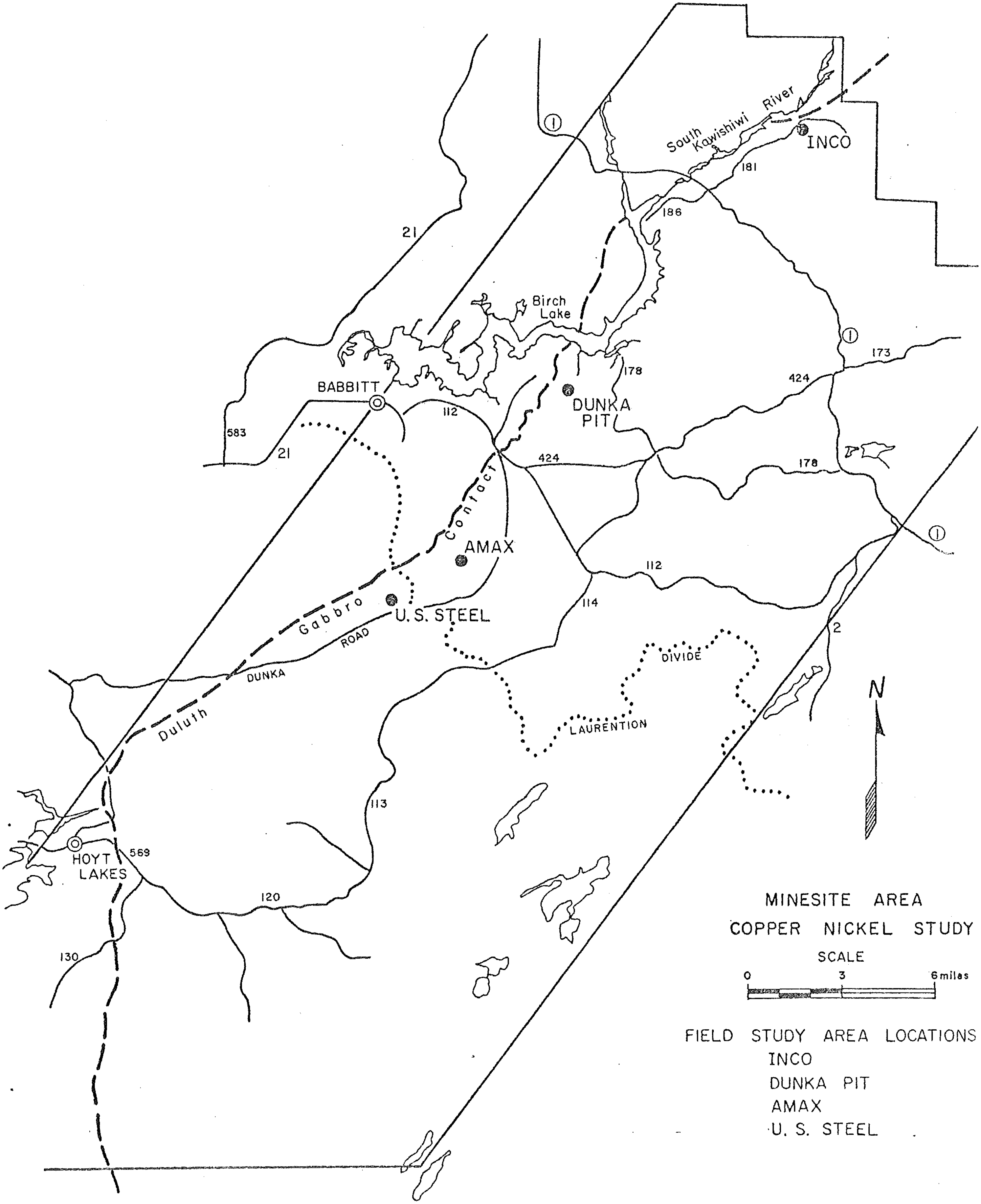
	New Brunswick from MECo (1972)		Ontario-from Hawley (1972a)			N.W.T.-from Falk et al (1973)		
	Brunswick 12 (partial treatment)	Heath Steele	#1	#2	#3	Giant	Echo Bay	Terra
N-Kjeldahl						0	0.97	4.9
N-Nitrate + Nitrite.						0.06	1.3	4.1
Organic carbon	5.5	5.0				40	9	19
C.O.D.	23.8	48.8	50	30				
Av.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

combined laboratory-field study. The overall objectives were to: 1. Determine the rates of release of various contituents; 2. Determine factors controlling release; and 3. Develop leachate models that could be used to predict the types of impacts that might occur in future mining situations. The laboratory program was designed to study the rate of release under controlled conditions and to study the effect of various factors on the release. The goals of the field studies were to measure rates of release under actual field conditions.

A brief discussion of the field areas is given in Table 2.2, and the locations are shown in Fig. 2.1. The only area that approaches full scale operation is at Erie Mining Company's Dunka Pit. This mine is an open pit taconite operation located along the intersection of the Biwabik iron formation and the Duluth gabbro. In order to remove the iron ore, some of the gabbro must be removed and stockpiled. The locations of these piles are shown in Figure 2.2. Approximate compositions and masses are presented in Table 2.3. Although these stockpiles are large, the total amount of gabbro that has been stockpiled in a 10-year period is less than that stockpiled in a 20 x 10^6 mpty open pit mine in <u>one</u> year. (The 20 x 10^6 mtpy open pit was a standard model operation used by the Regional Copper-Nickel Study to assess impacts). The Erie gabbro piles are composed of material $>$ 0.2% Cu, with an average concentration of 0.28%. Material containing much greater than 0.2% copper may also be included in the piles.

Strict segregation of material in any open pit mine is difficult, and high grade material may be present in the waste piles. As will be discussed later, rates of release obtained from these piles are

Figure 2.1



MINESITE AREA
COPPER NICKEL STUDY

FIELD STUDY AREA LOCATIONS
INCO
DUNKA PIT
AMAX
U. S. STEEL

Figure 2.2

DUNKA PIT STUDY

STOCKPILE AND SAMPLING SITE LOCATIONS

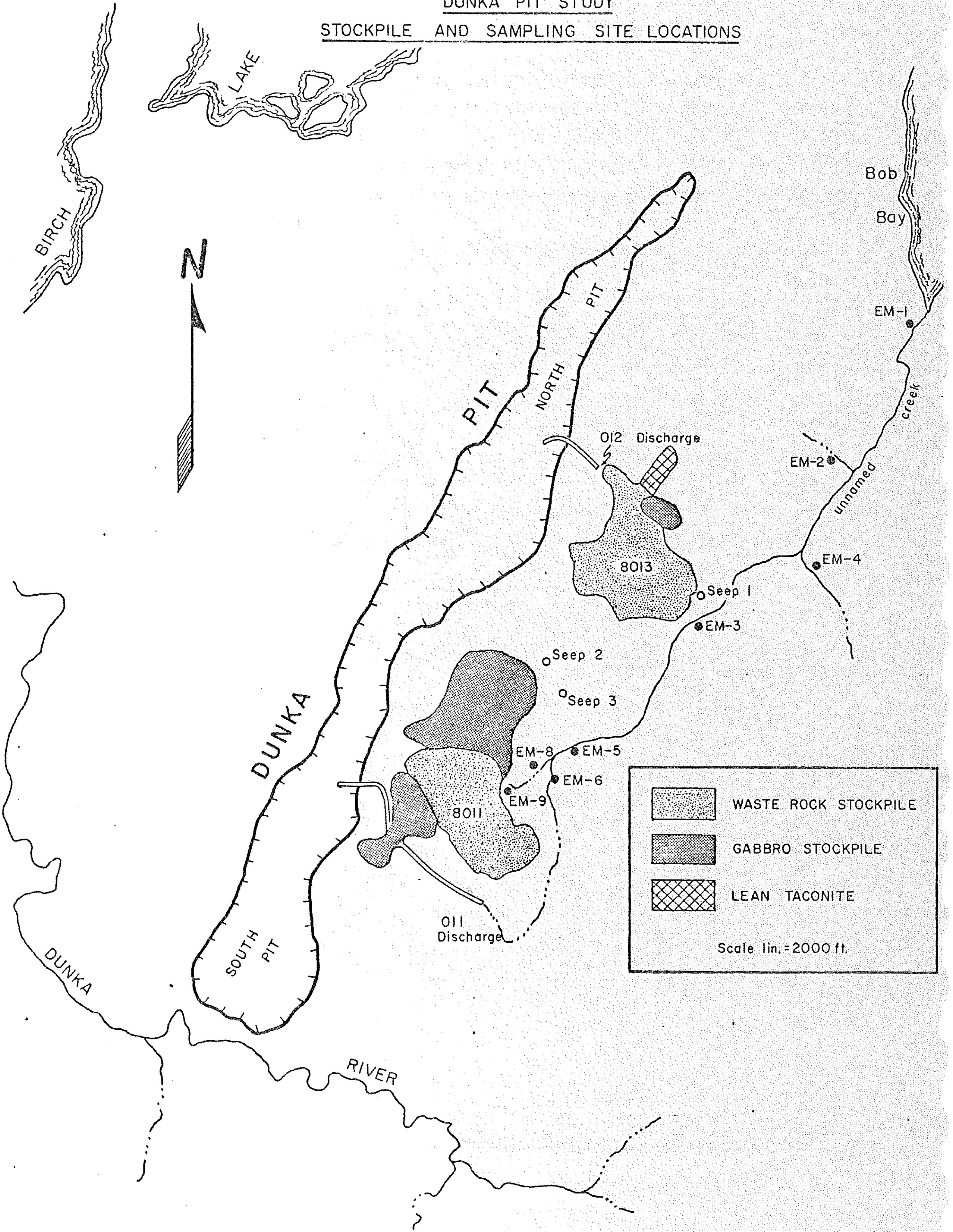


Figure 2.3. AMAX Test Piles

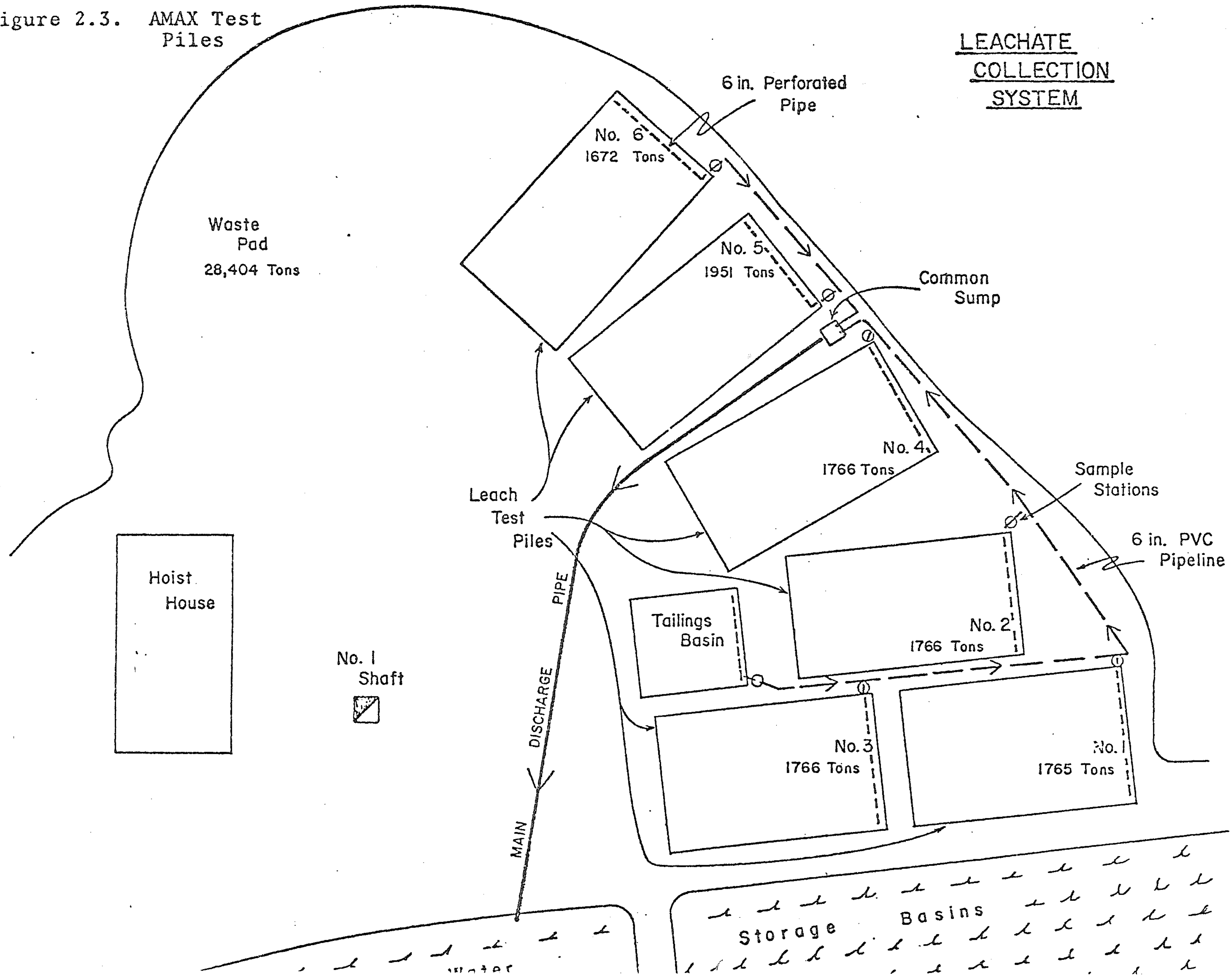


TABLE 2.2 Description of Field Study Areas

Field Study Area	Description
Erie Mining Company - Dunka Pit	Open pit taconite operation. The geological contact between the iron formation and the Duluth gabbro intersects this pit. Duluth gabbro, containing mineralization, has been removed and stockpiled on the eastern side of the pit. Two types of stockpiles have been formed: gabbro piles, which contain all rocks >.2% copper and waste rock piles, which are a mixture of gabbro(<.2% Cu) and waste rock from the iron formation. Three distinct sources of leachate have been identified (sites labeled Em8, Seep 3, and Seep 1). Water quality and quantity measurements were collected from July 1976 through August 1977. Some data collection is continuing.
Amax Exploration, Inc.	Six small test plots of lean ore material have been contructed. The base of these plots is impermeable so all runoff can be collected and monitored. Data were collected in 1977 by Amax. Revegetation work on three of the piles has begun. Data collection continues under a joint Amax-Department of Natural Resources program.
U.S. Steel	In 1972, a small bulk sample was removed (two samples were collected, one in August, the other in October). Approximately 300 tons of material were removed. The average grade of the sample was .53 percent copper, .17 percent nickel, and .9 percent sulfur (The maximum sulfur content found in core samples from this area was 1.3 percent). The site was a bedrock outcrop, and the resulting basin is completely in bedrock. The pit was abandoned and has since filled with rain and runoff. A limited amount of data was collected in 1976; the majority of the data was collected in 1977.
International Nickel Co. (Inco)	In January of 1974, a 10,000 ton bulk sample was removed from an exposed rock outcrop. Soil depth varied from 0 to 4 feet. After the sample was collected, the site was restored and revegetated. By 1975, subsidence had occurred and seepage began to flow from the site. Additional reclamation work was done during the fall of 1975, but seepage flow continued. Data were collected over the period 1975-1977.

comparable to laboratory rates and other field rates, indicating that there are no large abnormalities in stockpile composition.

Most of the field effort was concentrated at the Dunka Pit site. Since it was a full scale operation, the quantities of leachate produced were adequate to study the movement of the metals from the stockpile through the surrounding aquatic environment.

The Amax data were collected from six small test plots (Figure 2.3) having the compostions shown in Table 2.4. The piles were constructed on impermeable hypalon bases, thereby allowing efficient runoff collection. The chemical composition of the stockpiles is known, but due to the small stockpile size, extrapolation based on the data must be applied carefully. (The Amax study is discussed in detail in a progress report by Eger et al, 1979).

The U.S. Steel site is a small abandoned bulk sample pit (100 ft. long x 50 ft. wide x 10 ft. deep) which has filled with rain and runoff water. A bulk ore sample was taken in 1972 and the pit was abandoned. Due to its small size and probable high metal concentration in the pit walls, extrapolation to full scale operations must be made carefully.

Seepage from the Inco bulk sample site has also been analyzed. The area was covered and vegetated after a bulk sample was taken in 1974. Seepage was observed in the spring of 1975. Additional reclamation work was conducted in the fall, but the seepage continued. The rock composition is representative of ore so extrapolations based on these data may tend to overestimate typical leachate concentrations. One of the important conclusions from the Inco study is that the data support the general leaching behavior of the gabbro which was observed in other parts of the region.

Table 2.3

Stockpile composition, Dunka Pit.*

Stockpile No.	mat'l.	Date Started	tons gabbro	Composition (%)		Seep identified
				Cu	Ni	
8011	waste rock	Dec., 1965	9,976,107	.057	.014	Em8
8012	gabbro	March, 1967	1,162,341	.27	.07	-----
8014	gabbro	June, 1967	4,190,806	.29	.08	Seep 3
			15,329,254			
8013	waste rock	April, 1967	5,578,465	.043	.014	Seep 1
8022	iron ore	April, 1968	---------	----	----	------
8016	gabbro	Dec., 1968	629,577	.21	.06	------
			6,208,042			

* Stockpile tonnages as of January 1977.

TABLE 2.4 COMPONENTS OF FIELD LEACHING PILES - AMAX

Pile No.	Size (Tons)	Completion date	Average Mineral Content %Cu	% Ni	% S
1	1766	April 20, 1977	.33-.35	.075	0.6
2	1766	April 20, 1977	.33-.35	.075	0.6
3	1766	April 20, 1977	.33-.35	.075	0.6
4	1765	April 20, 1977	.33-.35	.076	0.6
5	1951	Sept. 10, 1977	0.29	0.09	1.45
6	1672	Sept. 30, 1977	0.38	0.09	0.83
Total piles 1-6	10,686		0.33	0.08	0.79

Treatments for Test Piles

Pile	Treatment
1	none, control
2	cover with top soil, revegetate
3	cover with overburden, revegetate
4	none, control
5	cover with overburden, revegetate
6	none, control

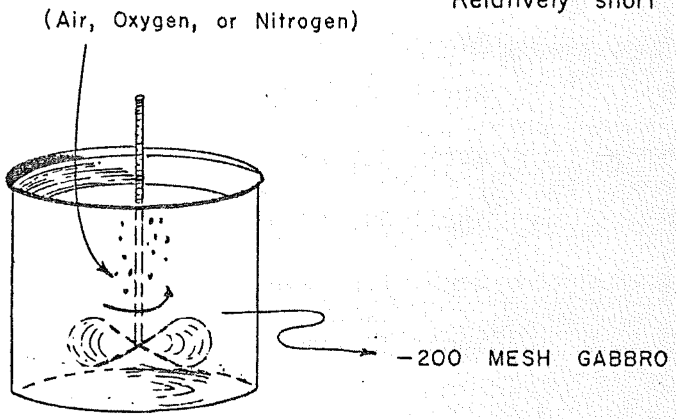
Figure 2.4

LABORATORY TESTS

1. BATCH REACTOR

Well mixed system, provides maximum contact between solution and rock particles

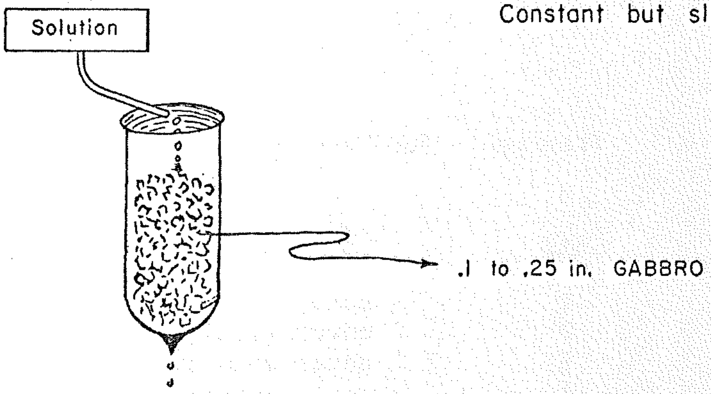
Relatively short term experiments < 1000 hours.



2. COLUMN

Long term, total time : 250 days

Constant but slow, solution addition



3. ENVIRONMENTAL LEACHING TEST

Short test (100 hours)

A standardized approach for comparing leaching potential of various samples.

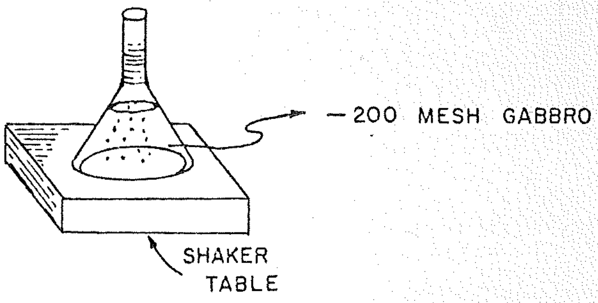


Table 2.5 Laboratory Tests, Variables Investigated

Variables examined	Parameters analyzed
Batch reactor	
Mass loading	Cu
pH	Ni
Ionic strength	
Disolved oxygen concentration	Fe
Particle size	SO_4
Gabbro composition	Ca
Effect of Citrate	Mg
Effect of phthalic acid	pH
Effect of natural bog and ground water	
column	
Gabbro composition (mineralized vs unmineralized)	Cu Ni Co Fe SO_4
solution composition (synthetic surface water synthetic ground water distilled water)	Mn pH
Environmental leaching Test	
Gabbro composition (mineralized and tailings samples from across the study area)	Cu Ni Co Zn Fe
solution composition (acid solution pH 3.5 synthetic natural water)	Mn Ca Mn Cd pH

Table 2.6 Composition of Duluth gabbro used in laboratory studies.

Samples from Dunka Pit

	Unmineralized	Mineralized	Models[+]	
%		(DP9002)	Lean Ore	Waste Rock
S	1.1	3.92	.655	.207
Cu	.24	1.4	.306	.100
Ni	.095	.36	.073	.023
Co	.082[a]	.039	.009	.002
Zn	<.0009	.012	.016	.0026

a = neutron activation analysis - this value is anomalously high.

\+ = model lean ore and waste rock as developed by Regional Copper-Nickel Study.

3.1 Introduction

This chapter presents the results of laboratory experiments investigating the factors controlling the leaching of Duluth gabbro, leaching defined as the net transfer of components from the solid mineral phase to the dissolved aqueous phase which results from contact of the phases. Water may contact mining products in stockpiles, underground and open pit mines and tailings basins; the change in water quality (leaching) due to this contact is a topic of environmental concern.

Topics will be discussed as follows:

Literature review
Model presentation
Experimental laboratory methods
Batch reactor experiments
Summary of batch reactor kinetic results
Column leach experiments
Tailings in batch experiments
Environmental leaching tests

The leaching process is discussed from a chemical viewpoint, examining theoretical considerations in conjuction with results of laboratory experiments designed to study the leaching behavior of Duluth gabbro. Dissolution models based on considerations of chemical theory are presented and laboratory results are discussed in light of the model. A chemical equilibrium approach, using the REDEQL 2 computer program, was incorporated to provide insight into leaching reactions and the ultimate fate of leached components (Vuceta and Morgan, 1978; Ferreira, 1973; Morel and Morgan, 1970; Morgan, 1967). Dr. Michael R. Hoffmann modified the program at the University of Minnesota and provided advice on its operation.

Additional detail regarding theoretical considerations and laboratory results is abailable in various study reports including a literature survey (Eisenrich et al. 1976) and individual laboratory reports (Hoffmann et al. 1979; Thorsen, 1978; Ryss and Hoffmann, 1979).

3.2 Literature Survey

3.2.1 Introduction

Trace metals such as copper, nickel, cobalt and zinc are present largely as sulfides in the Duluth gabbro. The metal sulfides are disseminated as small particles and veins in the interstices between silicates, included within silicates or intimately with the silicates (Weiblin and Morrey, 1976). Abbreviated chemical and mineralogical analyses of the gabbro used in laboratory sutdies are presented in Tables 3.1 and 3.2, respectively,

The unmineralized rock sample was randomly selected from waste rock stockpiles 8013 at the Erie Mining Company Dunka site. The mineralized sample (DP9002) was selected from the open pit wall at the Dunka site and represents an ore sample. Additional analyses of rock samples from the study area are presented by Stevenson et al. (1979).

Pyrrhotite is the major sulfide mineral in the Duluth gabbro. The dissolution of trace metal sulfides, such as chalcopyrite ($CuFeS_2$) and pentlandite ($(Fe,Ni)_9S_8$), is important since the release of copper, nickel, cobalt and zinc poses a greater potential for toxic effects on aquatic biota (Pickering, 1974; Rehowldt et al. 1971; Warnick and Bell, 1969; Toth, 1968). Removal mechanisms for metals are considered in the presentation of models since the net effect of dissolution, and precipitation and adsorption, reflects the degree of potential environmental impact.

Table 3.1. Chemical composition of gabbro (values in weight percent).

Element	Unmineralized	Mineralized
S[b]	1.1	3.92
Ni	0.095	0.36
Cu	0.24	1.4
Co[a]	0.082	0.039
Zn[a]	0.0009	0.012
Fe	10.4	17.2
Ca	2.6	2.3
Mg	2.0	1.9

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[a] Neutron Activation analyses.
[b] Analysis by Mineral Research Center, University of Minnesota

Table 3.2 Mineral analysis of gabbro.

Mineral	Formula	WEIGHTED MEAN VOLUME PERCENT Mineralized (DP 9002)
Penlandite	$(Fe,Ni)_9S_8$	0.34
Chalcopyrite-Cubanite	$CuFeS_2$ - $CuFe_2S_3$	1.3
Pyrrhotite	Fe_7S_8 - FeS	3.1
Ilmenite Magnetite	$FeTiO_3$ Fe_3O_4	3.1
Olivine	$(Fe,Mg)_2 SiO_4$	11
Clinopyroxene	$Ca(Fe,Mg)Si_2O_6$	26
Orthopyroxene	$(Fe,Mg)_2Si_2O_6$	2.3
Plagioclase	$NaAl Si_3O_8$ - $CaAl_2Si_2O_8$	47

3.2.2 Metal Sulfide Leaching

For significant release of trace metals such as Fe, Cu, Ni, Co and Zn to occur, the products indicated by reaction 1 must undergo further reaction. The equilibrium concentrations of iron, copper, nickel, cobalt and zinc with aqueous sulfide are low, having solubility products (K_{so} in equation 3.2) ranging from $10^{-36.2}$ for CuS to $10^{-17.5}$ for FeS (Table 3.3).

$$\mathrm{MeS(s)} \quad = \quad \mathrm{Me}^{2+} + \mathrm{S}^{=} \qquad (3.1)$$

$$(\mathrm{Me}^{2+})\ (\mathrm{S}^{=}) \quad = \quad K_{so} \qquad (3.2)$$

$$(\mathrm{Me}^{2+}) \quad = \quad K_{so} \,/\, (\mathrm{S}^{=}) \qquad (3.3)$$

$$(\mathrm{Me}^{2+}) \quad = \quad (K_{so})^{\frac{1}{2}} \qquad (3.4)$$

If the products of reaction 1 were strictly Me^{2+} and $\mathrm{S}^{=}$ the equilbrium concentration of Me^{2+} would be dictated by equation 3.3; resulting in concentrations ranging from $10^{-18.1}$ $\underline{M}$ for copper to $10^{-8.8}$ $\underline{M}$ for iron. Research on the recovery of metals from sulfide minerals indicates that in metallurgical processing sulfide reacts to form elemental sulfur or hydrogen sulfide. Woodcock (1961), Wadsworth (1972), Roman and Benner (1973) and Dutrizac and MacDonald (1974) discussed advances in the leaching of sulfides. Numerous studies indicated that dissolution occurs due to the oxidation of sulfide to elemental sulfur:

$$\mathrm{MeS(s)} \quad = \quad \mathrm{Me}^{2+}\mathrm{(aq)} + \mathrm{S}^{o} + 2e^{-} \qquad (3.13)$$

For the oxidation of sulfide to occur the presence of an oxidizing agent, such as ferric iron or oxygen, is required.

$$\mathrm{Fe}^{3+} + e^{-} \quad = \quad \mathrm{Fe}^{2+} \qquad (3.14)$$

$$\tfrac{1}{2}\mathrm{O}_2 + 2e^{-} \quad = \quad \mathrm{O}^{2-} \qquad (3.15)$$

In a review of metal sulfide leaching Woodcock (1961) observed that ferric iron was the more effective oxidizing agent although a strongly acidic

Table 3.3 Metal sulfide solubilities from Sillen and Martel (1964, 1971)

Equilibrium			-LOG K_{SO}	
$CuS(s)$	=	$Cu^{2+} + S^{=}$	36.2	(3.5)
α-$NiS(s)$	=	$Ni^{2+} + S^{=}$	20.8	(3.6)
γ-$NiS(s)$	=	$Ni^{2+} + S^{=}$	27.75	(3.7)
$CoS(s)$	=	$Co^{2+} + S^{=}$	21.3	(3.8)
$ZnS(s)$	=	$Zn^{2+} + S^{=}$	22.05	(3.9)
ZnS(wurtzite)	=	$Zn^{2+} + S^{=}$	22.80	(3.10)
ZnS(sphalerite)	=	$Zn^{2+} + S^{=}$	25.15	(3.11)
$FeS(s)$	=	$Fe^{2+} + S^{=}$	17.5	(3.12)

solution was required to maintain the Fe^{3+} in solution.

The major sulfide minerals present in the Duluth gabbro are pyrrhotite ($Fe_{1-x}S$, $0 \leq x \leq 0.2$), chalcopyrite ($CuFeS_2$), cubanite ($CuFe_2S_3$) and pentlandite ($(Fe,Ni)_9S_8$). Minor sulfide minerals include violarite (Ni_2FeS_4), mackinawite ($(Fe,Ni)_{1.1}S$), pyrite (FeS_2), sphalerite ($(Zn,Fe)S$), and bornite (Cu_5FeS_4) (Stevenson et al. 1979).

3.2.2.1 Dissolution of iron sulfides

The dissolution of pyrrhotite has been described by various reactions similar to both reactions 5 and 6. Ingraham et al. (1972) used reactions 3.16 and 3.17 to represent the dissolution of stoichiometric and iron deficient pyrrhotite in hydrochloric acid.

$$FeS + 2HCl = FeCl_2 + H_2S \tag{3.16}$$

$$Fe_7S_8 + 14HCl = 7FeCl_2 + 7H_2S + 8S^o \tag{3.17}$$

Lowe (1970) investigated the dissolution of pyrrhotite in acidified ferric sulfate solutions, observing linear kinetics and an apparent activation energy of 9 kcal/mole. The dissolution rate was independent of the ferric ion concentration over the range 0.025 to 0.208 M. Chemisorption on the sulfide surface was suggested as the rate controlling step and the dissolution reaction for $T<50^o$ C was

$$FeS + Fe_2(SO_4)_3 = 3FeSO_4 + S^o. \tag{3.18}$$

At temperature greater than 50^oC the rate decreased sharply due to direct acid attack of the sulfide and generation of H_2S.

Subraminian et al. (1972) represented the dissolution of pyrrhotite in acidified ferric sulfate solutions by

$$FeS_{1.15} + 2Fe^{3+} = 3Fe^{2+} + 1.15\ S^o. \tag{3.19}$$

Arai (1977) investigated the oxidative leaching of $Fe_{1-x}S$ ($0 \leq x \leq 0.08$) in acidic ferric chloride solution. The experimentally determined determined stoichiometry of the reaction was

$$Fe_{1-x}S + 2(1-x)Fe^{3+} = 3(1-x)Fe^{2+} + S^o. \qquad (3.20)$$

The reaction rate was proportional to the ferric iron concentration for pH < 1. For pH < 1 the rate varied directly with (Fe^{3+}) and inversely with (H^+). The author determined activation energies of 12 and 14.5 kcal/mole for x = 0.0004 and x = 0.0614 and the observed leaching rate for x = 0.0004 was twice that for x = 0.0614. It was observed for pH < 1 that reaction of Fe_{1-x} by H^+ with H_2S evolution competed with suppressed oxidative leaching.

3.2.2.2 Dissolution of copper sulfides

Sullivan examined the oxidative dissolution of copper sulfides in the 1930's. Reactions 3.21-3.25 were established for the ferric ion leaching of chalcopyrite (Sullivan, 1933; Brown and Sullivan, 1934), bornite (Sullivan, 1931, 1933), chalcocite (Cu_2S) (Sullivan, 1930a, 1933) and covellite (CuS) (Sullivan, 1930b).

[1]$CuFeS_2 + 4Fe^{3+} = Cu^{2+} + 5Fe^{2+} \quad 2S^o$ (3.21)

[1]$CuFeS_2 + 4Fe^{3+} + 2H_2O + 3O_2 = Cu^{2+} + 5Fe^{2+} + 2H_2SO_4$ (3.22)

$Cu_5FeS_4 + 12Fe^{3+} = 5Cu^{2+} + 13\ Fe^{2+} + CuS + 35^o$ (3.23)

[2]$Cu_2S + 2Fe^{3+} = Cu^{2+} + 2Fe^{2+} + CuS$ (3.24)

$CuS + 2Fe^{3+} = Cu^{2+} + 2Fe^{2+} + S^o$ (3.25)

Results of subsequent research verify these reactions.

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[1] 75% of the dissolution of chalcopyrite occurred according to reaction 3.21, and 25% by reaction 3.22.

[2] The CuS intermediate in reaction 3.24 was noted to be a mineral form other than covellite.

Bauer et al. (1972) and Stanczyk and Rampacek (1963) reported that chalcopyrite was more difficult to leach than other copper sulfides. Bauer et al. (1972) found the dissolution of chalcopyrite to proceed

$$CuFeS_2 = Cu^{2+} + Fe^{2+} + 2S^0 + 4e. \qquad (3.26)$$

Stanczyk and Rampacek (1963) reported covellite (CuS) and troilite (FeS) were formed in the autoclave leaching of chalcopyrite under varying oxygen partial pressures:

$$CuFeS_2 = CuS + FeS. \qquad (3.27)$$

Dutrizac et al. (1969) investigated the leaching of synthetic chalcopyrite between 50 and 94° C. Based on yields of sulphur and ferrous iron reaction 3.28 was proposed:

$$CuFeS_2 + 2Fe_2(SO_4)_3 = CuSO_4 + 5FeSO_4 + 2S^0 \qquad (3.28)$$

Parabolic kinetics were observed and the authors concluded that the reaction was controlled by ferric sulfate diffusion through a film of accumulating sulfur for $(Fe^{3+}) < 0.01\underline{M}$. An activation energy of 17 ± 3 kcal/mole was reported.

Haver and Wong (1971) examined the leaching of chalcopyrite concentrates using acidified ferric chloride solutions at temperatures between 30° and 106° C. The observed parabolic kinetics were explained in the same manner as Dutrizac and MacDonald (1969). The proposed reaction was also essentially the same as that determined in previous works with the exception of a cupric chloride reaction product.

$$CuFeS_2 + 3FeCl_3 = CuCl + 4FeCl_2 + 2S^0 \qquad (3.29)$$

Dobrakhotov and Maiorova (1962) conducted studies examining the autoclave leaching of chalcopyrite between 125° and 175° C using oxygen. An activation energy of 7 kcal/mole was determined and the variation of leaching rate with pH and oxygen was expressed as

$$\frac{d(Cu^{2+})}{dt} = k(H^+)\ (P_{O2})^{1/2} \qquad (3.30)$$

Autoclave leaching of chalcopyrite by Vizsolyi et al. (1967) resulted in 98% copper recovery and 85% elemental sulfur recovery with iron remaining as an insoluble oxide. Ferric oxide was also reported as a reaction product in the leaching of copper and zinc minerals (Evans et al. 1964).

Prater et al. (1972) studied the autoclave leaching of chalcopyrite in nitric acid and proposed the reaction

$$6\ CuFeS_2 + 10HNO_3 + 10H_2SO_4 = 6\ CuSO_4 + 10NO + 12S^o + (Fe_2O_3)_3 .4SO_3 .9H_2O + 6H_2O. \qquad (3.31).$$

An increase in pH was observed initially and explained by the reaction

$$S^= + \tfrac{1}{2}O_2 + 2H^+ = S^o + H_2O. \qquad (3.32)$$

The pH eventually stabilized due to the hydrolysis of iron. Increased nitric acid concentrations were observed to enhance the oxidation of elemental sulfur to sulfate.

Prater et al. (1970) studied the dissolution of chalcopyrite in hot sulfuric acid and proposed the reactions:

$$CuFeS_2 + 2H_2SO_4 = CuSO_4 + FeSO_4 + 2H_2S \qquad (3.33)$$

$$H_2S + H_2SO_4 = S^o + SO_2 + 2H_2O \qquad (3.34)$$

$$2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + SO_2 + 2H_2O \qquad (3.35)$$

Since only traces of H_2S were detected in the off gases, reaction 3.33 would have to proceed very rapidly which is contrary to observations of Pawlek (1969). It appears possible that two reactions, 3.28 and 3.33, were occurring simultaneously, although the presence of an oxidant for reaction 3.28 would be required.

Dutrizac et al. (1970) studied the ferric sulfate leaching of synthetic cubanite over the temperature range from 45° to 90° C. An activation energy of 11.6 ± 0.7 kcal/mole was determined for the reaction

$$CuFe_2S_3 + 3Fe_2(SO_4)_3 = CuSO_4 + 8FeSO_4 + 3S^0. \qquad (3.36)$$

Linear kinetics were observed with the reaction rate proportional to $(Fe^{3+})^{0.6}$, indicating that Fe^{3+} was directly involved in the rate controlling reaction. Thomas and Ingraham (1967) studied the rate of sintered synthetic covellite dissolution, as represented by reaction 3.25, and found the rate was linear. An activation energy of 22 kcal/mole was determined for $T<60^o$ C, decreasing to 4 kcal/mole at higher temperature, indicating solution transport control. Dutrizac and MacDonald (1974) conducted a similar study over the temperature range of 25° to 95° C using both pure synthetic CuS disks and high grade natural material. Relatively slow reaction rates were observed for both materials. The rates increased during the initial stages of reaction eventually becoming linear with a direct dependence on (Fe^{3+}) for ferric concentrations less than 0.005<u>M</u>. An activation energy of 17.8 ± 2.0 kcal/mole was determined. Bauer et al. (1972) observed that the rate of covellite dissolution decreased with time, an occurrence attributed to the accumulation of elemental sulfur on the surface.

3.2.2.3 Dissolution of pentlandite

Autoclave leaching of pentlandite under oxygen pressure was studied by Schneerson et al. (1966) who reported an activation energy of 14 kcal/mole and a reaction rate dependence on $(P_{O_2})^{\frac{1}{2}}$. Millerite (NiS) was identified as an intermediate phase.

Klets et al. (1966) studied the leaching of a mixture of pyrrhotite and pentlandite and observed elemental sulfur formation in the surface layers. Formation of millerite,beyrichite (NiS) and troilite (FeS) was also observed.

Dutrizac and MacDonald (1974) investigated the percolation leaching of pentlandite by acidified ferric sulfate. Based on the observation that almost all reacted sulfur was in the elemental state the dissolution was represented by

$$18Fe^{3+} + (Fe, Ni)_9S_8 = 27\,Fe^{2+} + 9\,Ni^{2+} + 8S^0 \qquad (3.37)$$

Linear kinetics were observed to be proportional to $(Fe^{3+})^{0.20}$ and an apparent activation energy of 9 kcal/mole was determined. Neither resting of the column (wet-dry cycling) nor the presence of bacteria had a significant effect on the dissolution rate. Nickel concentrations in the leach solutions decreased from 0.71 to 0.16 g/l due to cementation onto ground pyrrhotite. Corrans and Scholtz (1976) studied the dissolution of pentlandite and determined an activation energy of 14.5 kcal/mole. The rate model presented in equation 3.38was proposed based on both ferric ions and oxygen reacting as oxidizing agents

$$R = k_1(Fe^{3+})\,W^{0.833} + k_2(P_{O_2})^{\frac{1}{2}}\,(H^+)^0 \qquad (3.38)$$

where W = stirring rate.

The first set of terms on the right side of the equation represented the oxidation by ferric ions which was controlled by mass transport. The second set represented oxidation by oxygen which was controlled by adsorption of dissolved oxygen onto the mineral surface. Examinations of leach residues revealed that the unleached pentlandite was covered by a thin loosely bound layer containing pyrrhotite and sulfur. The authors proposed the anodic reaction sequence

$$NiFeS_{1.8} = Ni^{2+} + FeS_{1.8} + 2e^- \qquad (3.39)$$

$$FeS_{1.8} = Fe^{2+} + 1.8S^0 + 2e^- \qquad (3.40)$$

3.2.2.4 Dissolution of cobalt and zinc sulfides

Torma (1971, 1972) investigated the bacterial leaching of synthetic CoS in an iron free medium and expressed the leaching reaction.

$$CoS + H_2SO_4 + \tfrac{1}{2}O_2 \ \underline{\text{bacteria}\rightarrow} CoSO_4 + H_2O + S^o \qquad (3.41)$$

$$S^o + 3/2O_2 + H_2O \ \underline{\text{bacteria}\rightarrow} H_2SO_4 \qquad (3.42)$$

The author concluded that the leaching was the result of direct bacterial attack.

Scott and Dyson (1968) found certain metals to catalyze the pressure leaching of zinc sulfate.The catalysts of the acid leaching reaction, in order of increasing catalytic activity, were Fe<Mo<Ru<Bi<Cu. Zinc sulfide reacted according to

$$ZnS(s) + \tfrac{1}{2}O_2 + H_2SO_4 = ZnSO_4 + S^o + 2H_2O \qquad (3.43)$$

$$ZnS(s) + 2O_2 = ZnSO_4 \qquad (3.44)$$

with reaction 3.44 occurring in the absence of acid.

Pawlek (1969) determined that the pressure leaching of ZnS under acid conditions proceeded as

$$ZnS(s) + H_2SO_4 = ZnSO_4 + H_2S \qquad (3.45)$$

He observed that the reaction ceased when the equilibrium presented above was reached and proceeded once again upon release of H_2S from the leaching vessel. Locker and deBruyn (1969) studied the nonoxidative dissolution of ZnS and CdS under acid conditions. The authors proposed the reaction

$$MeS(s) + 2H^+ = Me^{2+} + H_2S(g) \qquad (3.46)$$

having activation energies of 9.5 and 14.2 kcal/mole for ZnS and CdS, respectively. The rate controlling reaction was determined as the adsorption of H^+ onto anionic sites.

Majima and Peters (1966) examined the oxidation rates of pyrite, pyrrhotite, chalcopyrite, chalocite, covellite, bornite, galena, sphalerite and stibnite at 120^{o}C using aqueous phosphate solutions buffered at pH 2.7, 7.1 and 11.2, in 1.0<u>M</u> NaOH and in ammonia containing solutions. The variation of oxygen consumption rates among the minerals in the phosphate buffered solutions was less than a factor of two with the exception of pyrrhotite, which initially oxidized very rapidly in acid solutions, and stibnite, which oxidized rapidly in basic solutions.

3.2.2.5 Leaching in the environment

The leaching conditions of low pH, elevated temperature, high oxygen pressure and increased ferric iron concentration used for metals recovery, are not typical environmental conditions. Research by Sato (1960a, 1960b), Pankow (1979) and Nelson (1978) was conducted under conditions more closely approximating those found naturally.

Sato (1960a) experimentally determined that the oxidation potential of the weathering environment is controlled by the H_2O_2-O_2 couple:

$$H_2O_2 = O_2 + 2H^+ + 2e^- \tag{3.47}$$

$$Eh = 0.632 - 0.0591\ pH + 0.0295 \log \frac{(P_{O_2})}{(H_2O_2)} \tag{3.48}$$

Most of the values measured in the zone of oxidation fell on or slightly above a line defined by

$$Eh = 0.682 - 0.0591\ pH. \tag{3.49}$$

This value is less than that for solutions containing high concentrations of ferric iron which is given by Peters (1970) as

$$Eh = 0.771 + 0.0591 \log \frac{(Fe^{3+})}{(Fe^{2+})}. \tag{3.50}$$

This comparison emphasizes the greater oxidative strength of high ferric concentrations relative to oxygen. Sato (1960b) studied the dissolution of sulfides of copper, lead, silver, iron and zinc under environmental conditions. He reported that oxidation of simple sulfides involved the release of metal ions to solution while elemental sulfur remained in the solid phase. When only sulfur remained it underwent a series of reactions, the final product being sulfate.

Pankow (1979) and Nelson (1978) studied the dissolution of synthetically prepared iron sulfides under conditions more closely approximating those in the environment.

Pankow (1979) studied the dissolution of mackinawite in anoxic aqueous systems with 3 pH 7, 5° T $35^{\circ}C$, and ionic strength from 0.05 to 0.60M. The flux from the surface was described by the equation

$$F_s = k_1 a_{H^+} + k_2 \qquad (3.51)$$

Where $k_1 = 0.13$ cm/min., $k_2 = 1.1 * 10^{-9}$ moles/cm^2-min and a_{H+}, the hydrogen ion activity in moles/cm^3.

The k_1 term is dominant for pH <4.3 and k_2 dominates at pH >5.6 with the region from 4.3 to 5.6 being a transition region. k_1 reflects the attack of H^+ at the FeS surface, and k_2 represents the normal thermal vibrations and H_2O solvation effects which influence the release of lattice constitutents. The oxidative dissolution of FeS was investigated by Nelson (1978) whose results were approximated by the relationship

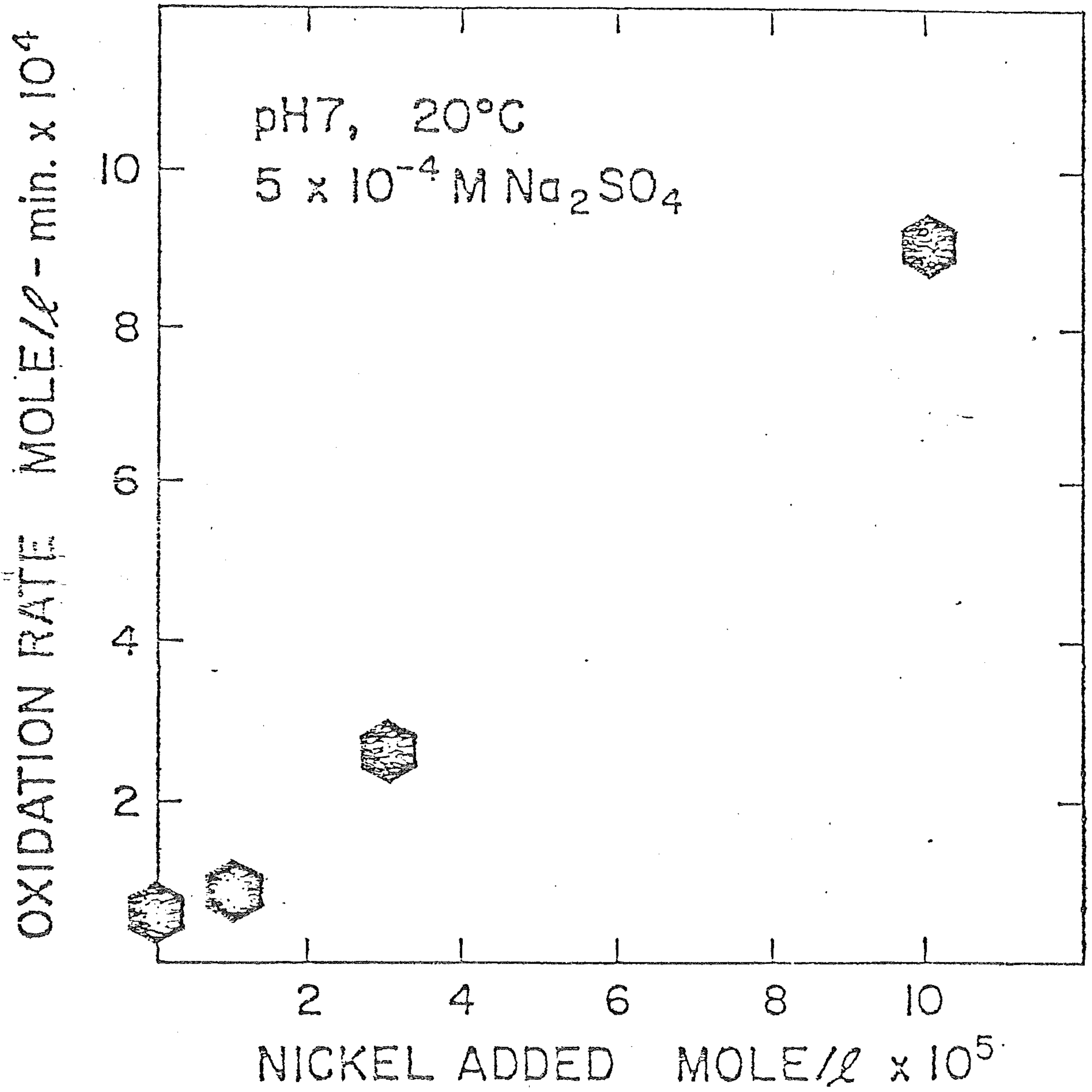
$$-d(FeS)/dt = kA_s P_{O_2} (H^+)^{1/4} \qquad (3.52)$$

The oxidation rate was proportional to surface area and exhibited a pseudo-first order dependence on oxygen at lower oxygen concentrations. The oxidation rate was relatively insensitive to changes in pH, increasing by a factor of 5 between pH 9 and pH 6.5. Nickel, at concentrations greater than $1 * 10^{-5}$M, was an effective catalyst of the oxidation as is presented in Figure 3.1. The proposed rate limiting reaction was the conversion of a surface complex formed by the adsorption of oxygen onto the sulfide surface. The oxidation rates observed ranged from $1.14 * 10^{-6}$ to $4.03 * 10^{-6}$ moles/m^2-min.

3.2.3 Silicate leaching

The mineralogical structure of the gabbro suggests that silicate dissolution may play a role in the release of metals bound as sulfides. Due to the intimate contact of the two mineral phases silicate dissolution may be necessary to

Figure 3.1. Rate of oxidation of FeS(s) as a function of the concentration of nickel present at pH 7, 20°C. From Nelson, 1978



expose additional metal sulfide surface. A second effect of silicate dissolution is an increase in ionic strength which increases the solubility of metal sulfides and other solid phases (Stumm and Morgan, 1970). A third factor is the effect of calcium and magnesium on oxidation (Chen and Morris, 1972). If aqueous sulfide oxidation were the rate limiting step in the release of copper or nickel, the presence of calcium or magnesium would tend to accelerate the release.

Silicates and their dissolution may also have inhibitive effects on the net release to solution of metals associated with sulfide minerals. The silicate surface can adsorb metals from solution:

$Me^{+n} + n(-SiOH) = Me(OSi-)_n + nH^+$ (Dugger et al., 1964). (3.53)

The behavior of the silicate surface in this reaction is similar to that of the hydroxyl ion in the reaction (Dugger et al., 1964)

$Me^{n+} + OH^- = MeOH^{(n-1)+}$ (3.54)

Metals may also be removed in a similar manner by reacting with silicic acid in solution (Stumm and Morgan, 1970). Silicates also provide a pH buffering effect which may maintain the pH in a range which limits the mobility of metals such as copper, nickel and iron.

Silicate dissolution has been studied to a greater extent than metal sulfide dissolution under conditions which approximate those observed in the natural environment. In general, weathering of silicates is enhanced with increasing acidity, pE (oxidizing conditions) and tendency for complex formation (Stumm and Morgan, 1970). Increasing pE is effective largely due to its tendency to decrease pH. The reactions occurring in the dissolution process of anorthite are presented in Table 3.4.

Table 3.4 Feldspar dissolution reactions

Initial Ion Exchange

$CaAl_2Si_2O_8(s) + 2H^+ = Ca^{2+} + H_2Al_2Si_2O_8(s)$ (3.55)

Dissolution Phase for Anorthite

Inorganic reactions

$CaAl_2Si_2O_8(s) + 2H^+ + H_2O =$ (3.56)[a]

$Al_2Si_2O_5(OH)_3(s) + Ca^{2+}$; $\log k = 14.4$

$Al_2Si_2O_5(OH)_4(s) + 5H_2O =$ (3.57)[a]

$2H_4SiO_4 + \underset{\text{gibbsite}}{Al_2O_3 \cdot 3H_2O(s)}$; $\log k = 9.4$[a]

$CaAl_2Si_2O_8(s) + 2H^+ + 6H_2O =$ (3.58)[a]

$2H_4SiO_4 + Al_2O_3 \cdot 3H_2O(s) + Ca^{2+}$; $\log k = 9.4$

Organic Ligand Y^-. effect on kaolinite dissolution

$Al_2Si_2O_5(OH)_4 + 2Y^- = 2AlY(aq) + 2H_4SiO_4 + H_2O$ (3.59)[a]

$CaAl_2Si_2O_8(s) + 8H^+ + 2Y^+ + H_2O =$ (3.60)

$Ca^{2+} + 2AlY(aq) + 2H_4SiO_4$

Additional Reactions

$Al_2O_3 \cdot 3H_2O(s) = 2Al^{3+} + 6OH^-$ $\log k = -68.0$[a] (3.61)[a]

$Al_2O_3 \cdot 3H_2O(s) + OH^- = Al(OH)_4-$ $\log k = -1.0$[a] (3.62)[a]

SiO_2 (amorph) $+ H_2O = H_4SiO_4$ $\log K = -2.7$[a] (3.63)[a]

$H_4SiO_4 = SiO(OH)_3- + H^+$ $\log k = 9.46$ (3.64)[a]

$(-SiOH) = (-SiO^-) + H^+$ $pk_{int} = 6.8 \mp 0.2$ (3.65)[a,b]

$Me^n + (-SiOH) = Me(OSi-)_n + nH^+$ (3.66)[c]
similar to reaction of Me^{n+} with (OH^-)

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[a] Stumm and Morgan (1970)
[b] 0.1M $NaClO_4$, Schindler and Kamber (1968) in Stumm and Morgan
[c] Dugger, D.L., et al. (1964)

Several rate limiting reactions have been proposed to explain the parabolic kinetics observed for the dissolution of feldspars. Correns and Von Englehardt (1938) and Wollast (1967) hypothesized that the rate of feldspar dissolution was controlled by diffusion through an amorphous or gel precipitate layer forming on the mineral surface. Helgeson (1971) proposed rate control due to the formation of a crystalline precipitate layer of variable composition. Lagache et al. (1961) and Lagache (1965) did not incorporate a rate controlling precipitate layer, but rather propose a rate limiting surface reaction.

The initial reaction between feldspar minerals and water is a reversible ion exchange reaction between surface cations and protons (H^+) in solution (Garrels and Howard, 1976). The initial stagelasted approximately one minute followed by a stage characterized by rapid cation release lasting up to 4 days. The third stage was a diffusion controlled parabolic stage lasting approximately 19 days. The final stage involved a slow linear release of cations and silicic acid in a steady-state reaction. The linear calcium rate constants determined for the final stage are presented in Table 3.5. Microcrystalline halloysite was the only solid reaction product identified in the dissolution of the plagioclases (Busenberg, 1978).

The ion exchange phase of the reaction can be represented by reaction 3.55, indicating that the degree of release of calcium and magnesium is dependent upon the concentration of hydrogen ion. Wollast (1967) found the initial release rate of alumina and silica from orthoclase proportional to the hydrogen concentration to the third power. Other exchangeable cations in solution may produce a similar effect. Reaction 3.58, the sum of reactions 3.56 and 3.57, represents the inorganic incongruent dissolution of anorthite and indicates a dependence of dissolution on hydrogen ion concentration with dissolution. Wollast (1967) observed an increased silica release with decreasing pH in the pH range from 4 to 8. Wollast (1967) also observed that release of silicic acid

Table 3.5 Linear rate constants for calcium, from Busenberg and Clemency (1976)

pH 5
particle size: d<37μm

FELDSPAR		LOADING	Ca	log k	k
	g/l	m^2/l*	wt%	mole $cm^{-2}sec^{-1}$	mole $cm^{-2}sec^{-1}$
Oligoclase	53	53.4	5.0	-16.051	$8.9*10^{-17}$
Labradorite	43.5	45.1	10.63	-15.961	$1.1*10^{-16}$
Bytownite	53	60.3	15.66	-15.890	$1.2*10^{-16}$
Anorthite	53	97.3	20.11	-15.662	$2.2*10^{-16}$

* determined by one point B.E.T. method

was greater at pH 10 than pH 8, evidently due to the reactions such as 3.62, 3.63 and 3.64. The enhancement of silica dissolution at high pH may also enhance the release of calcium and magnesium.

Organic ligands may also enhance the dissolution of silicate minerals (Schalscha et al. 1967). Reaction 3.60, the sum of reactions 3.56 and 3.59, represents this dissolution. In addition to enhancing dissolution the ligands also provide a means of increasing the aqueous mobility of metals released from both silicate and sulfide minerals.

Luce et al. (1971) investigated the dissolution of forsterite, serpentine and enstatite and concluded that the dissolution reactions were controlled by transport within the mineral lattice. Parabolic kinetics were reported and the diffusion coefficients calculated decreased in the order forsterite> serpentine> enstatite.

3.3 Model Presentation

Evidence exists which indicates that the kinetics and mechanisms of dissolution for the various metal sulfides present in the Duluth gabbro are similar. Majima and Peters (1966) observed similar dissolution rates for several sulfide minerals, a relevant exception being the rapid initial rate of oxidation of pyrrhotite in acid solution. Researchers from the areas of mining and metallurgy, geology, electrochemistry and environmental chemistry propose similar mechanisms for dissolution. Based on these observations and the compositional complexity of the systems analyzed in this study, the dissolution of the various metal sulfides will be treated as one general model. Refinement of the general case will be added when possible.

Based on the available literature, three potential mechanisms influence metal sulfide dissolution. These are presented in generalized form in reactions

3.67 to 3.69.

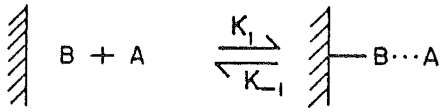
$$MeS = Me^{2+} + S^{0} + 2e^{-} \qquad (3.67)$$

$$MeS = Me^{2+} + S^{=} \qquad (3.68)$$

$$MeS + H^{+} = Me^{2+} + HS^{-} \qquad (3.69)$$

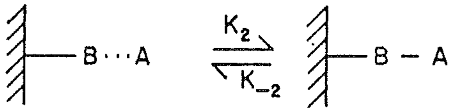
Reaction 3.67 indicates that trace metal release occurs upon oxidation of sulfide to elemental sulfur. The results of Nelson (1978) suggest that the rate of this reaction is controlled by the conversion of a surface complex formed by the adsorption of oxygen onto the ferrous sulfide surface. Nelson (1978) presented reactions 3.70 to 3.72 as a general model for the adsorption reactions occurring in sulfide oxidation.

Adsorption of reactant A onto reactive site B



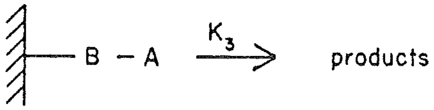
[3.70]

Molecular and/or electronic rearrangement



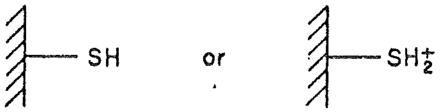
[3.71]

Formation of products (rate limiting)



[3.72]

In the case of sulfide oxidation
the reactive site B can be either



and

reactant A represents O_2

Sato (1960b) found that the elemental sulfur eventually reacted to form sulfate in oxidizing environments.

$$S^o + \frac{3}{2} O_2 + H_2O = SO_4^= + 2H^+ \qquad (3.73)$$

A stability field diagram for sulfur species is presented in Figure 3.2. When reactions 3.67 and 3.73 are added the overall reaction becomes

$$MeS + 2O_2 = Me^{2+} + SO_4^= \qquad (3.74)$$

According to Pankow (1979) the anoxic dissolution rate of FeS is described by the function

$$F_s = k_1 A_{H+} + k_2 \qquad (3.75)$$

Where F_s = flux in moles/cm^2-min
k_1 = 0.13 cm/min
k_2 = $1.1*10^{-9}$ moles/cm^2-min

Reaction 3.76 dominates at pH > 5.6 and reaction 3.77 at pH < 4.3.

$$FeS = Fe^{2+} + S^= \qquad (3.76)$$

$$FeS + H^+ = Fe^{2+} + HS^- \qquad (3.77)$$

Locker and deBruyn (1969) cited a reaction similar to reaction 3.77 as one step in the dissolution of ZnS and CdS under acid conditions.

Reactions subsequent to the initial dissolution of minerals must be considered for evaluation of the net change in water quality. If the aqueous sulfide concentration is not limiting aqueous metal concentrations, it is necessary to consider reactions between metals and other aqueous components. Solubilities of metal oxides, hydroxides and carbonates are presented in Table 3.6.

Figure 3.2. Stability field diagram for sulfur species in water at 25°C., total sulfur of 10^{-4}M. From Nelson, 1978

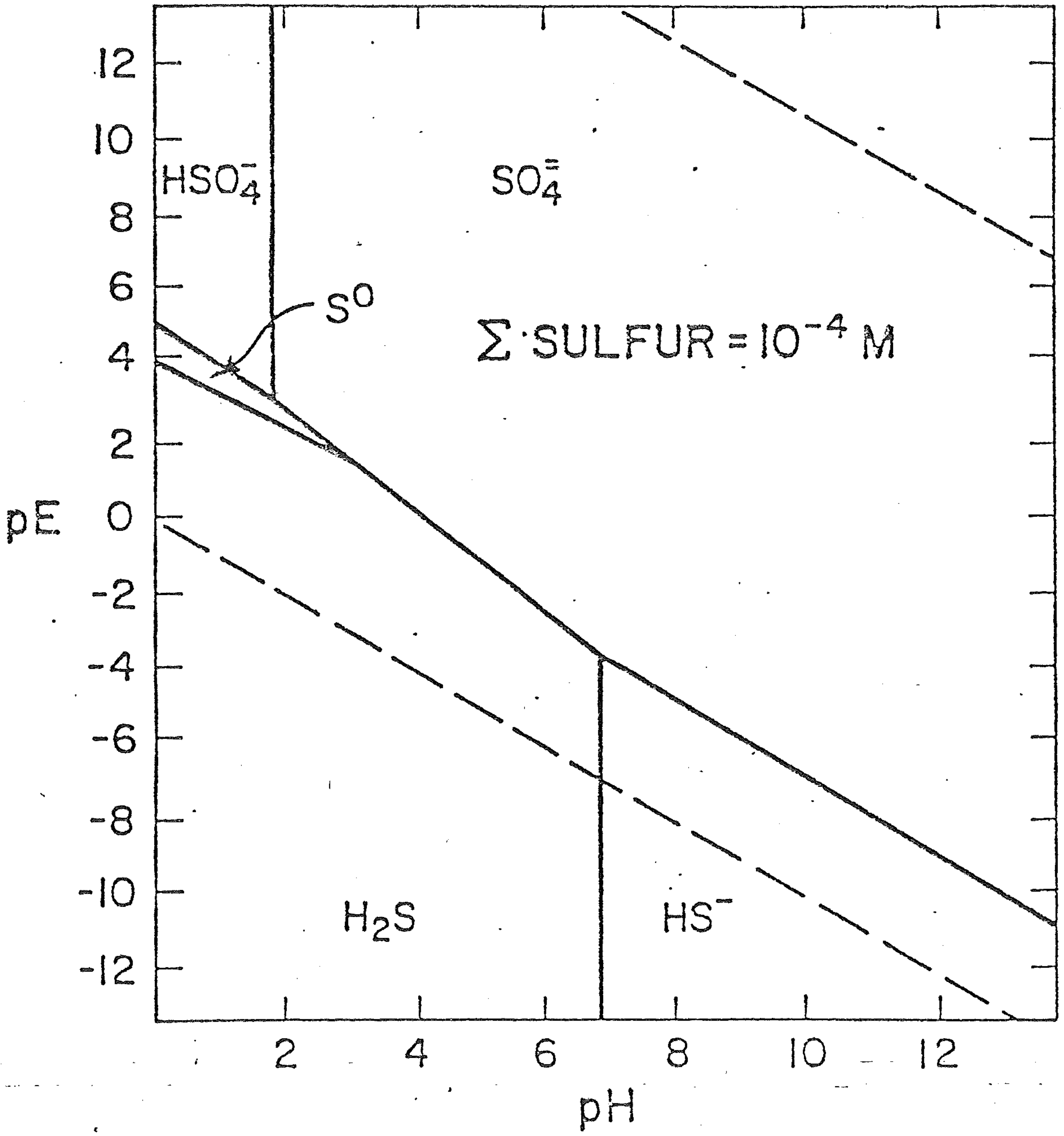


Table 3.6 Solubilities of metal oxides, hydroxides and carbonates [1]

Equilibrium			Symbol for k	Log K (25°C)	
$Cu(OH)_2(s)$	=	$Cu^{2+} + 2OH^-$	K_{so}	-18.7	(3.78)
$Cu^{2+} + OH^-$	=	$CuOH^+$	K_1	6.0 (18°C)	(3.79)
$2Cu^{2+} + 2OH^-$	=	$Cu_2(OH)_2^{2+}$	K_{22}	17.0 (18°C)	(3.80)
$Cu^{2+} + 3OH^-$	=	$Cu(OH)_3^-$	K_3	15.2	(3.81)
$Cu^{2+} + 4OH^-$	=	$Cu(OH)_4^{2-}$	K_4	16.1	(3.82)
$CuO(s) + 2H^+$	=	$Cu^{2+} + H_2O$	$^*K_{so}$	7.65	(3.83)
$Cu(OH)(CO_3)_{0.5} + 2H^+$	=	$Cu^{2+} + \frac{3}{2}H_2O + \frac{1}{2} CO_2(g)$	$^*K_{pso}$	7.08	(3.84)
$Cu_3(OH)_2(CO_3)_2 + 6H^+$	=	$3Cu^{2+} + 4H_2O + 2CO_2(g)$	$^*K_{pso}$	21.24	(3.85)
$Cu^{2+} + CO_3^{2-}$	=	$CuCO_3(aq)$	K	6.77	(3.86)
$Cu^{2+} + 2CO_3^{2-}$	=	$Cu(CO_3)_2^{2-}(aq)$	K	10.01	(3.87)
$Ni(OH)_2(s)$	=	$Ni^{2+} + 2OH^-$	K_{so}	-14.7	(3.88)
$Ni^{2+} + OH^-$	=	$NiOH^+$	K_1	3.4	(3.89)
$Ni^{2+} + 2OH^-$	=	$Ni(OH)_2(aq)$	K_2	10.0	(3.90)
$Ni^{2+} + 3OH^-$	=	$Ni(OH)_3^-$	K_3	13.0	(3.91)
$Co(OH)_2(s)$	=	$Co^{2+} + 2OH^-$	K_{so}	-14.9	(3.92)
$Co^{2+} + H_2O$	=	$Co(OH)^+ + H^+$	$^*K_1$	-9.6	(3.93)
$Co(OH^+) + H_2O$	=	$Co(OH)_2(aq) + H^+$	$^*K_2$	-9.2	(3.94)
$Co(OH)_2(s)$	=	$Co(OH)_2(aq)$	K_{s2}	-5.7	(3.95)
$Co(OH)_2 + H_2O$	=	$Co(OH)_3^- + H^+$	$^*K_3$	-12.7	(3.96)

Table 3.6 (Con't) Solubilities of metal oxides, hydroxides and carbonates[1]

Equilibrium	Symbol For K	log K (25°C.)	
$Zn(OH)_2(s) = Zn^{2+} + 2OH^-$	K_{so}	-15.52	(3.97)
$Zn^{2+} + OH^- = ZnOH^+$	K_1	4.95	(3.98)
$Zn^{2+} + 2OH^- = Zn(OH)_2(aq)$	K_2	12.89	(3.99)
$Zn^{2+} + 3OH^- = Zn(OH)_3^-$	K_3	14.22	(3.100)
$Zn^{2+} + 4OH^- = Zn(OH)_4^{2-}$	K_4	15.48	(3.101)
$ZnO(s) + 2H^+ = Zn^{2+} + H_2O$	$^*K_{so}$	11.18	(3.102)
$ZnCO_3(s) = Zn^{2+} + CO_3^{2-}$	K_{so}	-10.00	(3.103)
$Zn^{2+} + SO_4^{2-} = ZnSO_4(aq)$	K	2.8	(3.104)
$Zn^{2+} + Cl^- = ZnCl^+$	K	-0.56	(3.105)
$(am)\ Fe(OH)_3(s) = Fe^{3+} + 3OH^-$	K_{so}	-38.7	(3.106)
$(am)\ Fe(OH)_3(s) = FeOH^{2+} + 2OH^-$	K_{s1}	-27.5	(3.107)
$(am)\ Fe(OH)_3(s) = Fe(OH)_2^+ + OH^-$	K_{s2}	-16.6	(3.108)
$(am)\ Fe(OH)_3(s) + OH^- = Fe(OH)_4^-$	K_{s4}	-4.5	(3.109)
$2(am)\ Fe(OH)_3(s) = Fe_2(OH)_4^{4+} + 4OH^-$	K_{s22}	-51.9	(3.110)
$(am)\ FeOOH(s) + 3H^+ = Fe^{3+} + 2H_2O$	$^*K_{so}$	3.55	(3.111)
$-FeOOH(s) + 3H^+ = Fe^{3+} + 2H_2O$	$^*K_{so}$	1.6	(3.112)

[1] K values from Sillén and Martel (1964, 1971), Schindler (1967), Butler (1964)

A more effective method of presenting thermodynamic equilibria is the pC-pH diagram. Diagrams for copper, nickel, cobalt and zinc were constructed with the aid of the REDEQL 2 computer program (McDuff and Morel, 1973). The input concentrations were observed at the U. S. Steel bulk sample site in the Copper-Nickel Study area and are presented in Table 3.7.

Table 3.8 indicates that virtually all iron is removed from solution. Predicted copper concentrations decrease as pH increases above pH 6, as is presented in Figure 3.3. The predominant solid phase between pH 6 and 6.5 is malachite ($Cu_2(OH)_2CO_3$) and above pH 6.5 copper hydroxide is dominant. The initial total carbonate in the system is low ($2*10^{-5}\underline{M}$) and is essentially removed by malachite precipitation. At higher values of C_T malachite formation would proceed to further remove copper from solution (Table 3.8).

Nickel, cobalt and zinc are more mobile than copper (Figures 3.4 to 3.6). Cobalt carbonate precipitation at pH 8 is the only solid formation predicted for these metals.

This particular model ignores the presence of complexing organics and adsorbing surfaces. Complexing organics would tend to maintain higher concentrations of copper in solution while the presence of surfaces such as SiO_2, TiO_2, MnO_2 and FeOOH would tend to increase the removal of copper, nickel, cobalt and zinc from solution.

Table 3.7 Input data for REDEQL 2*

Parameter	CONC(mgl^{-1})	conc M	-Log (CONC M)
SO_4	538	5.604 x10^{-3}	2.251
Ni	37.4	6.371 x10^{-4}	3.196
Cu	22.7	3.575 x10^{-4}	3.447
Zn	0.24	3.671 x10^{-6}	5.435
Co	1.16	2.138 x10^{-5}	4.670
Fe^{3+}	1.19	2.128* 10^{-5}	4.672
Fe^{2+}	$2.73 \mathrm{x} 10^{-3}$	4.909* 10^{-8}	7.309
Ca	84.6	2.110* 10^{-3}	2.676
Mg	84.4	3.473* 10^{-3}	2.459
Cl	6.57	1.853* 10^{-4}	3.732
Mn	10.2	1.857* 10^{-4}	3.731
Cr	0.077	1.481* 10^{-6}	5.830

pE = 4.0

$Fe^{2+} = Fe^{3+} + e^-$ redox considered

ionic strength calculated within program

Variable Conditions

	USSa	USSb	USSc
pH	4.5	7.0	3.5-8.0
C_t:M* 10^{-5} mgl^{-1} as $CaCO_3$	0.001-20	0.001-20	2.0

* inorganic model, no organic ligands were included since dissolved organic carbon concentrations were essentially zero in field samples.

Table 3.8

Precipitate formation predicted by REDEQL 2

MODEL USSb pH 7.0

$C:\underline{M}*10^{-5}$	PRECIPITATE FORMED:	(MOLE/L)*10 5		Cu in Solution mgl^{-1}
	$Cu(OH)_2$	$Cu_2(OH)_2CO_3$	$Fe(OH)_3$	
0.001	34.0	0	2.13	1.11
0.0032	34.0	0	2.13	1.11
0.01	34.0	0	2.13	1.11
0.01	34.0	0	2.13	1.11
1	32.5	0.784	2.13	1.07
10	14.5	9.78	2.13	1.07
20	0	17.6	2.13	0.348

Model USSc $C_t = 2* 10^{-5}\ \underline{M}$

pH	PRECIPITATE FORMED: MOLE/L $^{1}*10^{5}$				mgl^{-1} in solution	
	$Cu(OH)_2$	$Cu_2(OH)_2CO_3$	$Fe(OH)_3$	$CoCO_3$	Cu	Co
3.5	0	0	0	0	22.7	1.26
4.0	0	0	0	0	22.7	1.26
4.5	0	0	0	0	22.7	1.26
5.0	0	0	0	0	22.7	1.26
5.5	0	0	0	0	22.7	1.26
6.0	0	1.67	1.86	0	20.6	1.26
6.5	22.6	1.91	2.12	0	5.92	1.26
7.0	30.5	1.36	2.13	0	1.07	1.26
7.5	32.1	1.36	2.13	0	0.589	1.26
8.0	34.9	0	2.13	0.949	0.538	0.701

Figure 3.3

USSC MODEL FOR SPECIATION OF METALS

COPPER

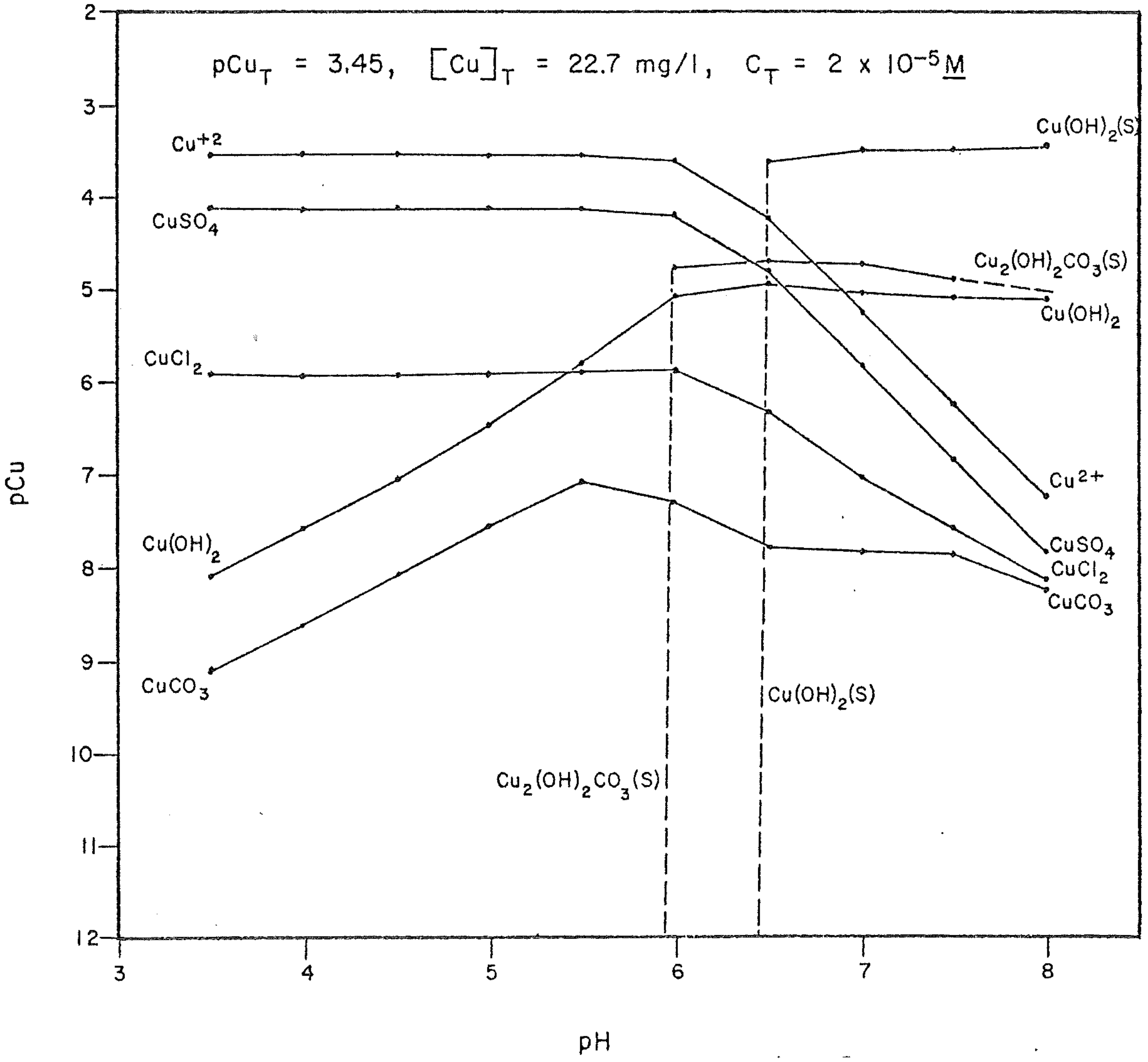


Figure 3.4

USSC MODEL FOR SPECIATION OF METALS

NICKEL

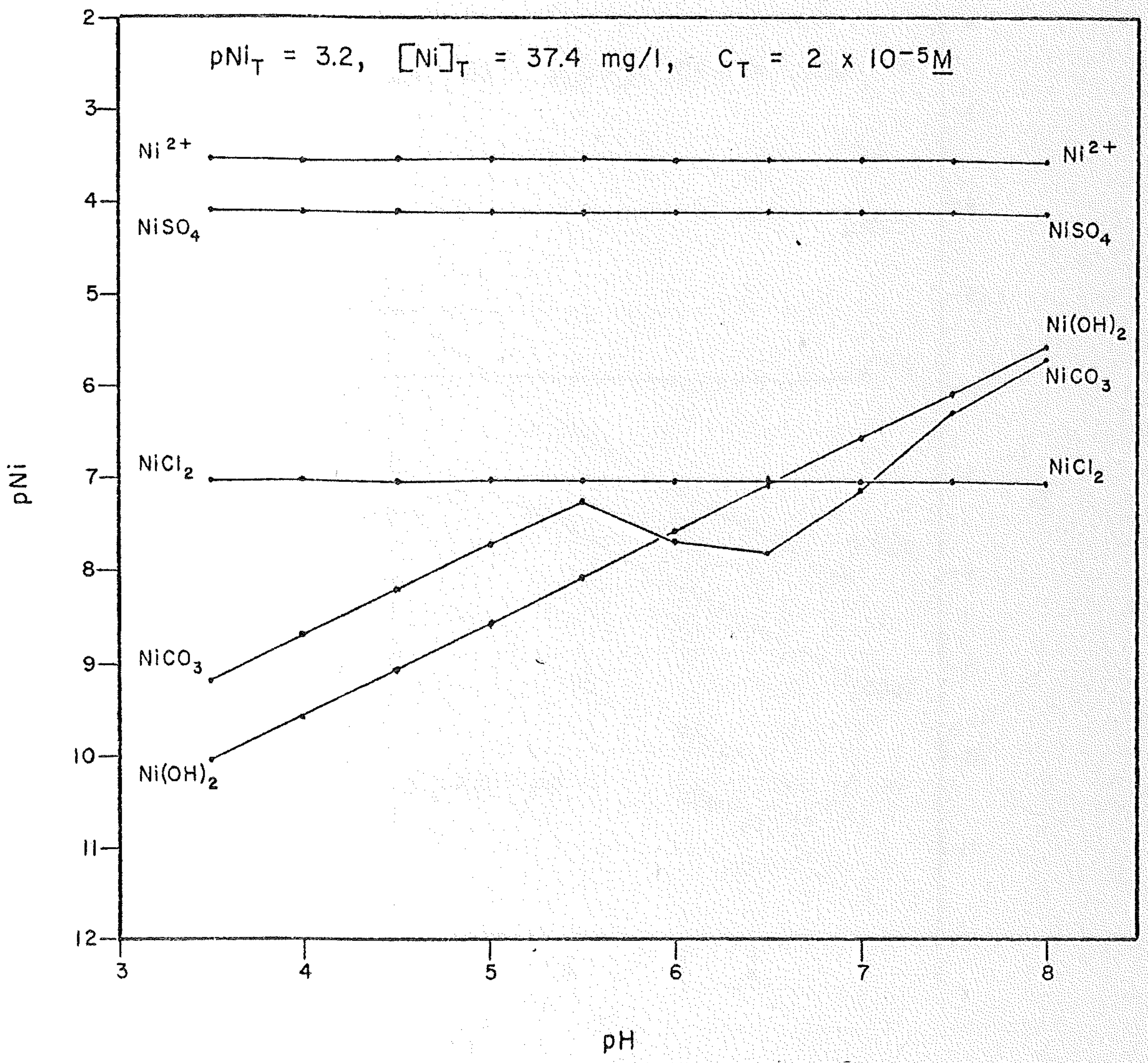


Figure 3.5

USSC MODEL FOR SPECIATION OF METALS

COBALT

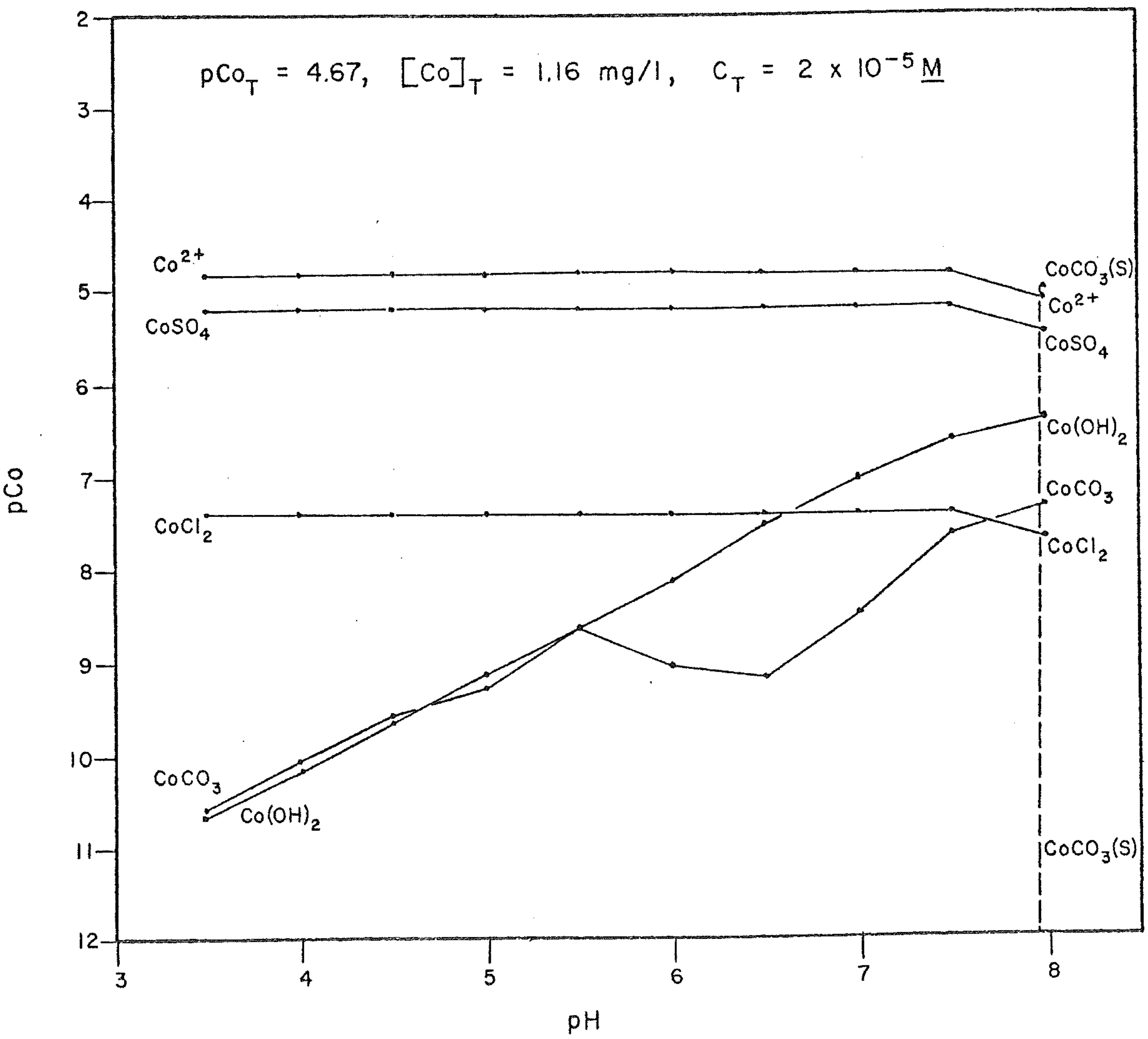
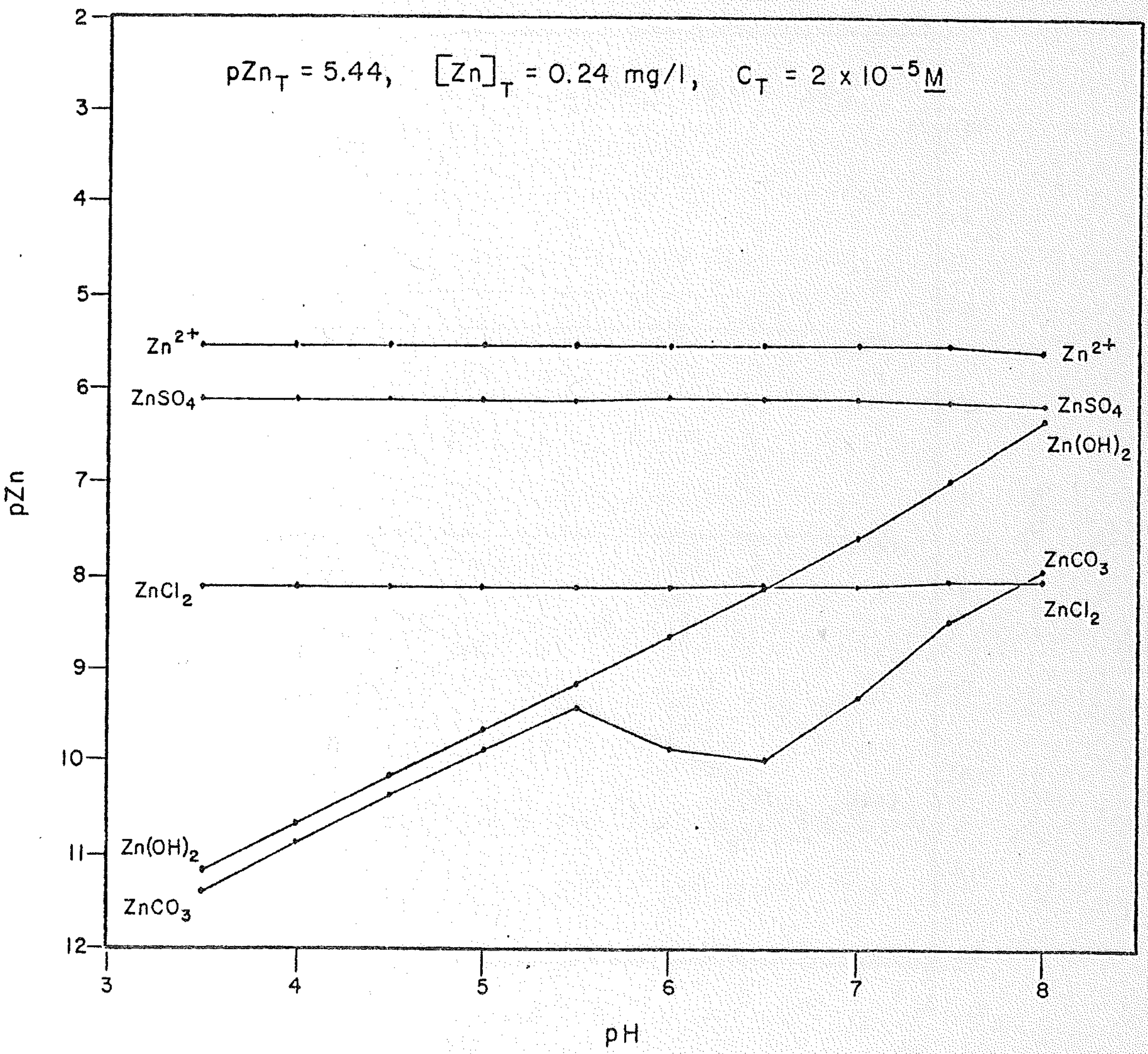


Figure 3.6

USSC MODEL FOR SPECIATION OF METALS

ZINC



3.4 Experimental methods

Laboratory studies are presented in four parts for discussion of both experimental procedures and results. The experimental divisions are:

1) batch reactor leaching of unmineralized and mineralized gabbro
2) column leaching of unmineralized and mineralized gabbro
3) batch reactor leaching of tailings
4) the environmental leaching test (ELT) which compared the leaching behavior of various solids, both host rock and tailings

3.4.1 Batch reactor leaching of unmineralized and mineralized gabbro

d<0.074mm (-200 mesh),were placed into well-mixed reactors at loadings from 2 to 100 gl^{-1}. Air was introduced to reactors through gas dispersion tubes. Solid phase and solution phase characteristics were varied to investigate their effects.

Solid phase variations included:

1) Solids loading.

   Unmineralized gabbro loadings of 2, 10, 50 and 100 gl^{-1} were used to investigate the variation of leaching with loading.

2) Particle size.

   Four size fractions with estimated surface areas and chemical composition are presented in Table 3.9. The specific surface areas were obtained using the slope, k, of the size distribution curves of the individual fractions in the equation.

$S_{r_1}^{r2} = \frac{3k}{\gamma} \ln \frac{r2}{r1}$, where $S_{r_1}^{r^2}$ is the surface area of particles of radius r, and $r_1<r<r_2$. (3.113)

The initial estimate was multiplied by a correction factor. The correction factor was the ratio of -200 mesh fraction surface area as determined by the Fisher Sieve Sizer to the mathematical estimation (C_f = 1.9).

Table 3.9 Chemical Composition of size fractions: all values in mg/(g gabbro)

DIAMETER (mm)	Surface Area (cm^2g^{-1})	Ni	Cu	Fe	Ca	Mg
$d \leq 0.074$	1700	3.55	14.1	172.	22.7	19.2
$0.074 < d \leq 0.42$	190	1.82	8.25	155.	16.6	18.2
$0.42 < d \leq 0.84$	62	4.52	12.8	259.	29.3	37.9
$0.84 < d \leq 2.38$	25	4.08	23.5	460.	47.3	80.2

3) Composition of gabbro.

Samples of unmineralized and mineralized gabbro were leached in batch reactors. The unmineralized rock sample was randomly selected from waste rock stockpile 8013 at the Erie Mining Company Dunka site. The mineralized sample (DP9002) was selected from the open pit wall at the Dunka site and represents an ore sample. Available chemical and mineralogical data are presented in Tables 3.1 and 3.2. Additional analyses of rock samples from the study area are presented by Stevenson et al. (1979).

Table 3.1 Chemical composition of gabbro (values in weight percent).

ELEMENT	UNMINERALIZED	(DP9002) MINERALIZED
S^b	1.1	3.92
Ni	0.095	0.36
Cu	0.24	1.4
Co^a	0.082	0.039
Zn^a	0.0009	0.012
Fe	10.4	17.2
Ca	2.6	2.3
Mg	2.0	1.9

[a] Neutron activation analyses.

[b] Analysis by MRRC.

Table 3.2 Mineral analysis of gabbro.

MINERAL	FORMULA	WEIGHTED MEAN VOLUME PERCENT Mineralized (DP 9002)
Pentlandite	$(Fe, Ni)_9S_8$	0.34
Chalcopyrite-Cubanite	$CuFeS_2$ - $CuFe_2S_3$	1.3
Pyrrhotite	Fe_7S_8 - FeS	3.1
Ilmenite Magnetite	$FeTiO_3$ Fe_3O_4	3.1
Olivine	$(Fe, Mg)\ Si_2O_6$	.11
Clinopyroxene	$Ca(Fe,Mg)Si_2O_6$	26
Orthopyroxene	$(Fe,Mg)_2Si_2O_6$	2.3
Plagioclase	$NaAlSi_3O_8$ - $CaAl_2Si_2O_8$	47

Variations in the aqueous phase composition included:

1) pH.

Two experiments were designed to investigate the effect of pH on leaching. In the first experiment varying amounts of acid were added in a single dose to 4 reactors containing unmineralized gabbro. Mineralized gabbro was used in the second experiment and the pH was regularly adjusted to 5, 6, 7, and 8 by addition of acid or base.

2) Dissolved oxygen (D.O.).

Dissolved oxygen concentration variation was attained by varying the flow of air, nitrogen and oxygen to four reactors containing mineralized gabbro. Gas flows were adjusted to achieve D. O. concentrations of 1, 5, 9.3 and 44 mgl^{-1}.

3) Ionic strength.

Sodium chloride concentrations of 0, 5×10^{-3} and 5×10^{-2} $\underline{M}$ were used to investigate the effect of ionic strength on the leaching of mineralized gabbro. A constant pH of 7 was maintained in all reactors.

4) Organics.

a. Citrate.

Citrate concentrations of 0, 1.29×10^{-4} and 1.29×10^{-3} $\underline{M}$ were used to investigate their effect on the leaching of unmineralized gabbro (2.86 gl^{-1}) at pH 7.

b. Phthalic acid.

Phthalic acid concentrations of 0, 1.29×10^{-4} and 1.29×10^{-3} $\underline{M}$ were used to investigate their effect on the leaching of mineralized gabbro (5.71 gl^{-1}) at pH 7.

c. Natural Waters.

The effects of bog water and ground water (collected from the study area) on the leaching of mineralized gabbro (5.71 gl^{-1}) were investigated. Abbreviated chemical analyses of the natural water are presented in Table 3.10.

Table 3.10 Natural concentrations in bog water and groundwater.

	Ni ug/1	Cu ug/1	Fe ug/1	Ca mg/1	Mg mg/1	SO_4 mg/1
Bog Water	1	3	160	7.8	8.9	3.9
Groundwater	4	4	37	18.9	10.2	6.4

Nickel and copper rates were calculated using concentrations observed during the first 50 hours of the experiment to minimize problems associated with subsequent metal removed. Nickel release was generally linear with time throughout the experiment. The concentration and time data were used to determine a linear equation of the form $(Me^{2+}) = at + b$ using the curve fitting program for the HP-97 calculator. Rate constants for nickel were calculated for all experiments. Rate constants for copper were calculated only for those reactors with pH $\leq$ 6 or reaction solution containing citrate. Copper release rates for other reactors were not calculated due to prohibitively low copper concentrations ($Cu < 0.005$ mgl^{-1}).

Sulfate release rates were calculated assuming linear release for $t > 150$ hours.

Calcium and magnesium release were fitted to the power equation $\left[Me^{2+}\right] = kt^n$ (Figure 3.7) using the curve fitting program for the HP-97. All data points in a given experiment were using. The slope of the curve varies with time and the slope at t = 500 hours was used as the linear release rate ($\frac{dc}{dt} = nkt^{n-1}$). This time was chosen as being representative of the steady-state linear release rate described in literature on silicate dissolution (Busenberg and Clemency, 1976).

3.4.2 Column leaching

The column leaching experiment was designed to investigate particular effects of solid and solution phase variation. Three kilograms of gabbro ($0.25 < d < 0.64$ cm) were placed into a column (d=5cm, 1=100cm) and subjected to a slow flow (approximately 150 ml day^{-1}) of various solutions. Three solutions (Table 3.11) were prepared to represent groundwater, surface water and rainwater (mega pure water). Both an unmineralized (DP9001) and mineralized sample (DP9002) were subjected to each of the leaching solutions (Tables 3.1, 3.2 and Stevenson et al. 1979).

Data collected on sample concentration, volume and time over the entire experiment were used to determine a relationship between cumulative mass leached and time. The curve fitting program of the HP-97 was used to determine the constants (a,b) for the best fit of the equation $M = at + b$ where M represents cumulative mass released and t is time. With the exception of some cases of copper and iron release, elemental release data agreed very well with the linear release concept.

Figure 3.7

[Ca] & [Mg] VS TIME

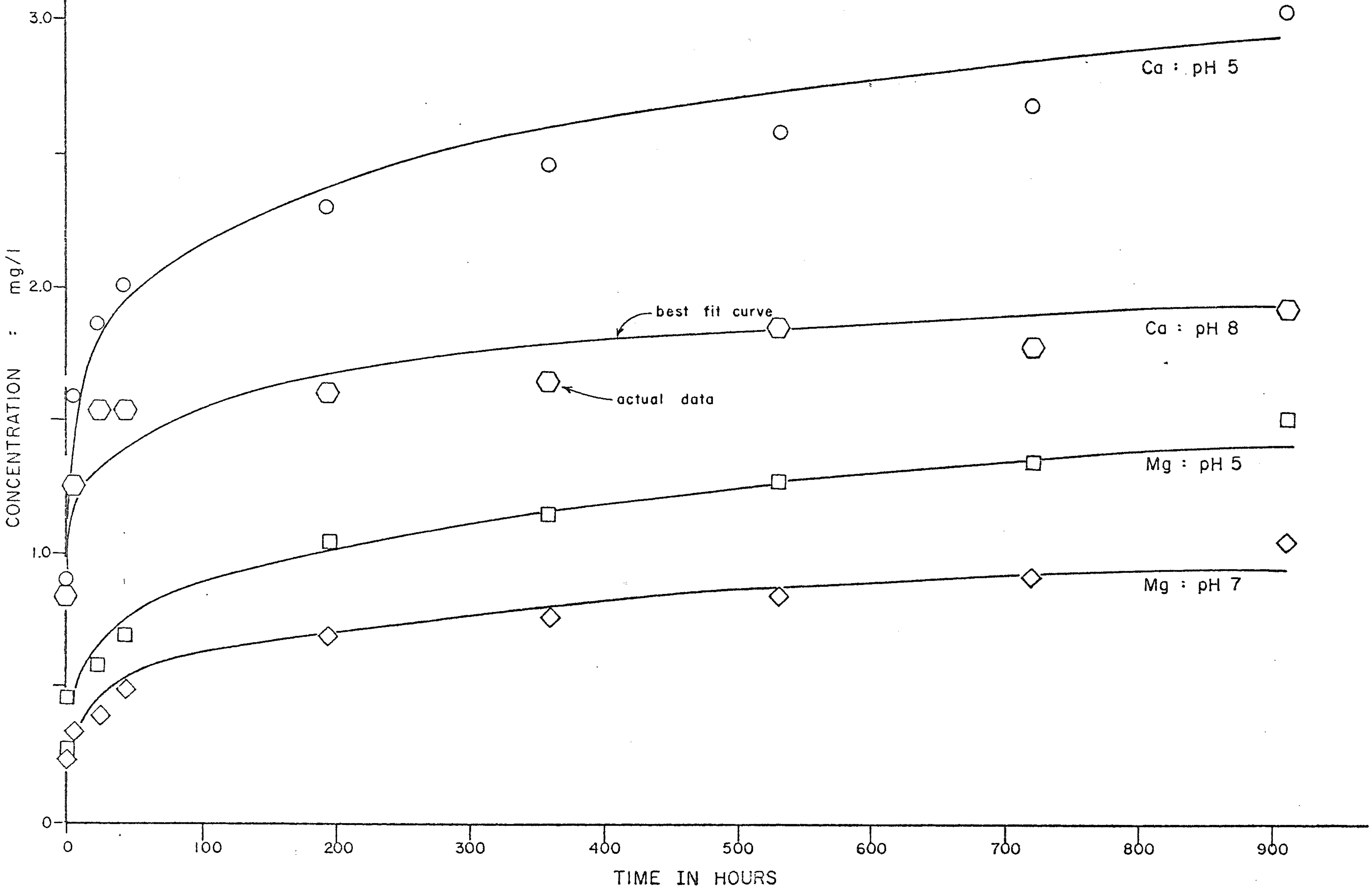


Table 3.11 Composition of synthetic groundwater and surface water

Concentrations in mgL^{-1}

COMPONENT	GROUNDWATER	SURFACE WATER
Na^+	24.5	11.2
K^+	2.0	2.0
Ca^{2+}	15	8.2
Mg^{2+}	25	5.0
HCO^-	46	25
$SO_4^=$	36	11.3
Cl^-	1.8	8.0
SiO_3 = (As Si)	5	4.0
NO_3^-	129	26
$PO_4^=$ as $PO_4^=$	0.5	0.5
Tannic Acid (as C)	0	10.0
Citric Acid (as C)	0	5.0

3.4.3 Batch reactor leaching of tailings

The leaching of tailings was studied under batch reactor conditions. Five reactors, each containing 100 g of -200 mesh tailings and two - liters of water, were employed to determine the effects of pH and natural water on metal release. The pH in two reactors was adjusted to 4 and 6, natural bog water and groundwater were used in two additional reactors with no pH adjustment, the fifth reactor was run as a control. Initial concentration of particular components in the natural waters are presented in Table 3.12. Reactors ran continously for 532 hours after which the solids were removed and air dried in a dessicator for 7 days. They were then returned to a fresh solution at the same solids to liquid ratio for an additional 190 hours.

Table 3.12 INITIAL CONCENTRATIONS (mgl^{-1}) in BOG WATER AND GROUNDWATER

	Ni	Cu	Fe	Ca	Mg	SO_4
BOG WATER	0	0.003	0.160	7.8	8.9	3.9
GROUNDWATER	0.004	0.004	0.037	18.9	10.2	6.4

3.4.4 Environmental leaching test

The environmental leaching test (ELT), developed by Professor S. Eisenreich, was designed to compare the leaching behavior of various solids, both host rock and tailings, under "worst case" and "probable " environmental conditions.

Selected metal release was determined following a 100 hour equilibration of finely ground ($d < 0.074$ mm) solid sample in:

a) a dilute sulfuric acid (H_2SO_4) solution at pH 3.5 ("worst case"), and,

b) a synthetic natural water (Table 3.13) at pH 7 ("probable case") under oxidizing conditions. The solid to solution ratio was 10 grams of -200 mesh solid per 100 ml solution.

Table 3.13 Chemical Composition of Synthetic Natural Water

1. Component	Concentration
Na^{+2}	11.2 mg/l
K^{+2}	2.0
Ca^{+2}	8.2
Mg^{+2}	5.0
HCO_3^-	25
$SO_4^=$	11.3
Cl^-	8.0
Si	4.0 as Si
Tannic Acid	10.0 as DOC
Citric Acid	5.0 as DOC
NO_3^-	26
PO_4^{-3}	0.5 as PO_4

3.5.1 Effect of pH

Release rates from mineralized gabbro were determined for SO_4, Cu, Ni, Ca and Mg over the pH range $5 \leq pH \leq 8$. For all parameters the rate of release increased with decreasing pH. The calculated rates are presented in Table 3.14.

Metal Sulfide Leaching

The rate of appearance of sulfate in solution increased with decreasing pH, as depicted in Figure 3.8. The dependence on (H^+) in the range $5 \leq pH \leq 8$ is described mathematically as

$$\frac{d(SO_4^=)}{dt} \;\alpha\; (H+)^{0.17},\; r^2 = 0.833. \qquad (3.14)$$

Examination of Figures 3.8 and 3.9 indicates that the pH dependence in the pH region 5 to 6 may be significantly different from that in the region 6 to 8. If this distinction is made the dependence on (H^+) for the two regions is

$$\frac{d(SO_4^=)}{dt} \;\alpha\; (H+)^{0.38} \quad \text{for } 5 \leq pH \leq 6, \text{ and} \qquad (3.115)$$

$$\frac{d(SO_4^=)}{dt} \;\alpha\; (H+)^{0.077} \quad \text{for } 6 \leq pH \leq 8 \qquad (3.116)$$

The rate of appearance of nickel in solution is presented in Figure 3.10, which indicates a general trend of increasing release with decreasing pH. This trend appears to reverse itself with release decreasing from pH 6 to pH 5 although the release rate during the first 25 hours is greatest at pH 5. A plot of k_{Ni} vs pH (Figure 3.11) indicates a dependence expressed as

$$k_{Ni} \;\alpha\; (H+)^{0.13},\; r^2 = 0.96 \qquad (3.117)$$

In a second experiment, with lower pH, the appearance of nickel decreased with decreasing pH in the range $4.0 \leq pH \leq 4.7$ (Figure 3.12).

Table 3.14 Rates as a function of pH: mole/cm^{2}min

				t = 1 hour		t = 500 hours	
pH	$SO_4^=*10^{13}$	$Cu*10^{15}$	$Ni*10^{14}$	$Ca*10^{12}$	$Mg*10^{12}$	$Ca*10^{14}$	Mg*10
5	4.9	9.2	4.2	6.7	4.9	3.2	4.2
6	2.1	1.8	3.3	6.3	4.2	3.5	3.9
7	1.7	0.66	2.0	4.6	3.5	1.7	2.4
8	1.4	0.11	1.8	3.9	3.1	1.5	1.7

Figure 3.8

$[SO_4^{=}]$ VS TIME : EFFECT OF pH

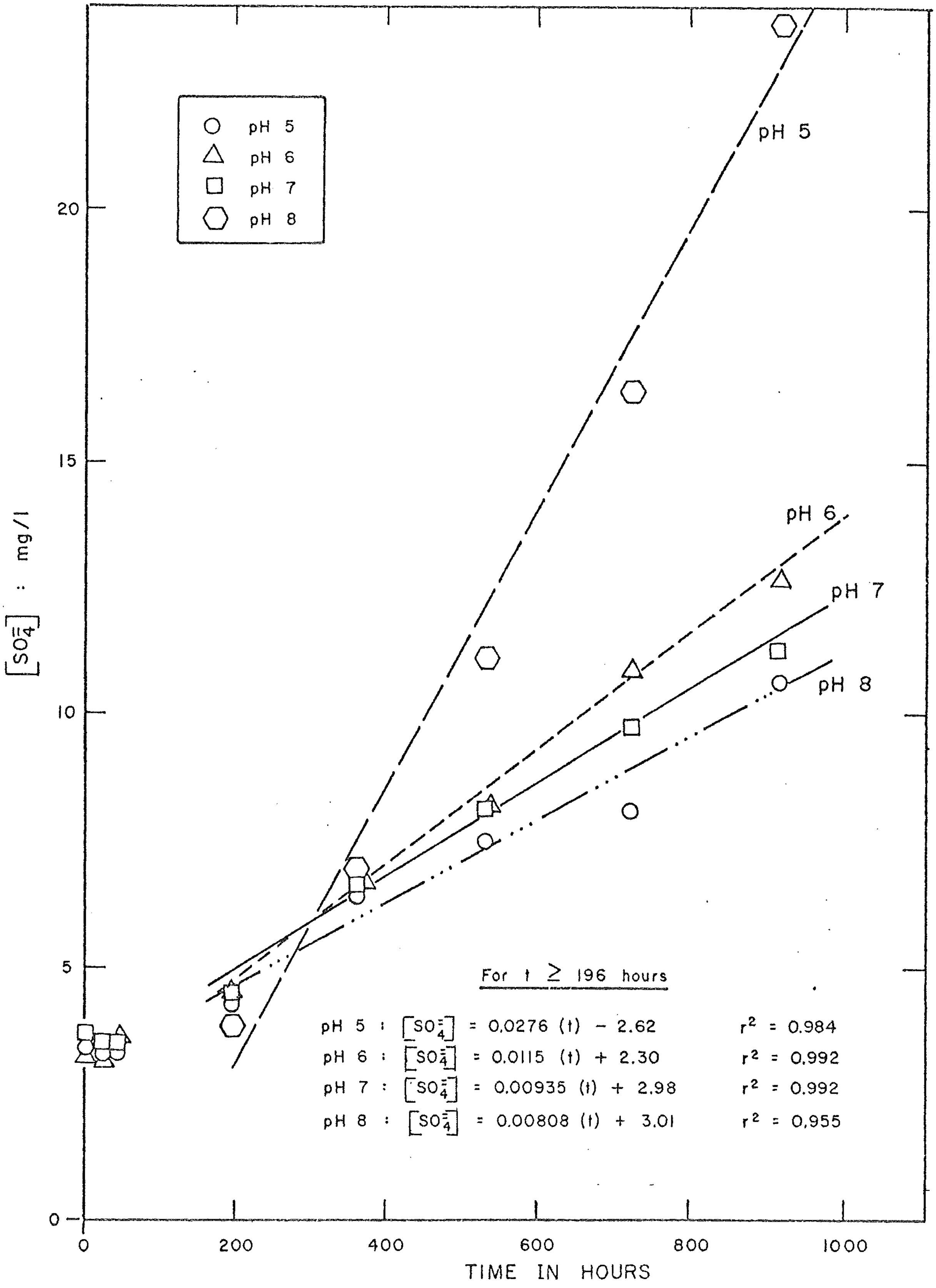
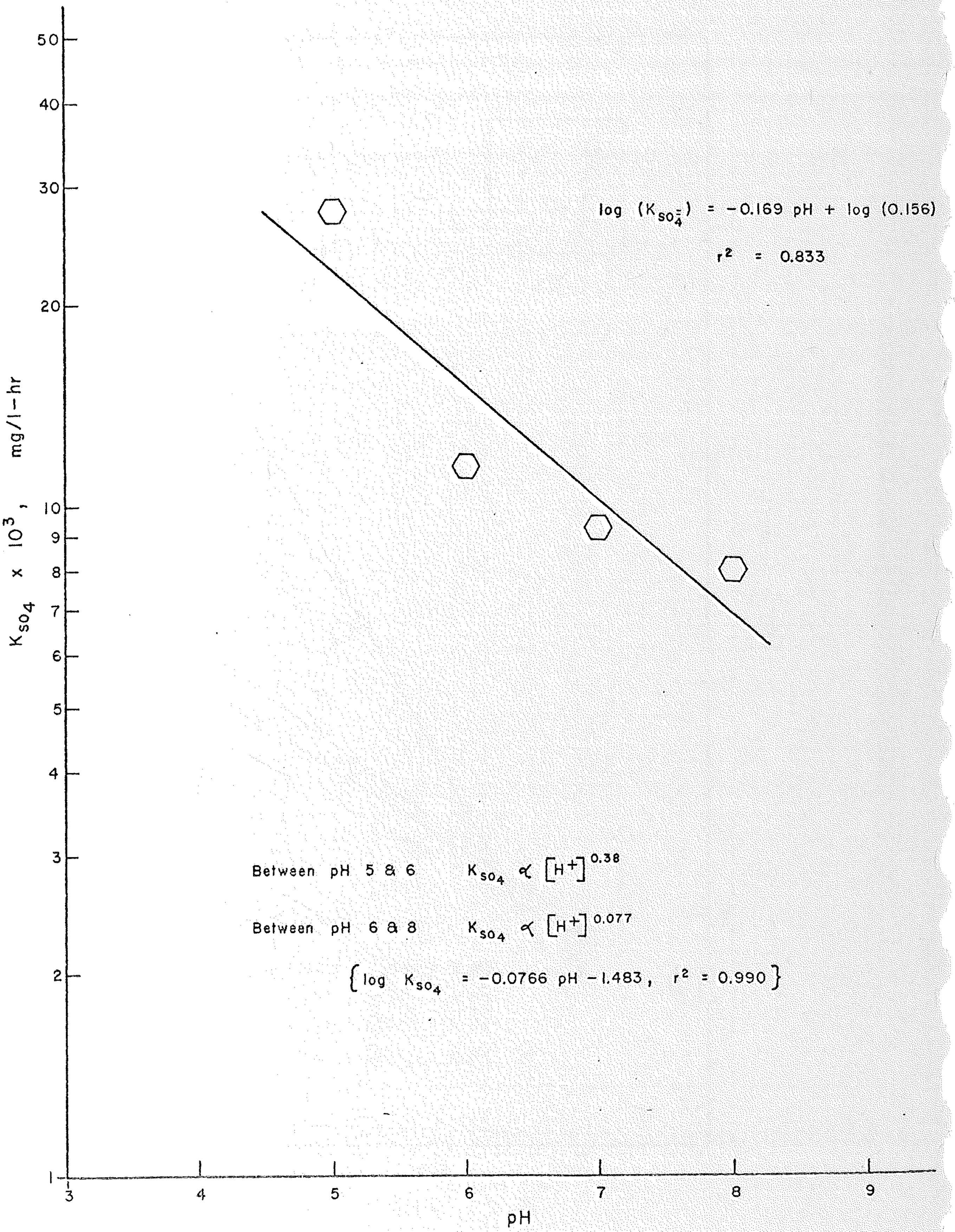


Figure 3.9

Log K_{SO_4} VS pH



$\log (K_{SO_4^=}) = -0.169\ \mathrm{pH} + \log (0.156)$

$r^2 = 0.833$

Between pH 5 & 6 $K_{SO_4} \propto [H^+]^{0.38}$

Between pH 6 & 8 $K_{SO_4} \propto [H^+]^{0.077}$

$\left\{ \log K_{SO_4} = -0.0766\ \mathrm{pH} - 1.483,\ r^2 = 0.990 \right\}$

Figure 3.10

EFFECT OF pH ON NICKEL RELEASE

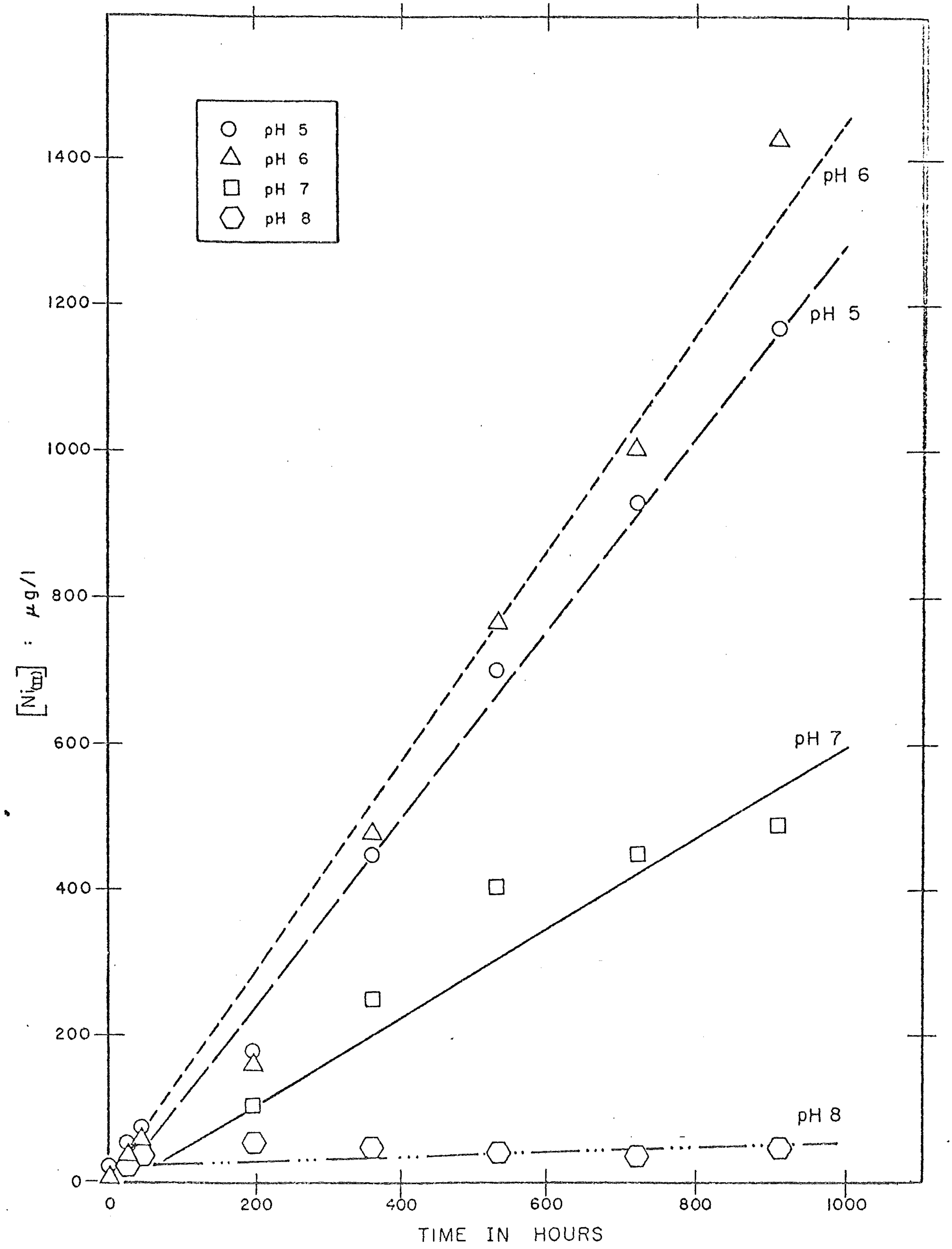


Figure 3.11

Log K_{Ni} VS pH

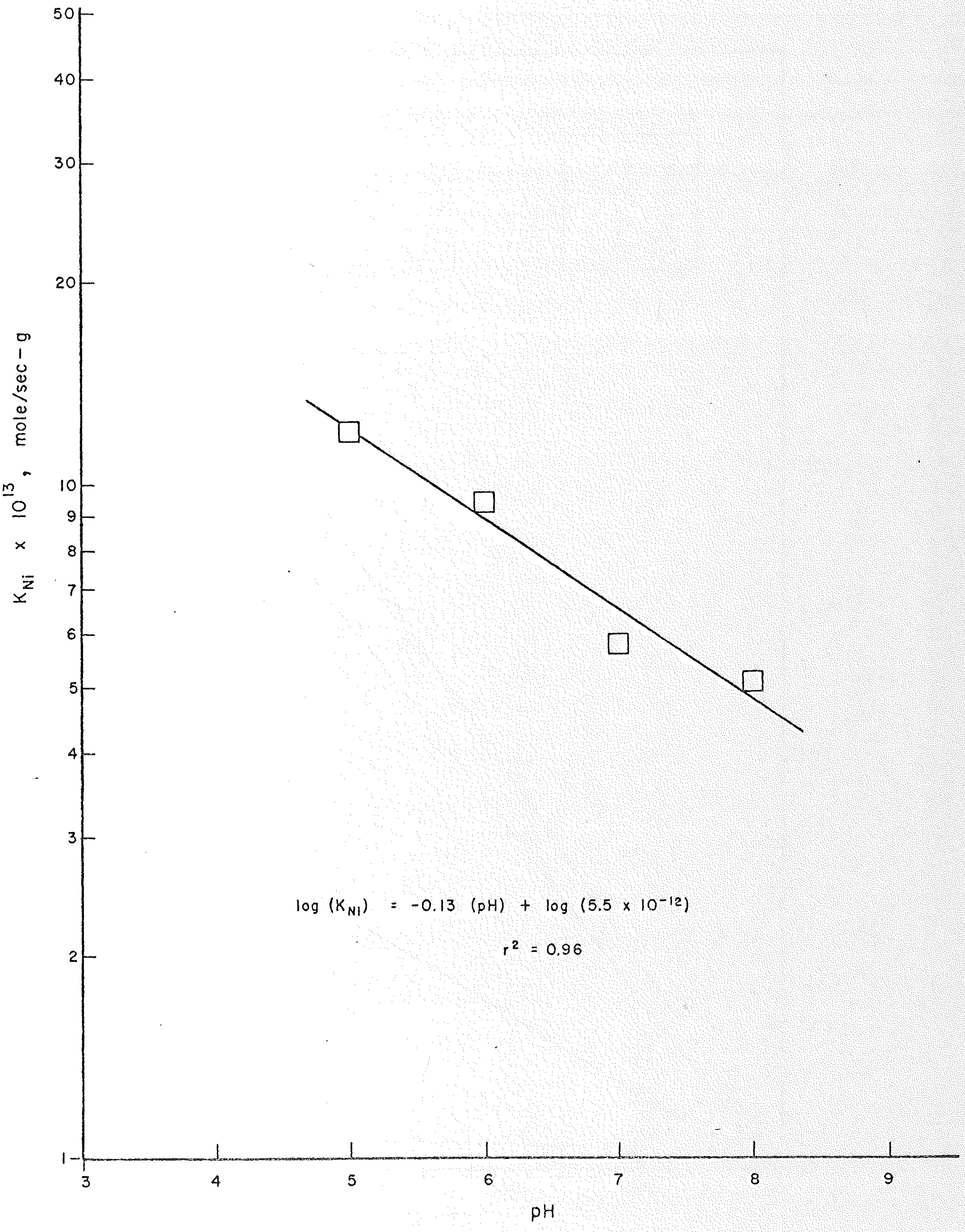
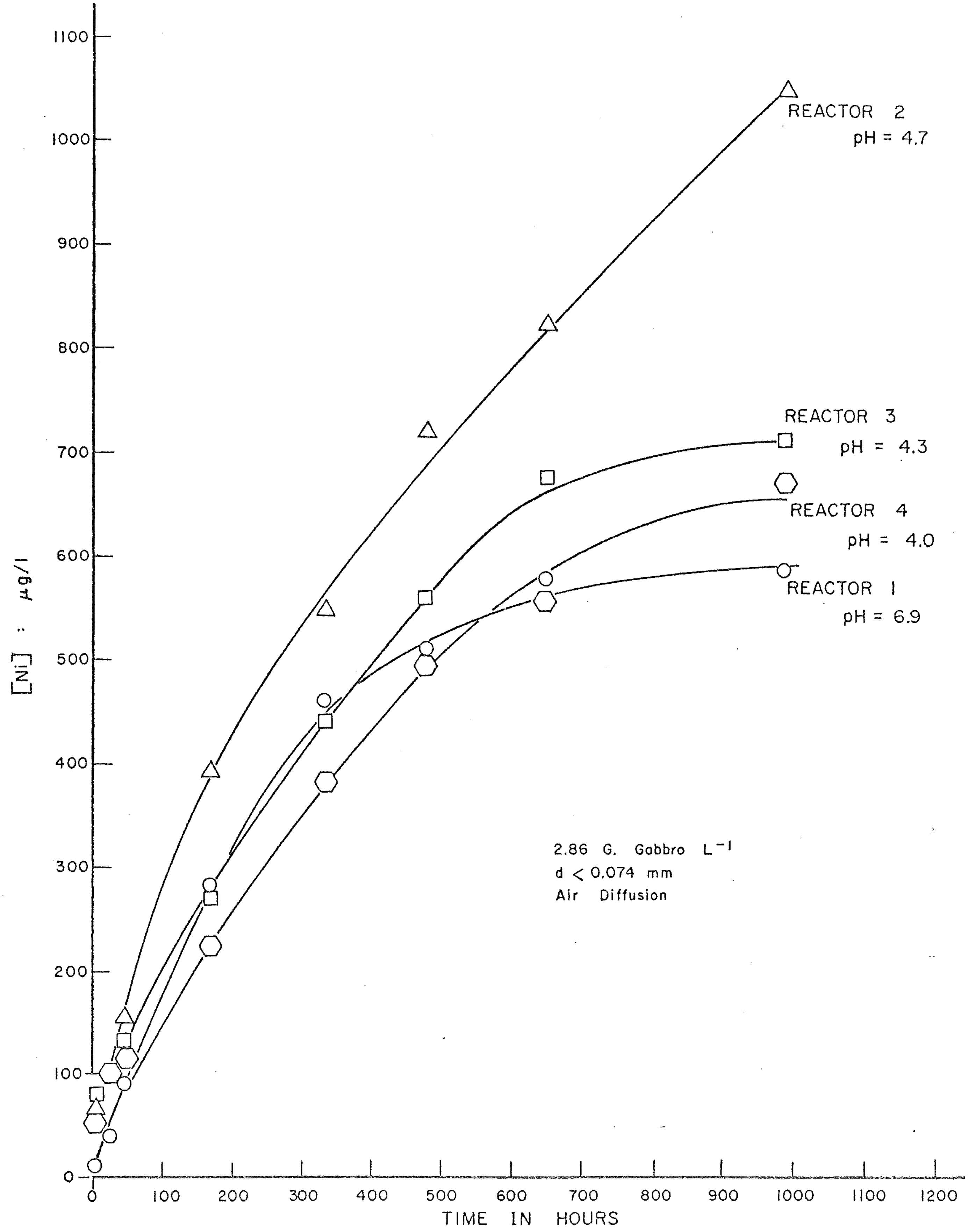


Figure 3.12

EFFECT OF pH ON UNMINERALIZED GABBRO

[Ni] VS TIME



The appearance of copper in solution for $5 \leq pH \leq 8$ is presented in Figure 3.13. The rate is more highly dependent on (H^+) than that of nickel or sulfate (Figure 3.14:

$$k_{Cu} \propto (H^+)^{0.62}, \quad r^2 = 0.995. \qquad (3.118)$$

Results from an experiment at lower pH indicate that copper release did not stictly increase with decreasing pH. Figure 3.15 shows that as pH decreased below 4.3 the rate of copper appearance in solution also decreased.

The variation of pH affected the ultimate phase distribution of metals released from the mineral phase. Figure 3.16 (constructed from data in Table 3.16) presents the results of adsorption tests conducted at the end of the experiment and indicates an increase in the solid phase fraction with increasing pH.

The rate of appearance of nickel and copper in solution was dependent upon both the initial dissolution of the sulfide mineral phase and subsequent reactions such as precipitation and adsorption. The appearance of sulfate in solution indicated an increase in the rate of sulfide oxidation with decreasing pH. The pH dependence of nickel was similar to that of sulfate (Table 3.15) suggesting that the secondary reactions were of lesser importance in nickel leaching. Data from Table 3.16 support this conclusion, indicating that the secondary reactions are dominant only at pH 8. Results from REDEQL 2 provide further support, predicting nickel removal only at pH 8.

The pH dependence of copper release was a function of reactions subsequent to the dissolution of the copper sulfide minerals. Data from Table 3.16 indicate dissolution of copper sulfide was relatively constant with pH but that copper in the aqueous phase decreased with

Figure 3.13 Cu vs time: Effect of pH

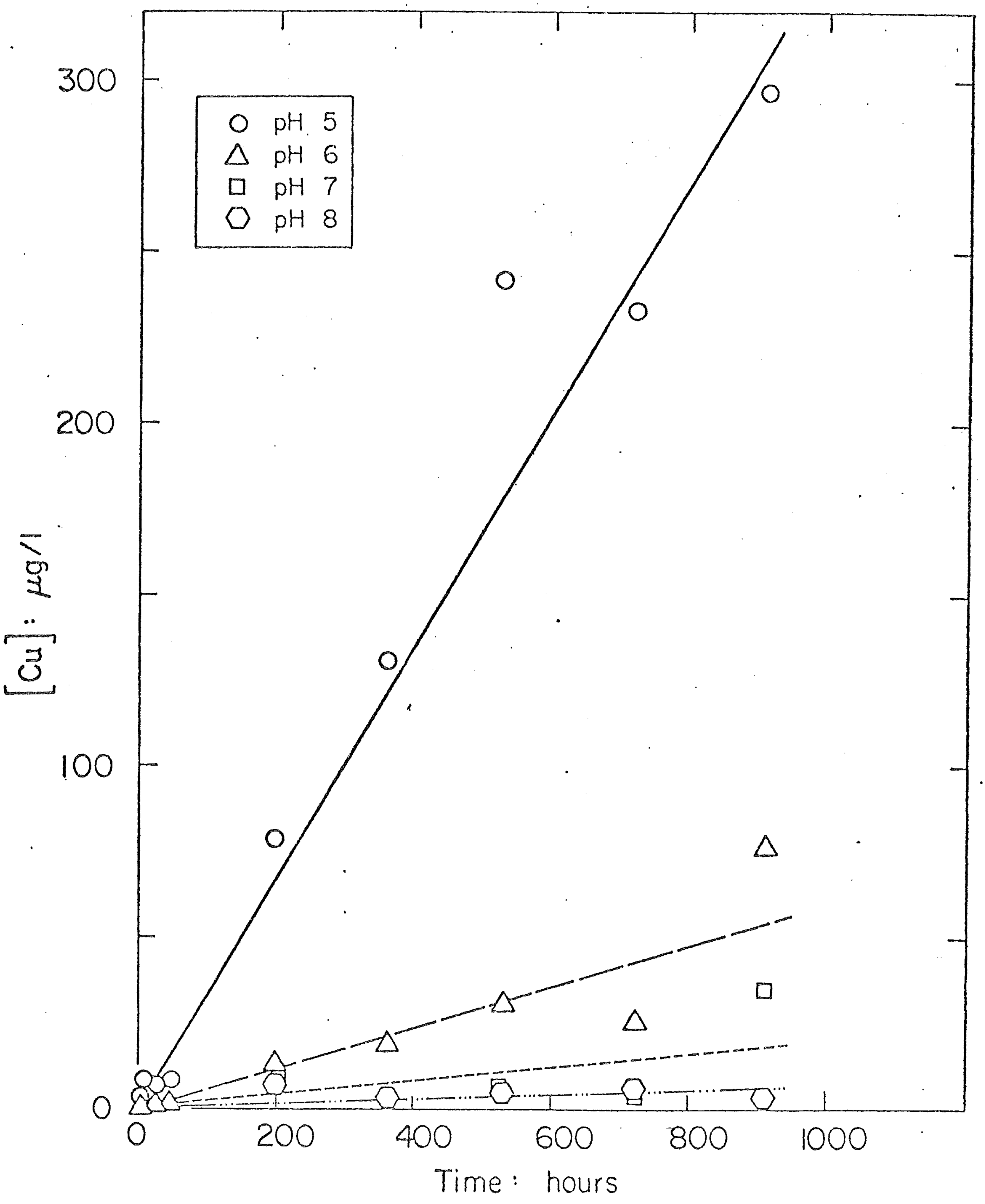


Figure 3.14

Log K_{Cu} VS pH

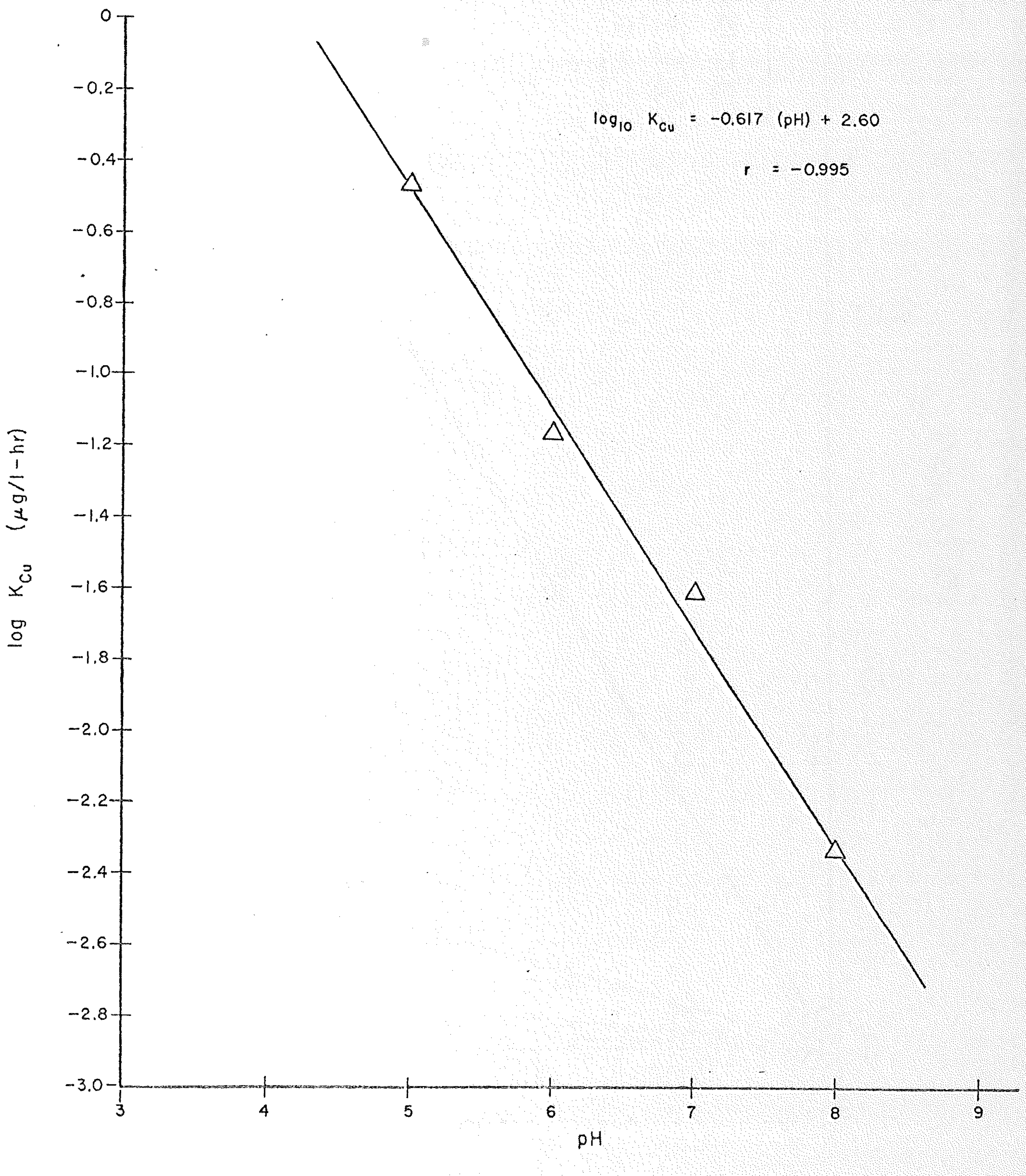


Figure 3.15

EFFECT OF pH ON UNMINERALIZED GABBRO
[Cu] VS TIME

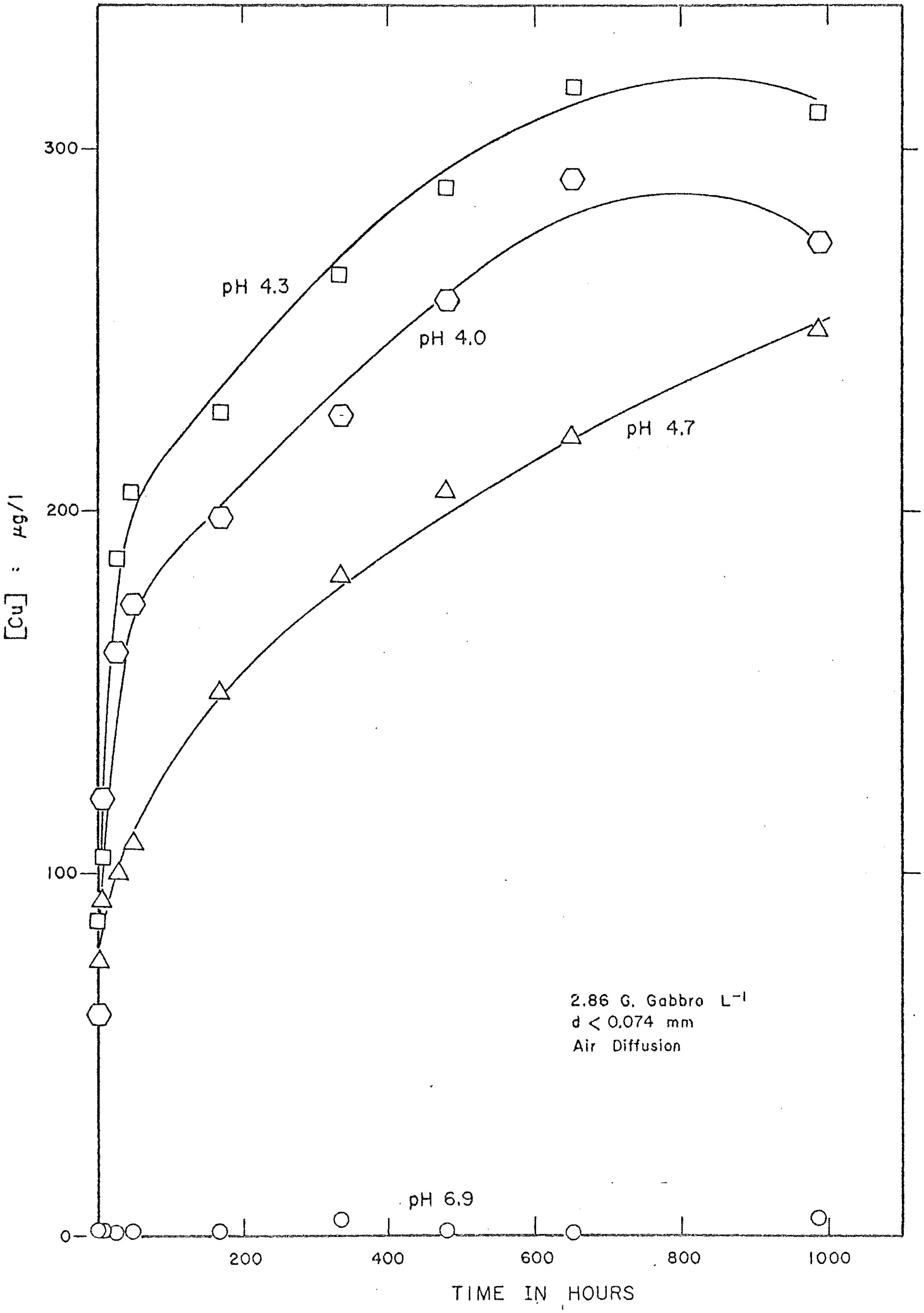


Figure 3.16. Phase distribution of metals released from mineral phase vs pH

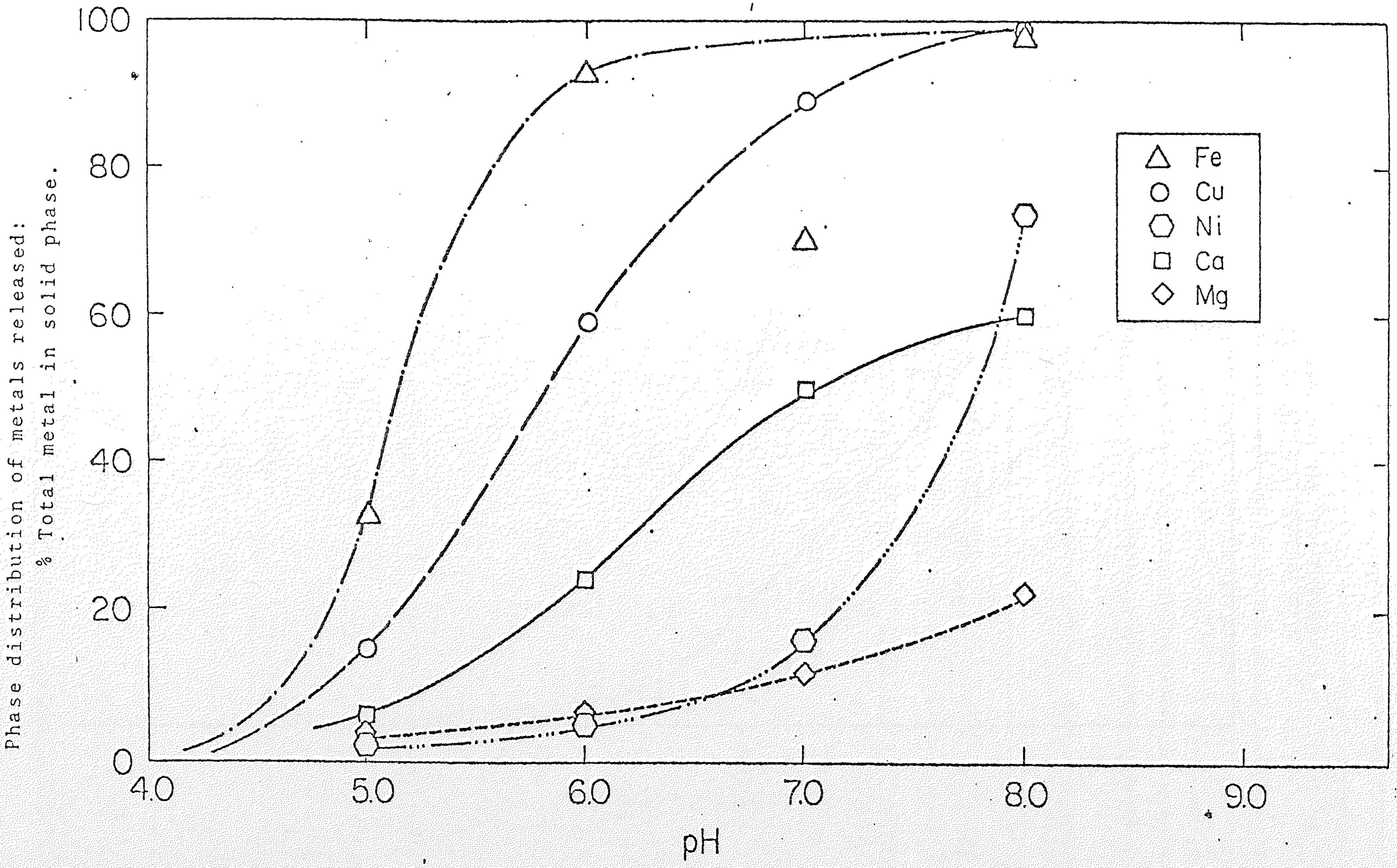


Table 3.15 Dependence of release rate on (H^+): $5 \leq \text{pH} \leq 8$

$k_x \alpha (H^+)^B$

PARAMETER	B	r^2
SO_4	0.17	0.83
Ni	0.13	0.96
Cu	0.62	0.99
Ca(t=1 hr)	0.085	0.94
Mg(t=1 hr)	0.069	0.99
Ca(t=500 hr)	0.13	0.81
Mg(t=500 hr)	0.14	0.94

Table 3.16 Total Release: Effect of pH; Mineralized Gabbro
Ad: Adsorbed and Precipitated, Sol: In solution, Tot: Total Release
All Values in Moles *10^6 per gram gabbro

pH	Ni_{Ad}	Ni_{Sol}	Ni_{Tot}	Cu_{Ad}	Cu_{Sol}	Cu_{Tot}	Fe_{Ad}	Fe_{Sol}	Fe_{Tot}	Ca_{Ad}	Ca_{Sol}	Ca_{Tot}	Mg_{Ad}	Mg_{Sol}	Mg_{Tot}	$SO_{4\,Tot}$
5.0	0.04	2.3	2.3	0.10	0.55	0.65	0.65	1.8	2.4	0.57	10	11	0.24	8.3	8.5	31
6.0	0.16	2.8	2.9	0.20	0.13	0.34	0.66	0.10	0.77	2.9	10	13	0.41	7.4	7.8	18
7.0	0.19	1.0	1.2	0.56	0.06	0.61	1.1	0.39	1.5	6.5	7.8	14	0.71	5.7	6.5	16
8.0	0.21	0.09	0.30	0.67	0.01	0.68	1.3	0.07	1.4	8.4	6.9	15	1.1	4.7	5.8	15

increasing pH. The equilibrium distribution predicted by REDEQL 2 (Figure 3.17) indicates that copper removal from solution increased with increasing pH due to precipitation of malachite and adsorption onto the silicate surface.

The trends observed in the low pH experiments indicated that the oxidation of copper and nickel sulfides was inhibited at low pH values. This trend was also observed by Dutrizac and MacDonald (1974) and Correns and Scholtz (1976) for the leaching of pentlandite in acidified ferric sulfate solutions.

Silicate dissolution

Release of calcium and magnesium from silicate minerals increased with decreasing pH. The results for calcium release are presented in Figure 3.18.

A power equation of the form $c = kt^n$ was used to describe the appearance of calcium and magnesium in solution. The rate of release based on the power equation is

$$\frac{dc}{dt} = nkt^{n-1} \tag{3.119}$$

and is dependent upon time. To account for the time dependence the rate was determined at 1 and 500 hours. These times were chosen to represent the initial stage and long term linear stage of reaction. The pH dependence of calcium and magnesium release were quite similar: at t = 1 hour

$$\frac{d(Ca^{2+})}{dt} \quad \alpha \quad (H^+)^{0.085} \tag{3.120}$$

$$\frac{d(Mg^{2+})}{dt} \quad \alpha \quad (H^+)^{0.069} \tag{3.121}$$

Figure 3.17

COPPER SPECIATION AS A FUNCTION OF pH

$pCu_T = 5.33$, $pC_T = 3.5$, $[ADSI] = 1\ m^2/l$

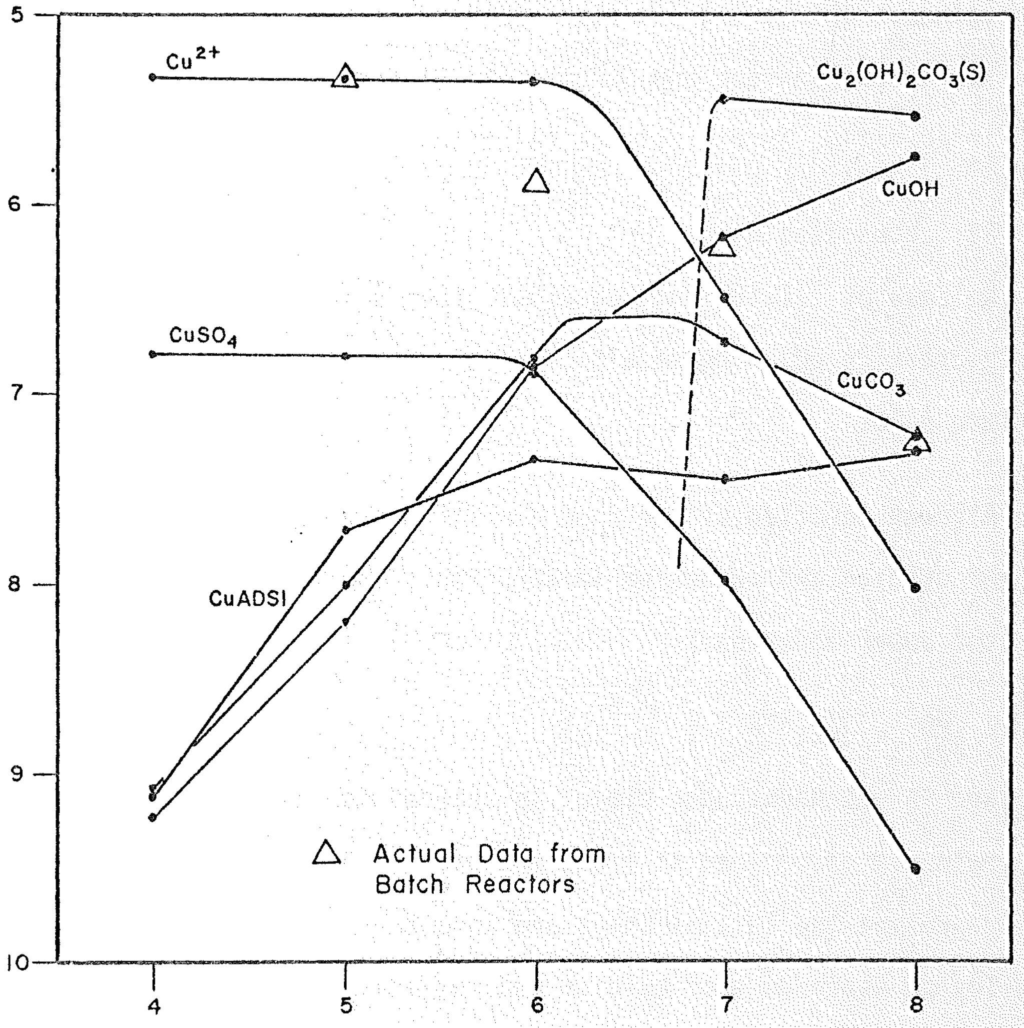
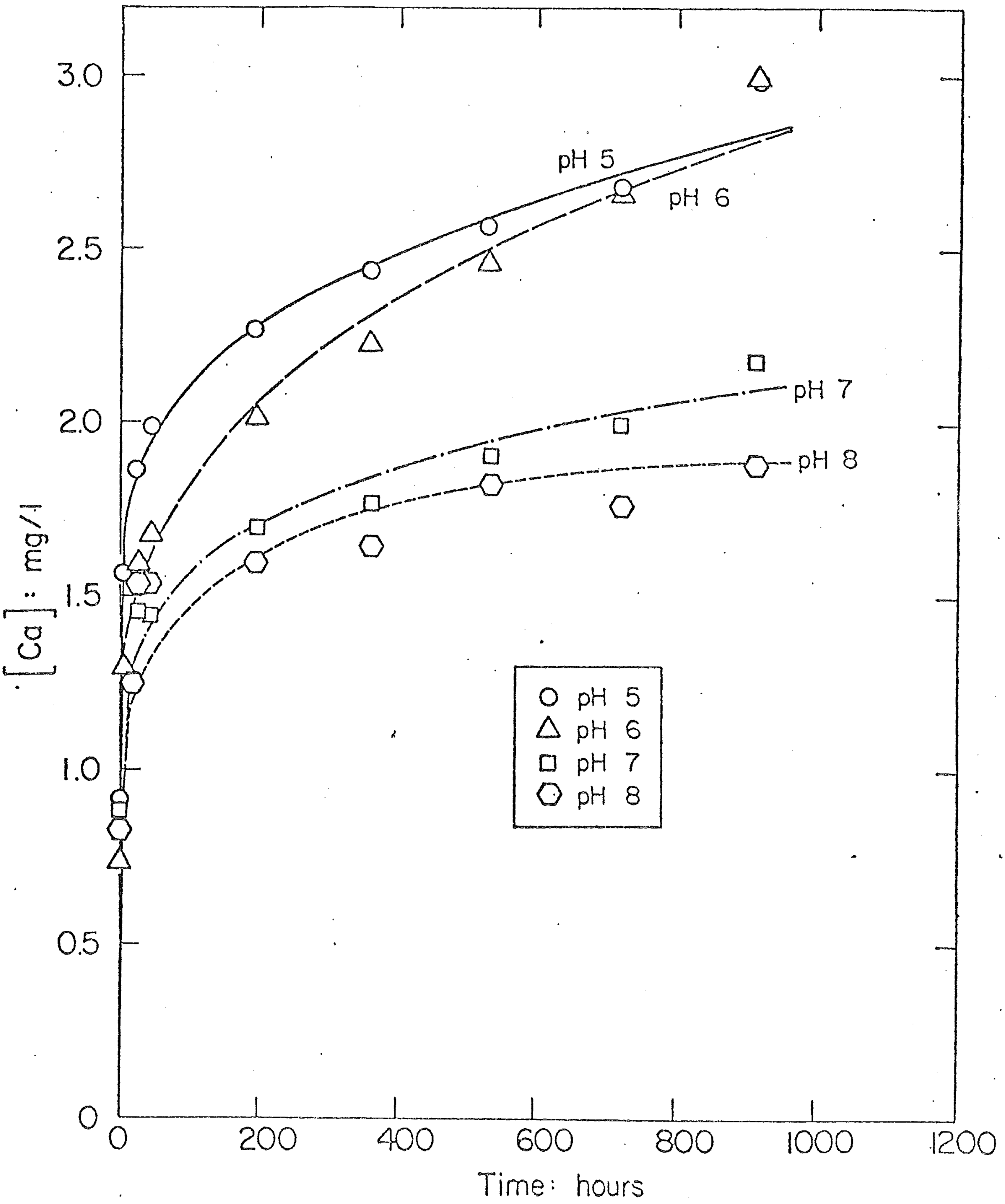


Figure 3.18 $\left[Ca^{2+}\right]$ vs Time: Effect of pH



and at t = 500 hours (see Figures 3.19 and 3.20)

$$\frac{d(Ca^{2+})}{dt} \qquad (H^+)^{0.13} \tag{3.122}$$

$$\frac{d(Mg^{2+})}{dt} \qquad (H^+)^{0.14} \tag{3.123}$$

The rates of calcium appearance at t = 500 hours (Table 3.17) were quite close to the value of $2.2 * 10^{-16}$ moles/cm^{2}sec determined by Busenberg and Clemency (1976) for the linear stage of anorthite dissolution. The pH dependence is consistent with observations reported in the literature on silicate dissolution.

Figure 3.19

$\left(\frac{d[Ca]}{dt}\right)$ VS pH at T = 1 hr. and T = 500 hrs.

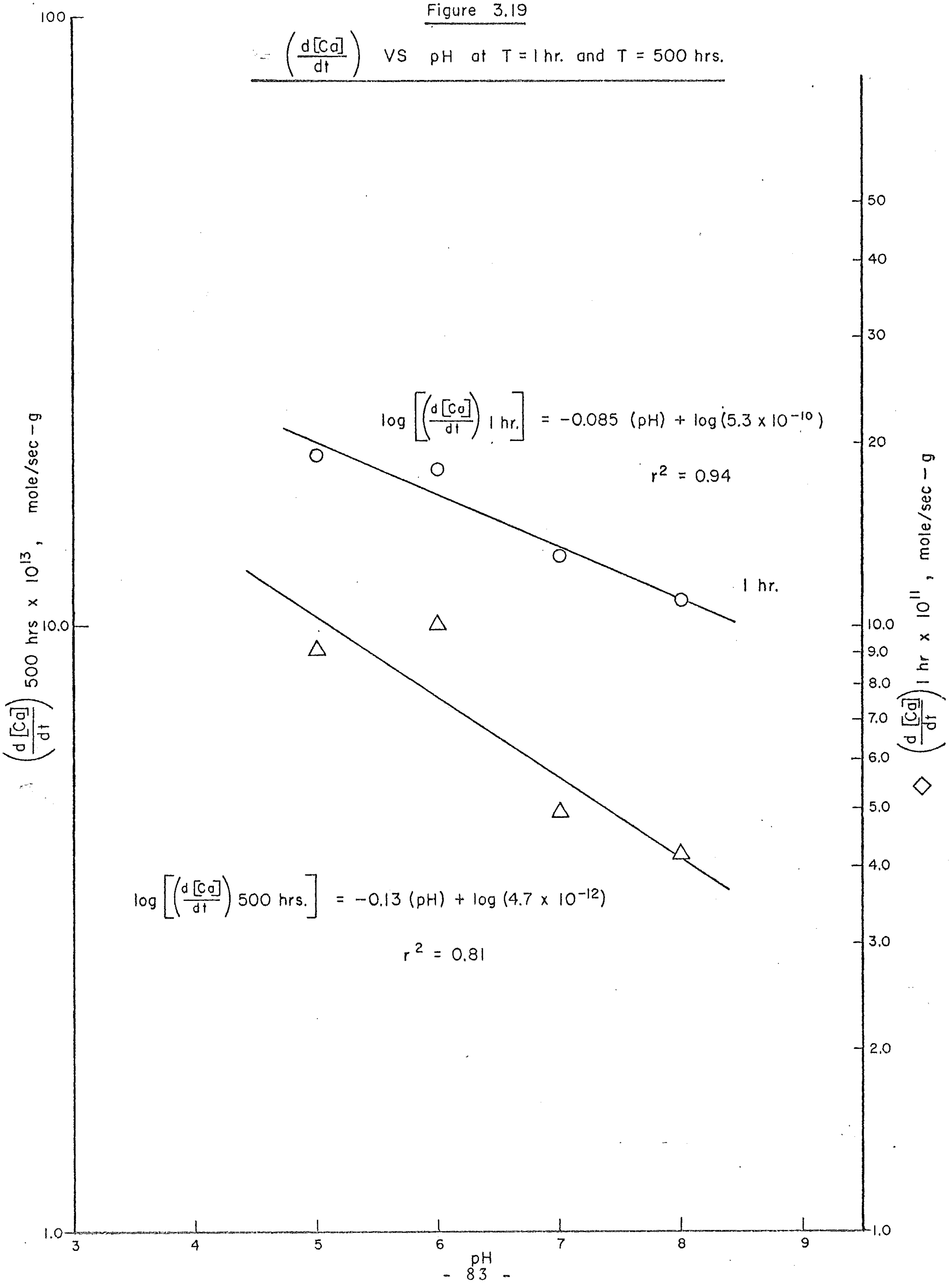
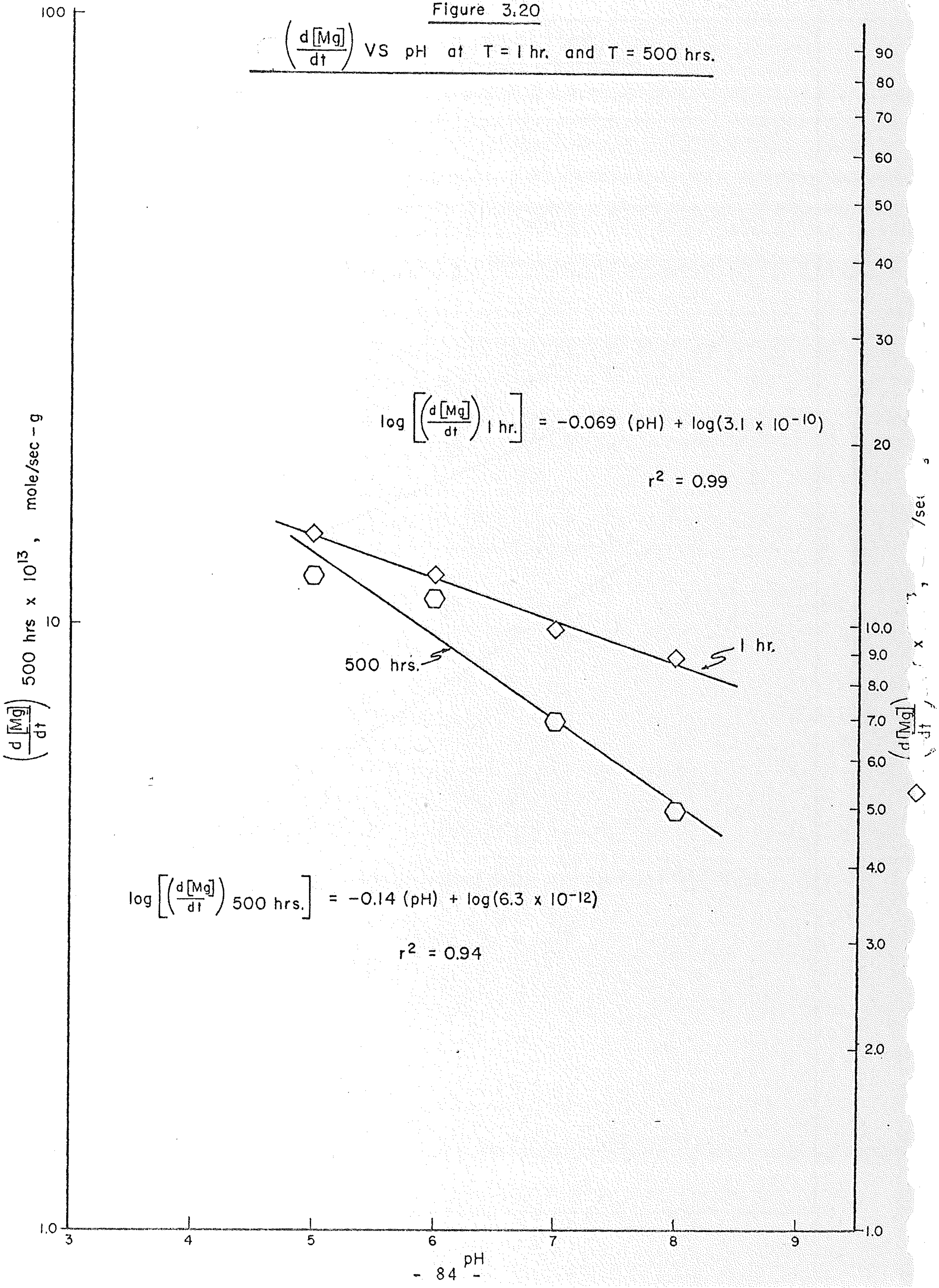


Figure 3.20

$\left(\frac{d[Mg]}{dt}\right)$ VS pH at T = 1 hr. and T = 500 hrs.



$\log\left[\left(\frac{d[Mg]}{dt}\right)_{1\ hr.}\right] = -0.069\ (pH) + \log(3.1 \times 10^{-10})$

$r^2 = 0.99$

$\log\left[\left(\frac{d[Mg]}{dt}\right)_{500\ hrs.}\right] = -0.14\ (pH) + \log(6.3 \times 10^{-12})$

$r^2 = 0.94$

Table 3.17 Rate constants for calcium and magnesium: Effect of pH

Calcium

pH	$k*10^5$	n	$(\frac{dc}{dt})_{1hr}$[1]	$(\frac{dc}{dt})_{500hr}$[1]	r^2
5	0.16	0.139	$1.1*10^{-13}$	$5.4*10^{-16}$	0.965
6	0.099	0.167	$1.1*10^{-13}$	$5.9*10^{-16}$	0.980
7	0.18	0.106	$7.6*10^{-14}$	$2.9*10^{-16}$	0.970
8	0.20	0.095	$6.5*10^{-14}$	$2.5*10^{-16}$	0.917

Magnesium

pH	$k*10^6$	n	$(\frac{dc}{dt})_{1hr}$[1]	$(\frac{dc}{dt})_{500hr}$[1]	r^2
5	0.33	0.230	$8.2*10^{-14}$	$7.1*10^{-16}$	0.996
6	0.26	0.239	$7.1*10^{-14}$	$6.5*10^{-16}$	0.997
7	0.33	0.203	$5.8*10^{-14}$	$4.1*10^{-16}$	0.986
8	0.49	0.166	$5.2*10^{-14}$	$2.9*10^{-16}$	0.991

1. rates in mole/cm^2-sec

3.5.2 Effects of Solids Loading

The effect of solids loading on leaching was examined on the basis of batch reactor data using gabbro loadings of 2, 10, 50 and 100 g unmineralized gabbro/liter. Theoretical considerations of loading variation are involved due to the myriad of potential reactions and the complexity of predicting the relative effects of these reactions. Mineral dissolution is enhanced due to increasing reactive surface area. Removal from solution is enhanced due to increasing adsorptive surface area. To predict the effect on leaching, the relative magnitude of these increases must be evaluated.

The effect of loading on pH was a dominant factor in determining the net effect of increased loading on leaching. Over the range of loadings from 2 to 100 gl^{-1}, pH increased with increased loading as indicated on Figure 3.21. The major influence occurred in the initial stage of reaction concurrent with the release of calcium and magnesium from the silicate mineral phase. This occurrence reflected the exchange of hydrogen ions in solution with the metals of the silicate minerals (see reaction 3.55 in Table 3.4).

Metal sulfide dissolution increased with increased loading as indicated by the observed sulfate concentrations presented in Figure 3.22. The rate constants calculated (assuming linear kinetics after t = 140 hours) are presented in Figure 3.23. The slope of the plot yields an average release rate of $2.2 * 10^{-11}$ mole/cm^2-(%S)-min.

Although oxidation of nickel sulfide apparently increased with increased loading a decrease in aqueous nickel concentrations was observed, as is presented in Figure 3.24. The hypothesis that nickel sulfide oxidation

Figure 3.21. Effect of gabbro loading on pH

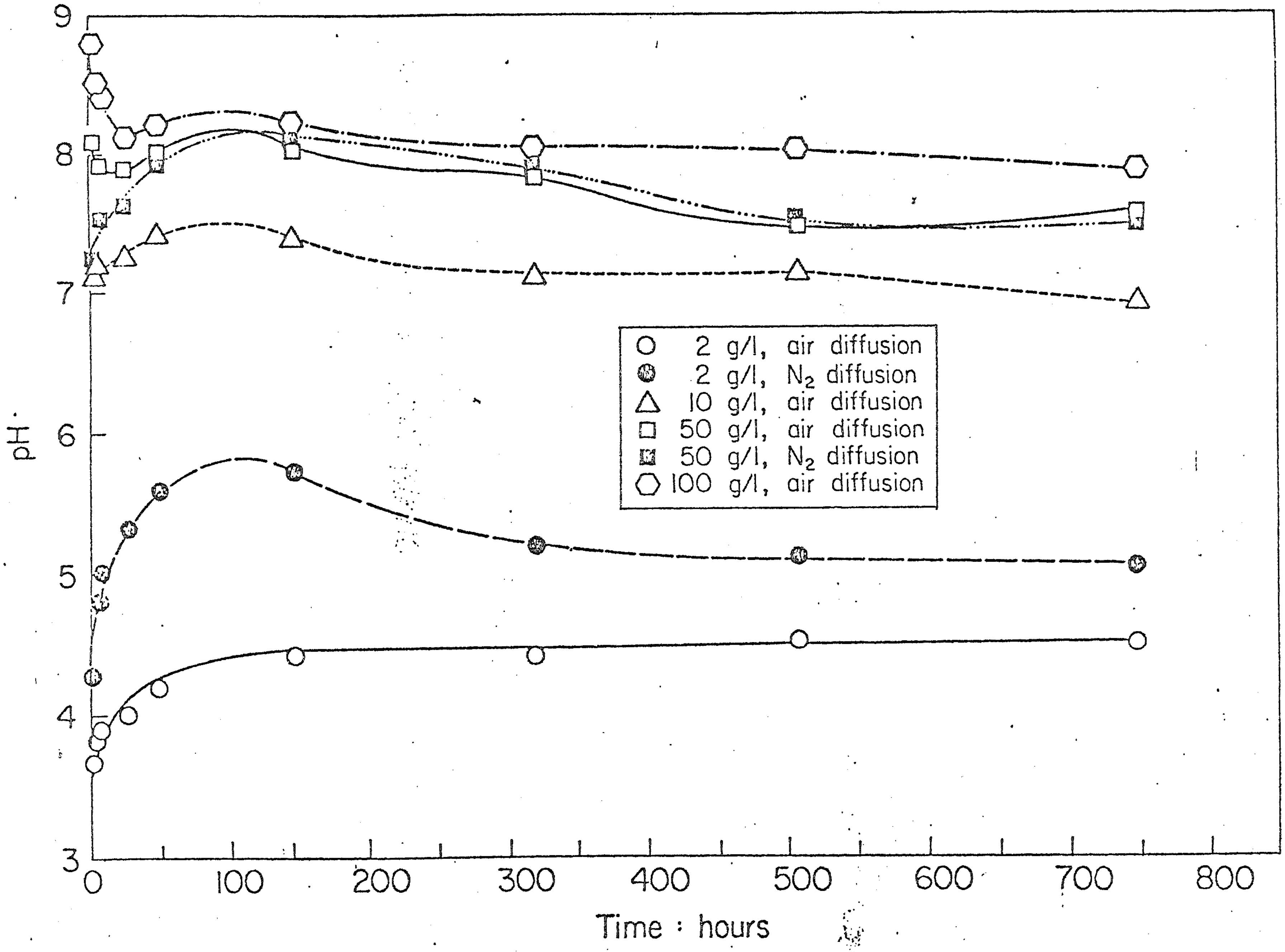


Figure 3.22

EFFECT OF LOADING : $[SO_4^=]$ VS TIME

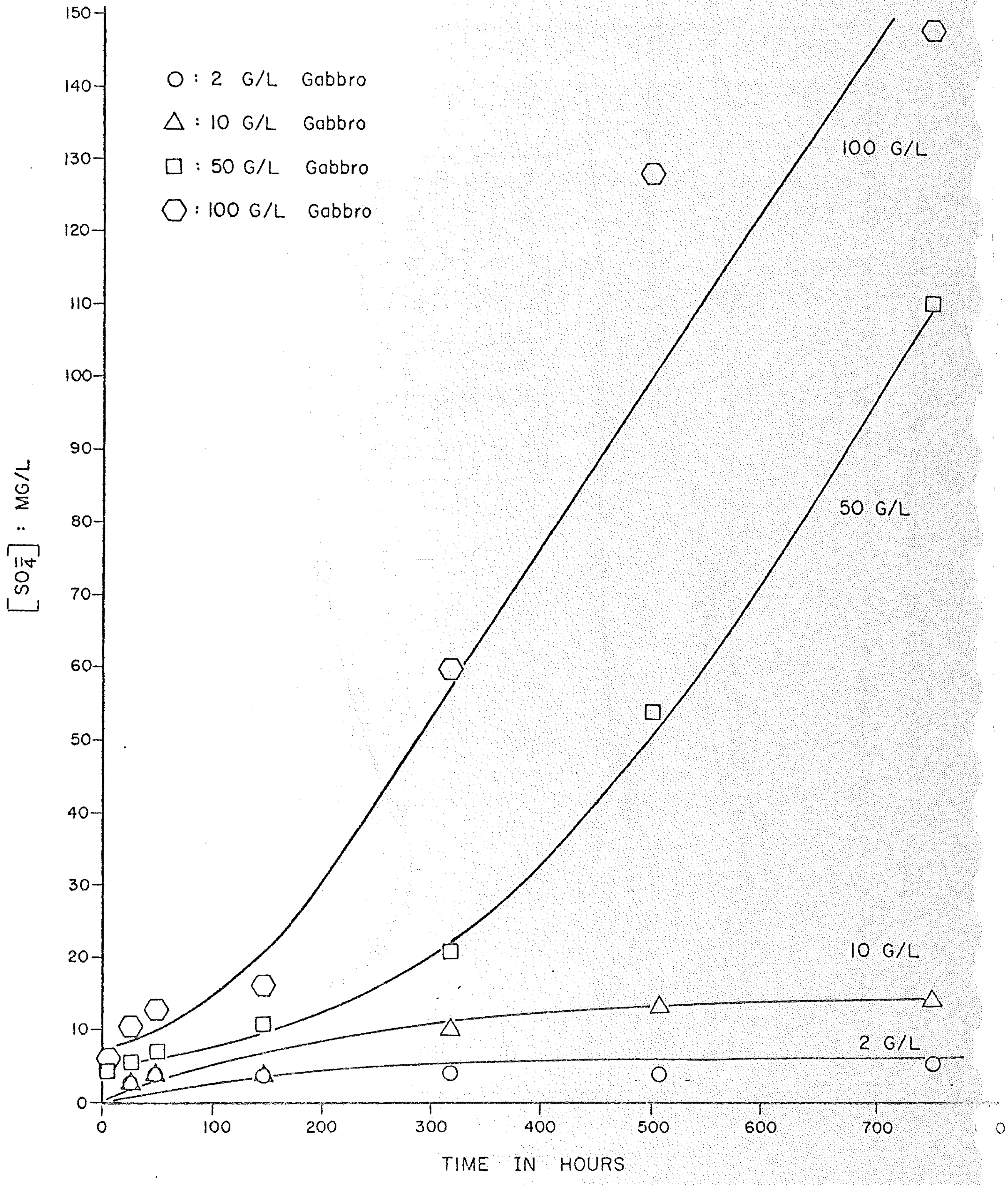
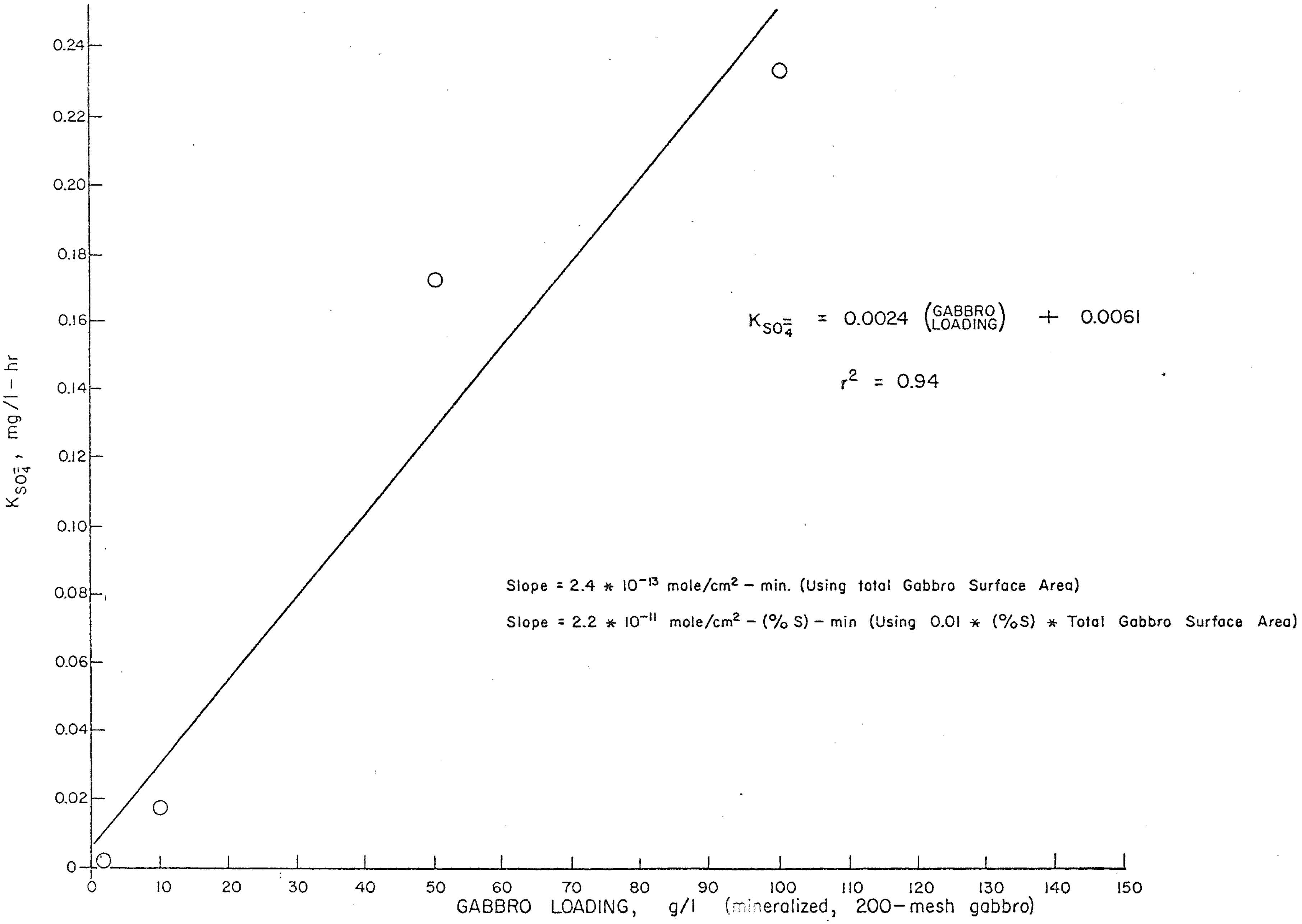


Figure 3.23

K_{SO_4} VS GABBRO LOADING



$K_{SO_4^=} = 0.0024 \left(\begin{smallmatrix}\text{GABBRO}\\ \text{LOADING}\end{smallmatrix}\right) + 0.0061$

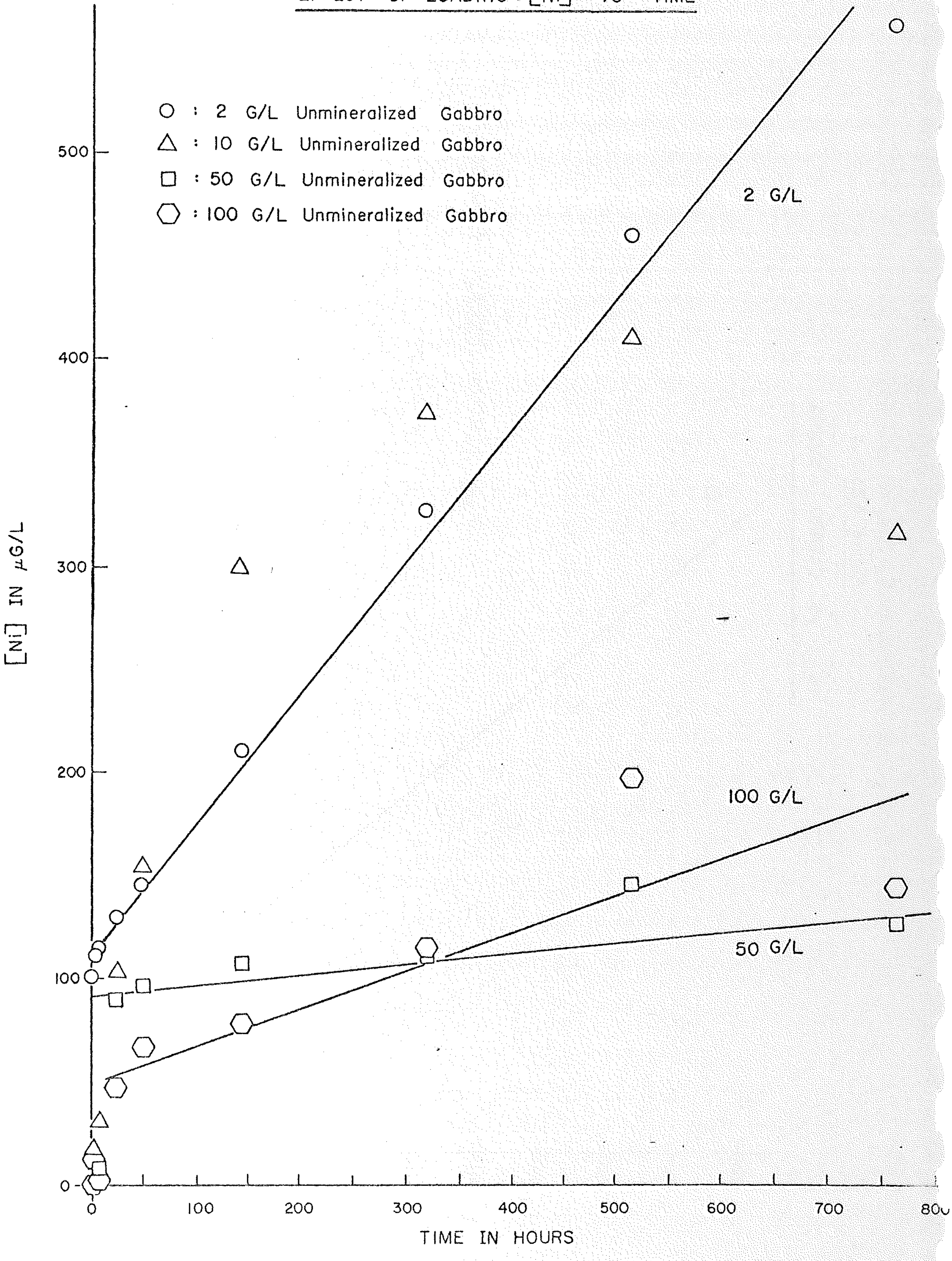
$r^2 = 0.94$

Slope = $2.4 * 10^{-13}$ mole/cm^2 – min. (Using total Gabbro Surface Area)

Slope = $2.2 * 10^{-11}$ mole/cm^2 – (% S) – min (Using 0.01 * (%S) * Total Gabbro Surface Area)

Figure 3.24

EFFECT OF LOADING : [Ni] VS TIME



increased with loading is supported by the observed sulfate concentrations (Figure 3.22) and data from total release determinations (Figure 3.25). Data from these tests indicate that although the nickel sulfide was oxidized, nickel was ultimately bound in a second solid phase. Due to the relatively high solubility of nickel with respect to hydroxide, oxide and carbonate solids, the secondary solid phase most likely involved adsorption onto surfaces present (e.g. SiO_2, MnO_2, TiO_2, iron oxides) or coprecipitation with iron.

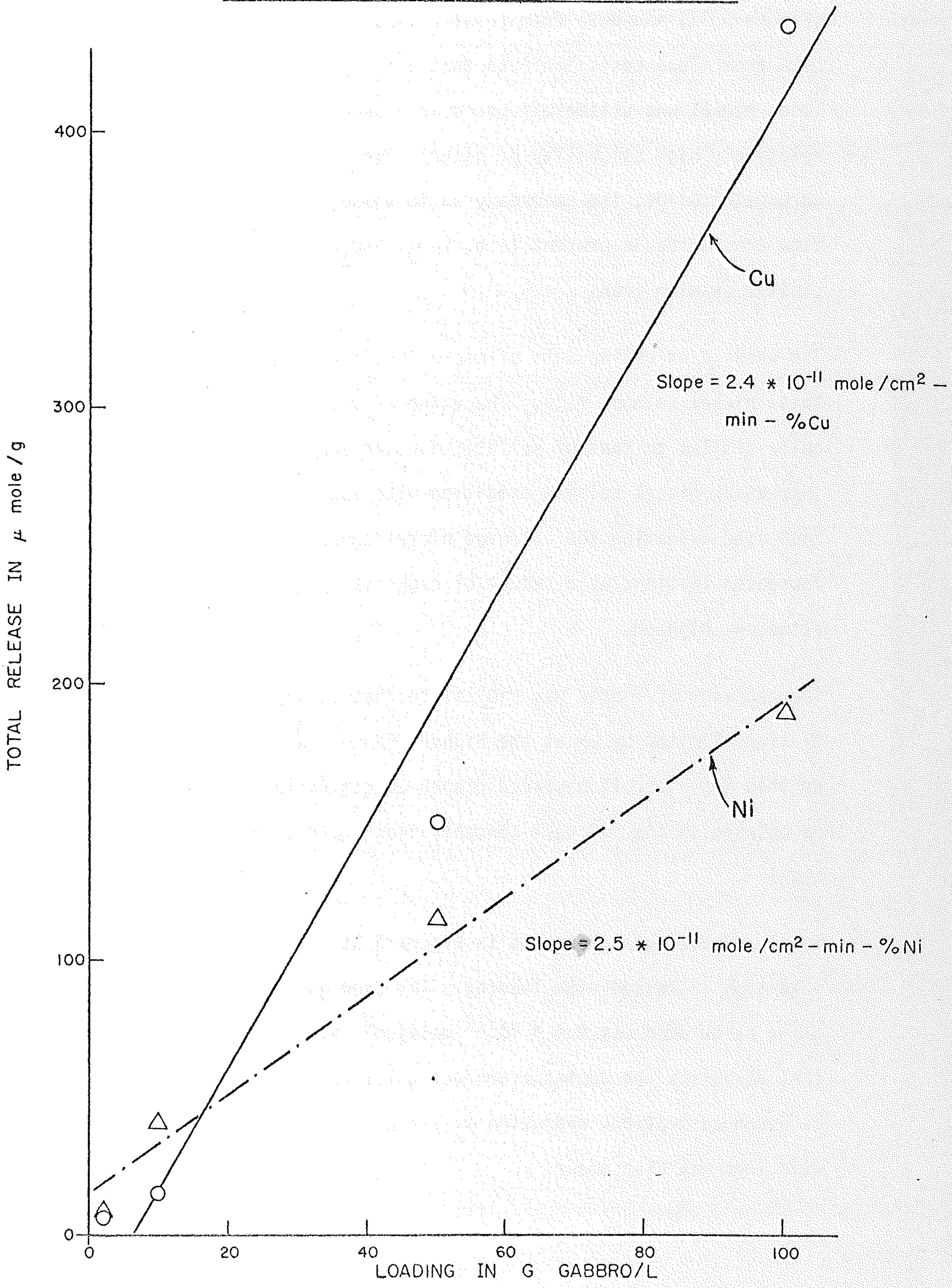
The average oxidation rate of nickel sulfide was determined based on the total nickel release data. The value of $2.5 * 10^{-11}$ mole/cm^2 (%Ni) -min was quite similar to that of sulfate, further supporting the hypothesis of increasing nickel sulfide oxidation with increased loading. Despite the increased oxidation the observed nickel concentrations decreased with increased loadings as a result of high adsorptive surface areas and the attendant high pH.

The behavior of copper was similar to that of nickel with observed concentrations limited by pH at the higher gabbro loadings. At loadings greater than 2 g gabbro/l observed copper concentrations were below 5 ug/l as opposed to the 530 ug/l concentration observed at the loading of 2 g gabbro/l.

Total release data presented in Figure 3.25 indicate that copper sulfide oxidation increased with loading. The average rate of copper sulfide oxidation calculated was $2.4 * 10^{-11}$ mole/cm^2 (%Cu)-min. Based on thermodynamic considerations the dominant product solid phase is probably malachite, although adsorption, hydroxide or oxide precipitation and coprecipitation with iron may also occur.

Figure 3.25

TOTAL Cu, Ni RELEASE VS GABBRO LOADING



The effect of gabbro loading on calcium release is presented in Figure 3.26. Release increased with increased loading. Magnesium behaved similarly reflecting a similarity in dissolution of silicate minerals and the relatively high aqueous mobility of calcium and magnesium.

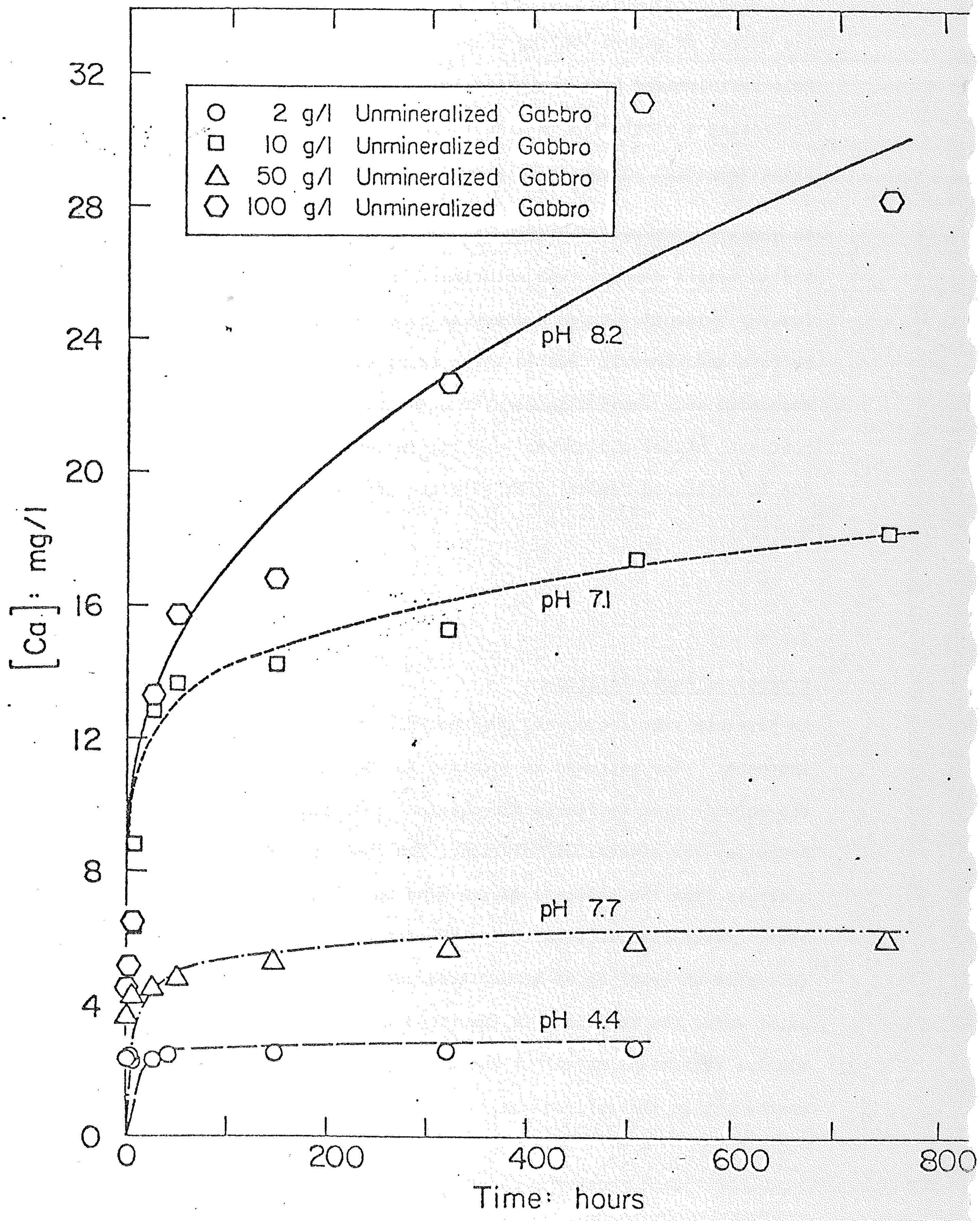
In summary, increased loading caused increases in mineral dissolution and in metals removal from solution. The increase of pH with increased loading evidently played a dominant role in determining the net effect of release and removal. Due to their relatively high mobility, calcium and magnesium were leached in greater quantities at increased loadings. In contrast, nickel and copper leaching decreased with increased loading, due to increased removal from solution of these metals of lower relative mobility.

3.5.3

Effects of Particle Size

As particle size decreases, the specific surface area (area per unit mass) increases. The increase in specific surface area provides an increase in the surface area available for chemical reaction, thus enhancing the potential for mineral dissolution. The physical liberation of sulfide minerals from the silicate matrix also increases with decreasing particle size. Batch reactor results are presented to examine the effect of particle size on leaching of mineralized gabbro. Compositional differences exist among the various size fractions and are presented in Table 3.18. Similar variations may occur due to physical abrasion, blasting, and weathering in the environment.

Figure 3.26. [Ca] vs Time: Effect of loading



Experimental results indicate that particle size affected dissolution of both sulfide and silicate minerals and consequently solution pH. Release to solution of sulfate and nickel increased with decreasing particle size as presented in Figures 3.27 and 3.28. A log-log plot of the sulfate release rate against surface area was defined by the function

$$k_{SO_4} \alpha \ A_s^{0.98}, \quad r^2 = 0.710 \qquad (3.124)$$

indicating that the rate of metal sulfide oxidation was proportional to surface area (Figure 3.29). A plot of k_{SO_4} vs A_s resulted in an average sulfate release rate of $2.5 * 10^{-13}$ mole/cm^2-min. Nickel release was proportional to $A_s^{0.4}$.

Release of metals from silicate minerals also increased as particle size decreased as is demonstrated by the behavior of calcium in Figure 3.30. The rate constants for calcium and magnesium release are presented in Table 3.19 and indicate a similarity in the behavior of the two metals. Plots of log release rate vs log surface area yielded the following functions:

$$\left(\frac{d(Ca)}{dt}\right)_{1\ hr} \alpha \ A_s^{0.25} \quad r^2 = 0.986 \qquad (3.125)$$

$$\left(\frac{d(Ca)}{dt}\right)_{500\ hr} \alpha \ A_s^{0.28}, \quad r^2 = 0.767 \qquad (3.126)$$

$$\left(\frac{d(Mg)}{dt}\right)_{1\ hr} \alpha \ A_s^{0.44} \quad r^2 = 0.914 \qquad (3.127)$$

$$\left(\frac{d(Mg)}{dt}\right)_{500\ hr} \alpha \ A_s^{0.40}, \quad r^2 = 0.621 \qquad (3.128)$$

Table 3.18

Chemical Composition of Size Fractions

COMPOSITION: All Values in mg-(gabbro)$^{-1}$

Diameter (mm)	Ni	Cu	Fe	Ca	Mg	As(cm^2/g)
$d \leq 0.074$	3.55	14.1	172.	22.7	19.2	1700
$0.074 < d \leq 0.42$	1.82	8.25	155.	17.6	18.2	190
$0.42 < d \leq 0.84$	4.52	12.8	259.	29.3	37.9	62
$0.84 < d \leq 2.38$	4.08	23.5	460.	47.3	80.2	25

Figure 3.27. Sulfate concentration vs Time: Effect of particle size

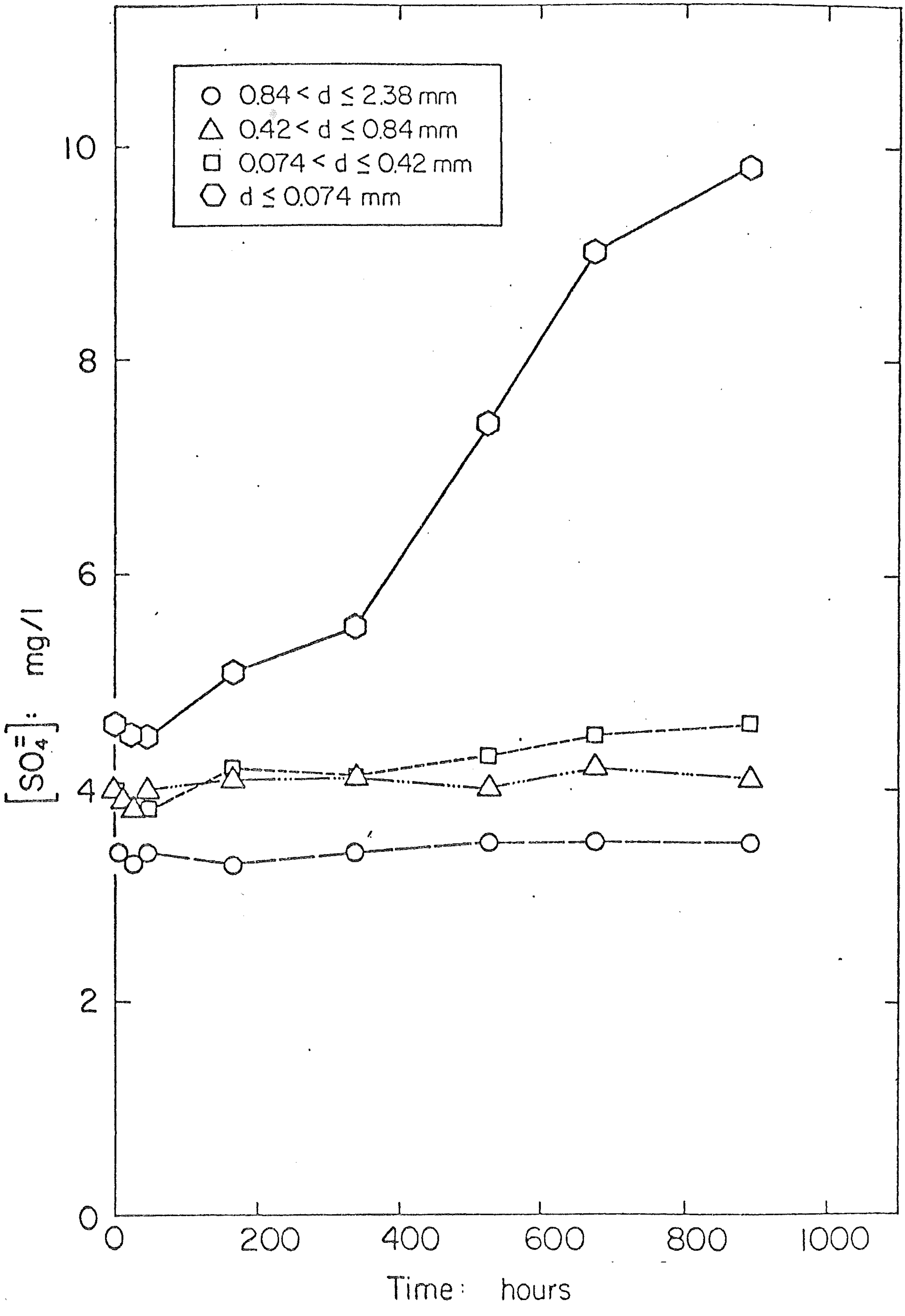


Figure 3.28. Nickel Concentration vs Time: Effect of particle size

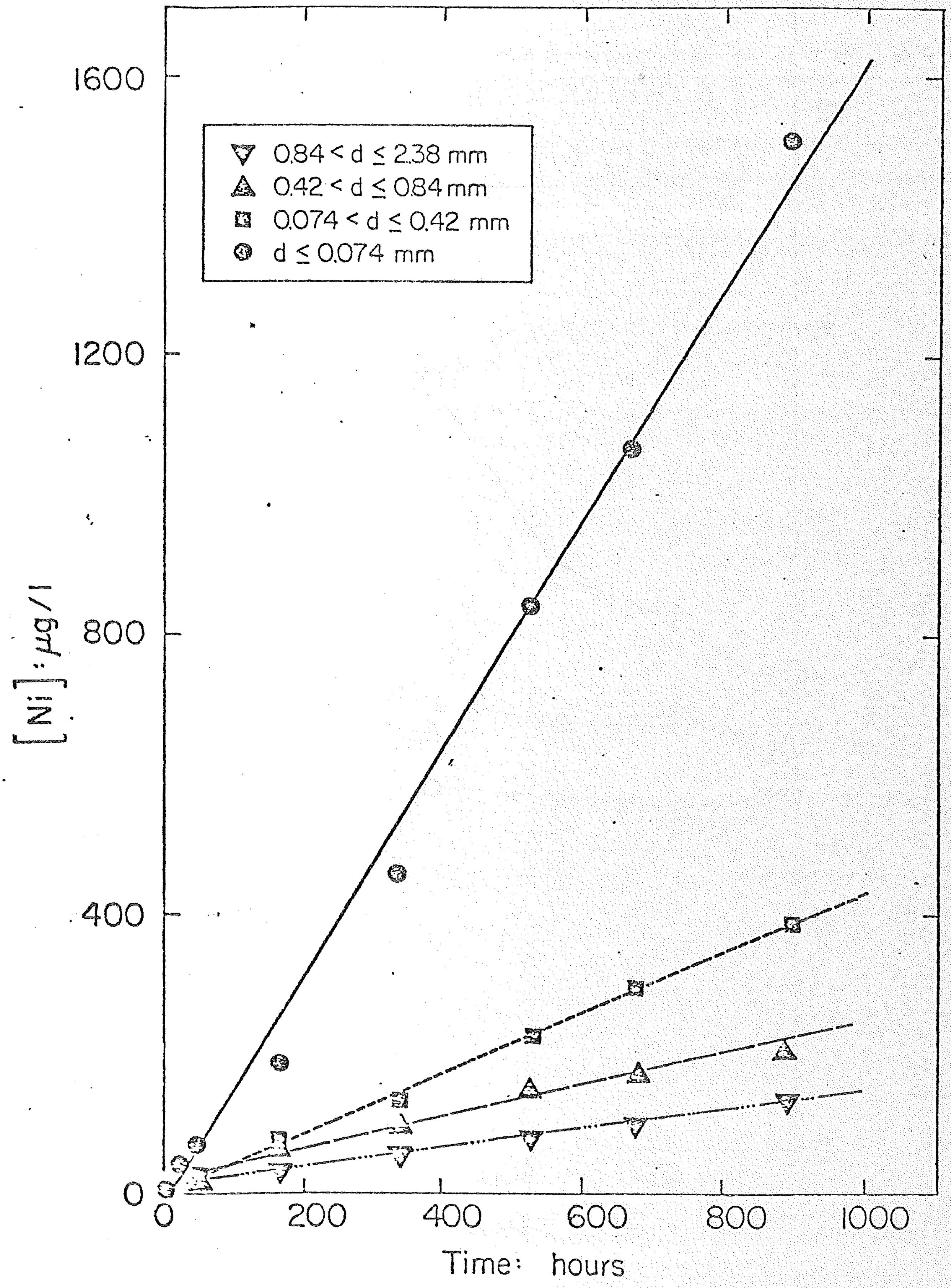


Figure 3.29

Log K_{SO_4} VS As

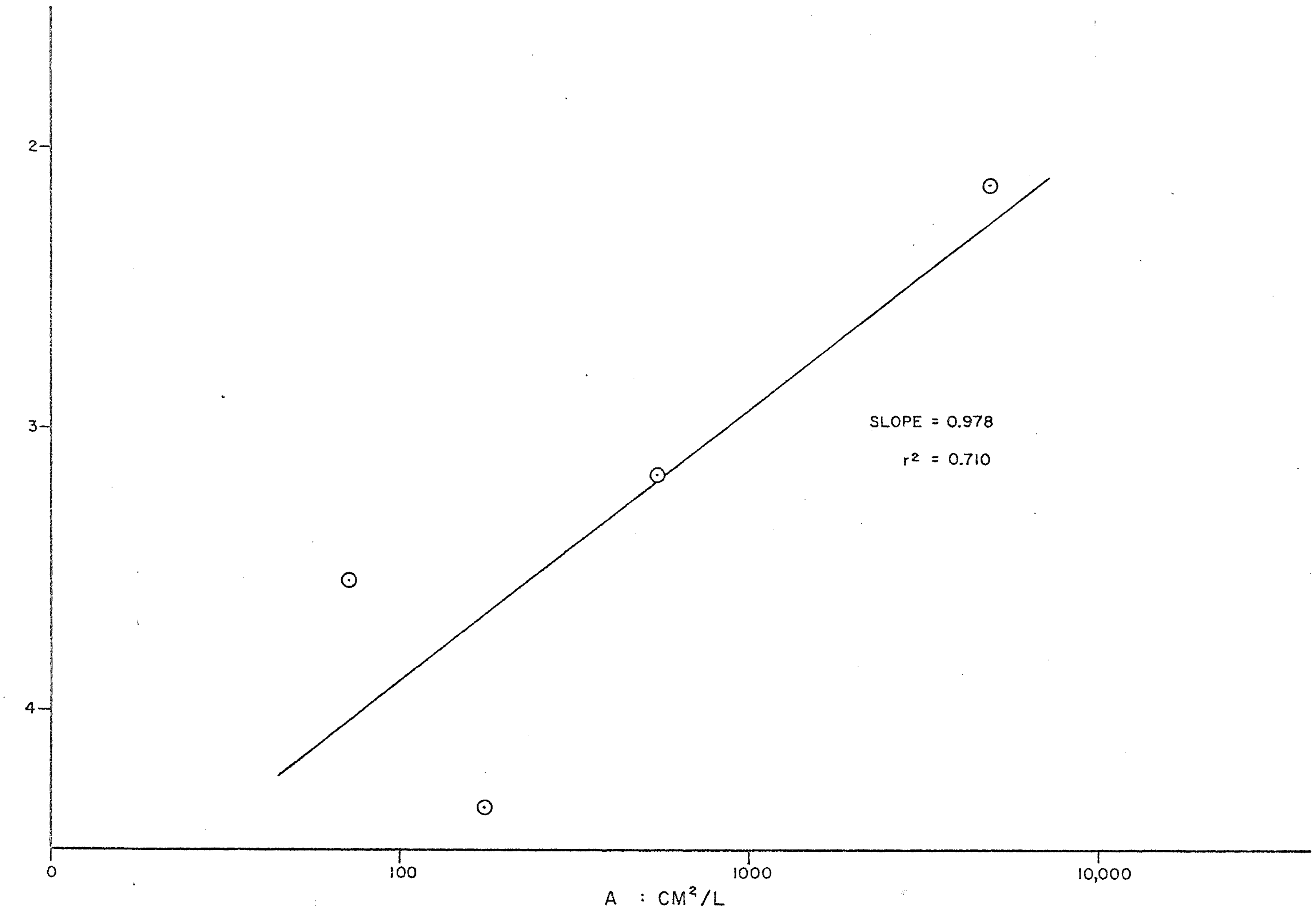


Figure 3.30 Calcium Concentration vs Time: Effect particle size.

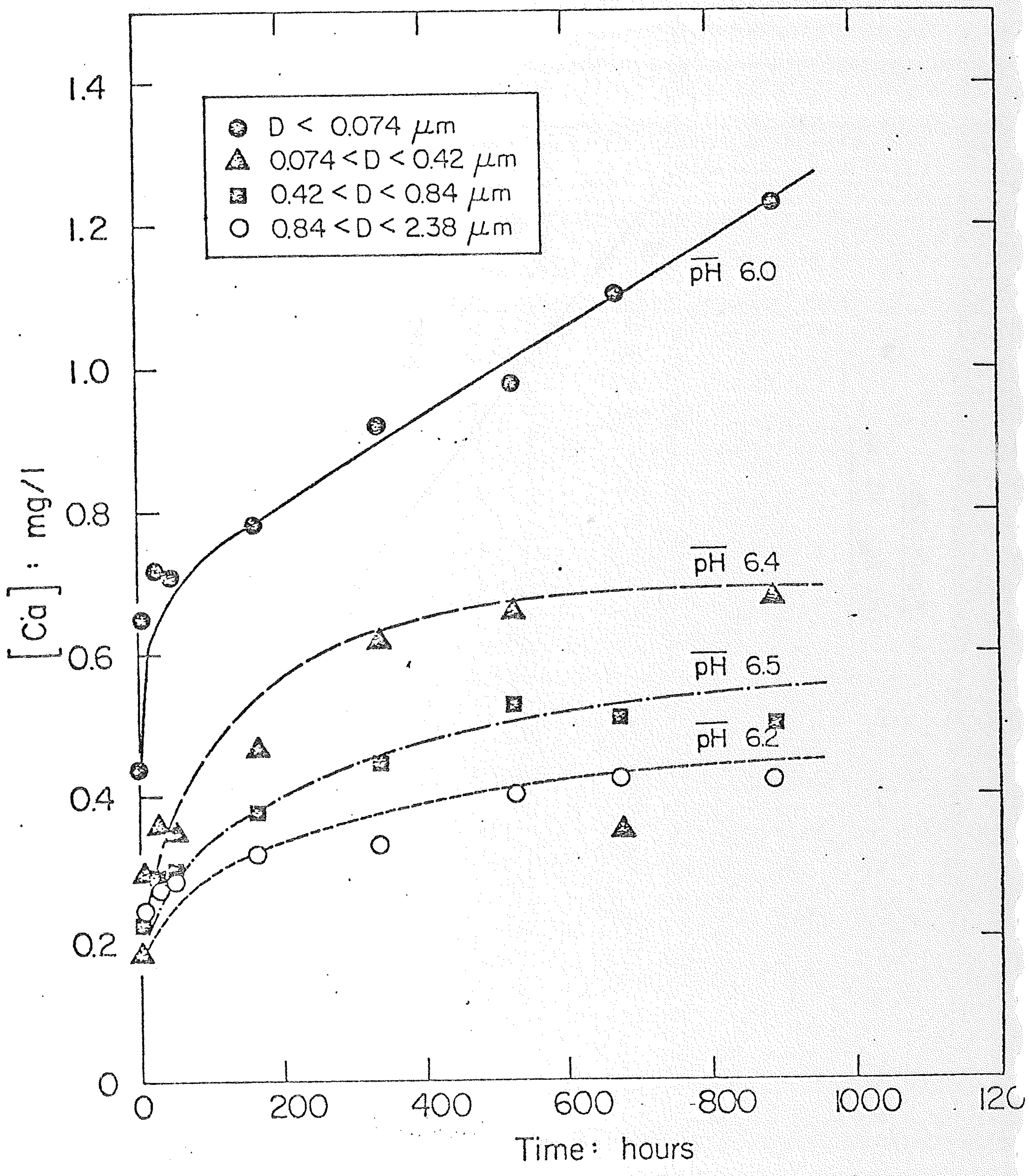


Table 3.19 Rate of Appearance of Calcium and Magnesium: Effect of Particle Size

k: $\text{mole/cm}^2\text{-min}^{-n}$
n: dimensionless

CALCIUM

A_s	k	n	r^2	$\frac{dc}{dt}$ 1 hr	$\frac{dc}{dt}$ 500 hr	$\frac{dc}{dt}$ 1 hr	$\frac{dc}{dt}$ 500 hr
$cm^2/1$				$\text{mole/cm}^2\text{-min}$		mole/g-min	
	$*10^9$			$*10^{12}$	$*10^{14}$	$*10^9$	$*10^{11}$
4860	1.51	0.119	0.931	4.87	2.04	8.3	3.5
543	4.36	0.180	0.974	27.3	16.7	5.2	3.2
177	17.4	0.129	0.884	63.4	28.3	3.9	1.8
72	51.3	0.0908	0.901	112	39.6	2.8	0.99

MAGNESIUM

A_s	k	n	r^2	$\frac{dc}{dt}$ 1 hr	$\frac{dc}{dt}$ 500 hr	$\frac{dc}{dt}$ 1 hr	$\frac{dc}{dt}$ 500 hr
$cm^2/1$				$\text{mole/cm}^2\text{-min}$		mole/g-min	
	$*10^9$			$*10^{12}$	$*10^{14}$	$*10^9$	$*10^{11}$
4860	0.263	0.247	0.965	2.98	2.76	5.1	4.7
543	0.602	0.293	0.937	9.76	12.0	1.9	2.3
177	0.224	0.481	0.945	12.9	51.1	0.80	3.2
72	6.16	0.178	0.864	37.9	22.9	0.95	0.57

The dissolution of sulfide and silicate minerals affected the solution pH as is indicated by Figure 3.31. The pH was initially dominated by the dissolution of silicate minerals. Initial pH increased with increasing surface area due to the reaction

$$Me^{z+}(\text{silicate}) + zH^{+} = Me^{z+} + (H)_{z}(\text{silicate}) \qquad (3.129)$$

as is illustrated in Figure 3.32. As time increased the rate of silicate dissolution decreased and the rate of iron sulfide dissolution eventually exceeded the rate of silicate dissolution causing a drop in pH. At the end of the experiment the relationship between pH and surface area had essentially reversed itself reflecting increased iron sulfide dissolution with increased surface area.

Figure 3.31. Effect of particle size on pH

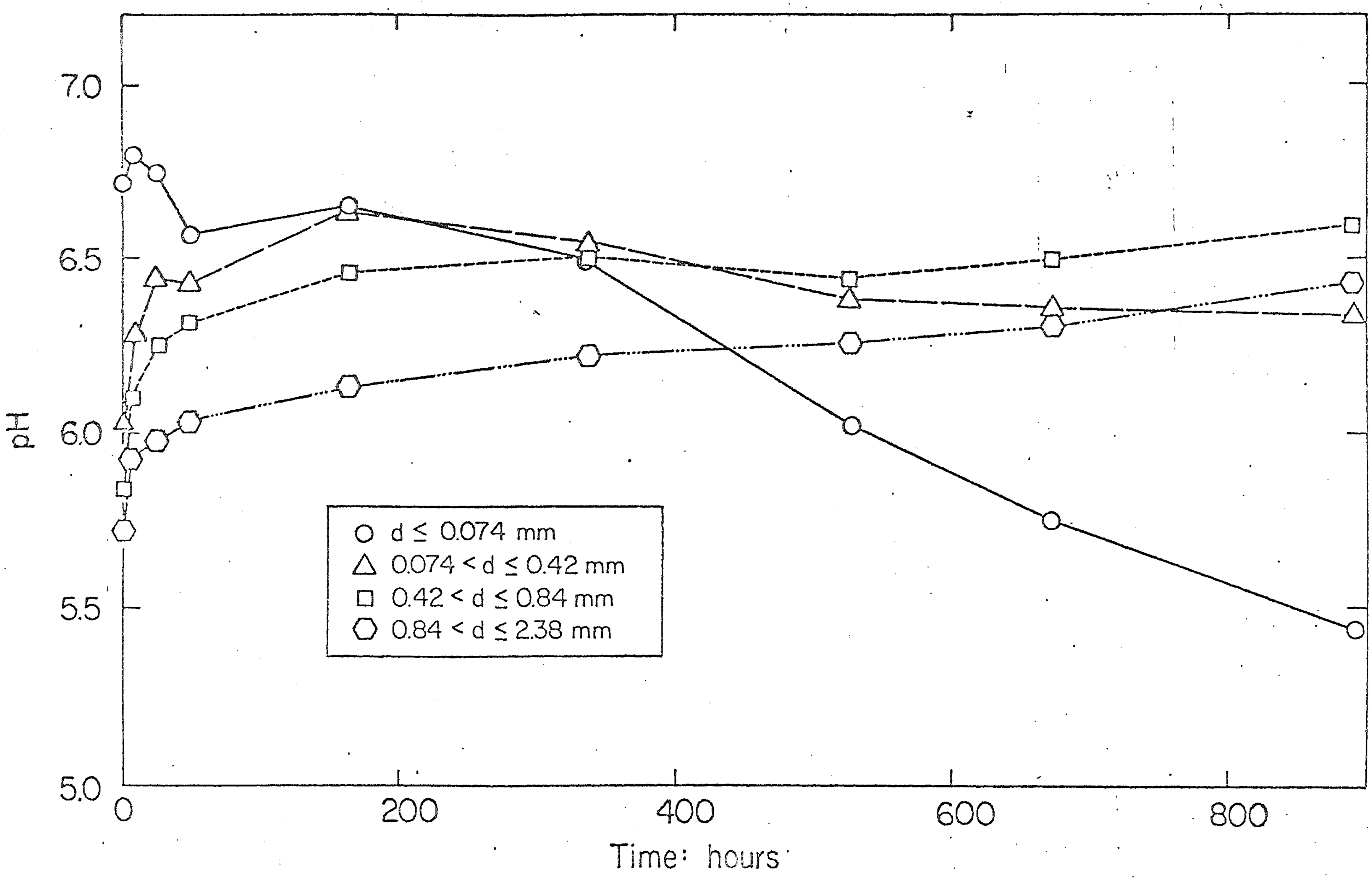
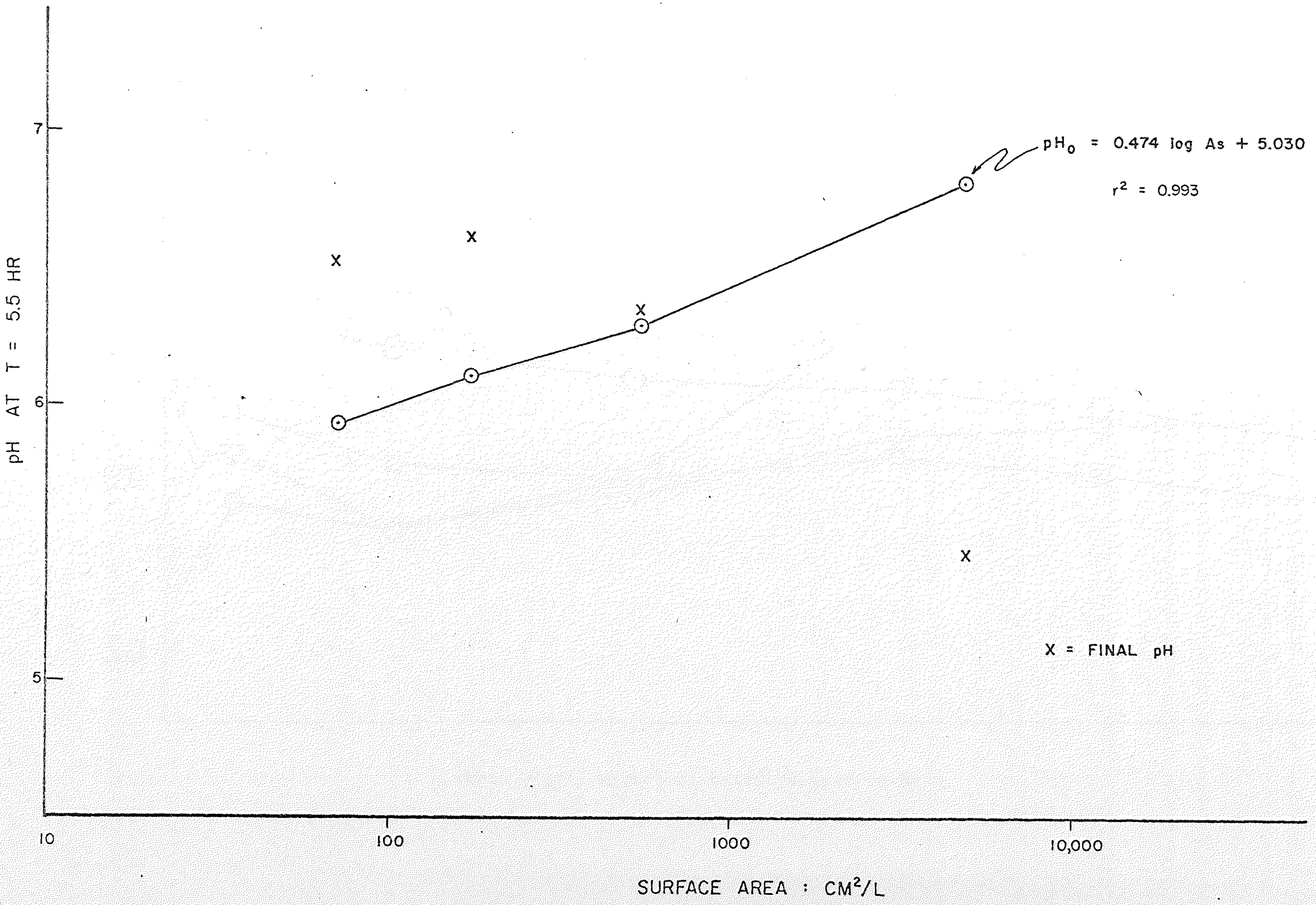


Figure 3.32

pH VS Surface Area



3.5.4

Effects of Rock Composition

Solid composition can affect the leaching process. As the mass of a given component increases, the potential for leaching increases. The amount of leaching which occurs may also be limited by factors other than available mass.

The chemical and mineralogical composition data from the batch reactor experiment are presented in Tables 3.1, 3.2 and the leaching data in figures 3.33 and 3.34. As can be seen in Figure 3.33 the mineralized gabbro produced a lower pH, evidently due to increased iron sulfide oxidation, a hypothesis supported by the observed sulfate concentrations. Observed concentrations of copper and nickel were also greater in the reactors containing mineralized gabbro, as is presented in Figure 3.34. The increase in copper concentration was most likely due to the drop in pH with the mineralized gabbro.

Calcium and magnesium release to solution was greater from the unmineralized than the mineralized gabbro. Likewise, calcium and magnesium concentrations in the unmineralized gabbro were slightly higher than those in the mineralized gabbro, but the solid phase chemical composition alone does not seem to be sufficient to account for the difference in release. Quantification of release as a function of composition based on two samples would be tenuous. The results in conjunction with experiments on surface area do indicate an increase in sulfide oxidation with metal sulfide surface area, which implies an increase in acid producing potential with increased iron sulfide content.

Figure 3.33

pH, [Ca], [SO$_4$] VS TIME : Effect of Rock Composition

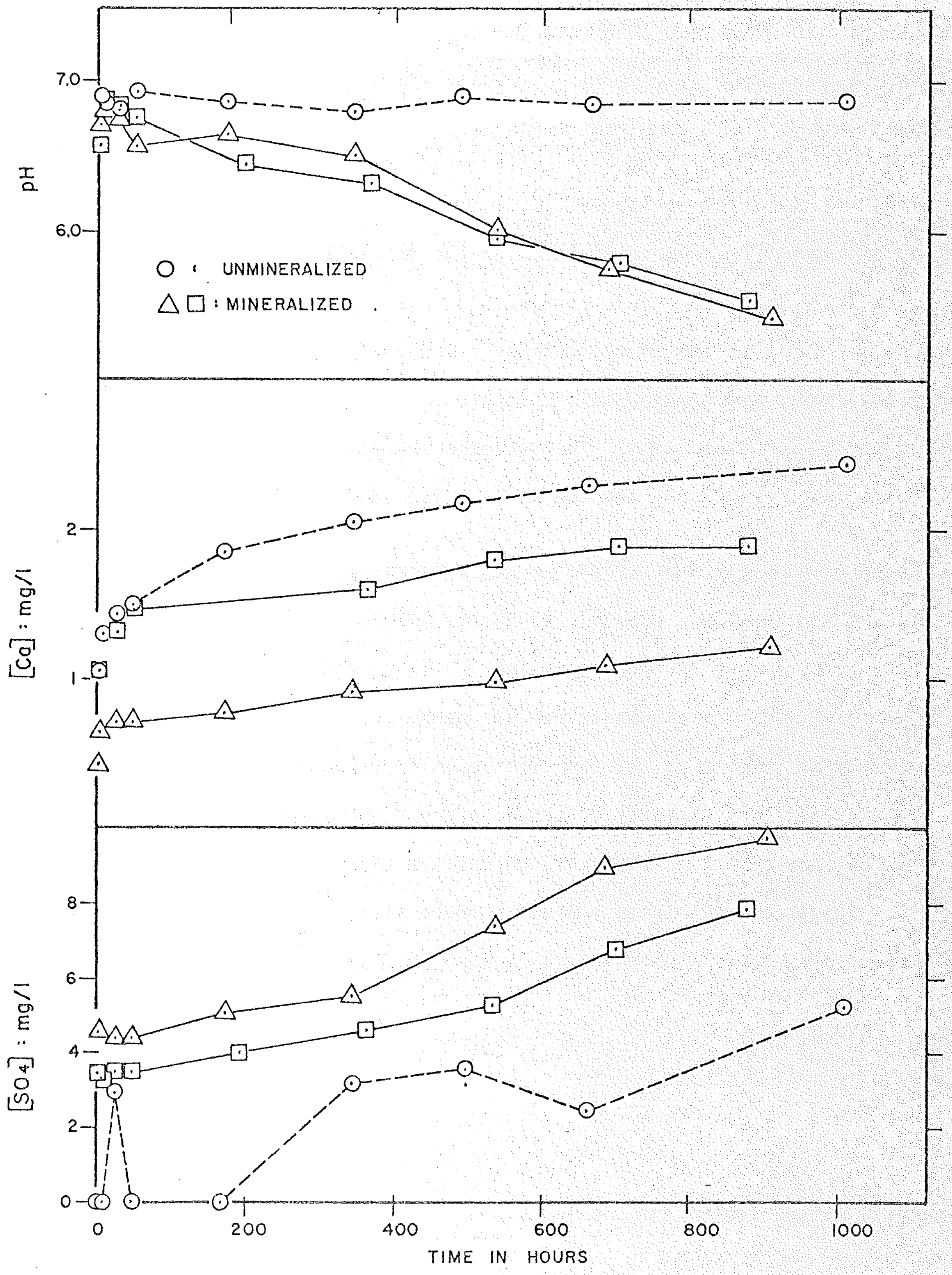
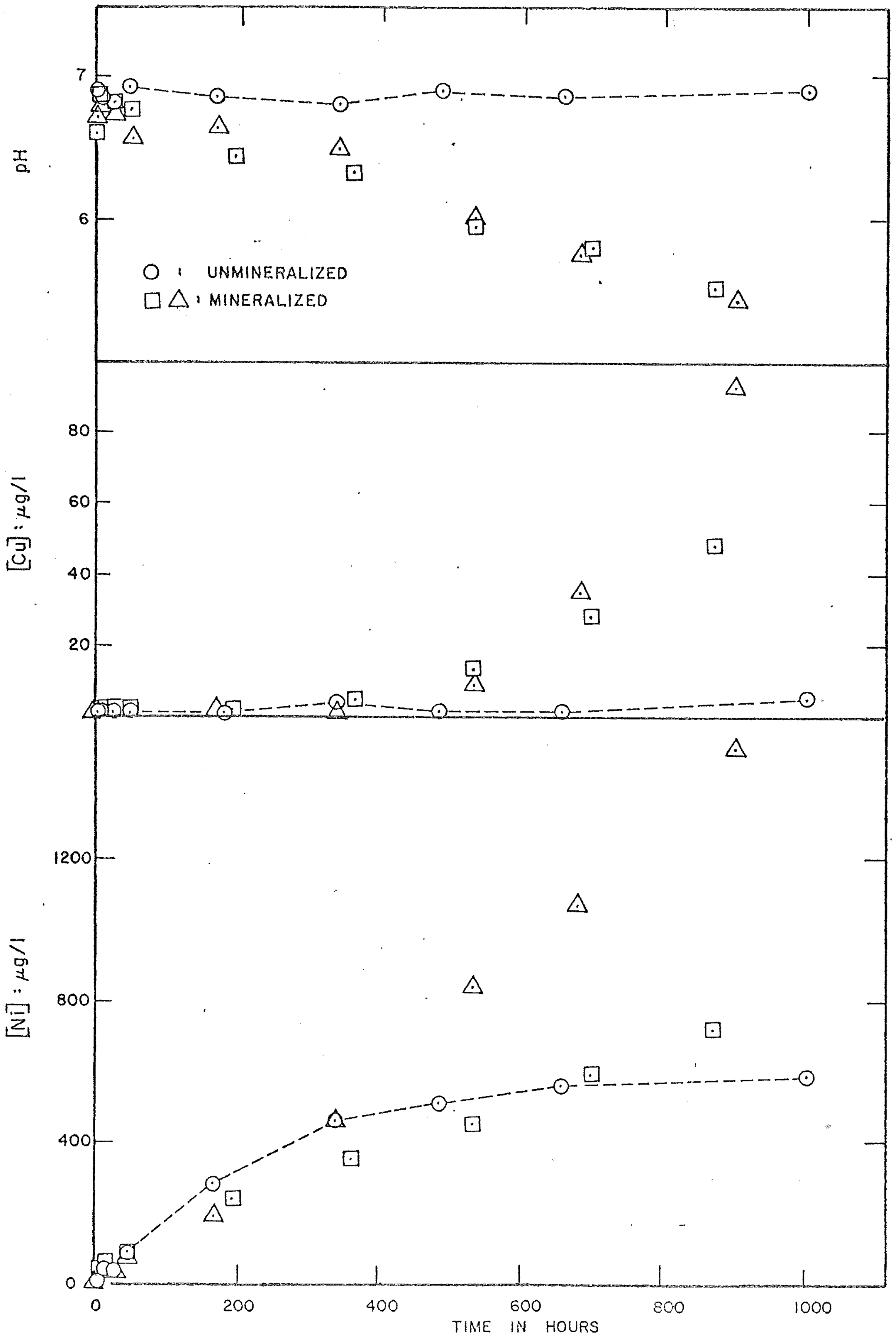


Figure 3.34

pH, [Cu], [Ni] VS TIME: Effect of Rock Composition



3.5.5 Variation of dissolved oxygen concentration

Experimental results indicate that dissolved oxygen concentration had a direct effect on metal sulfide oxidation and an indirect effect on silicate mineral dissolution. Sulfate release demonstrated little variation over the dissolved oxygen range of 1 to 9 mg/l but increased significantly when the dissolved oxygen concentration was increased to 44 mg/l (Figure 3.35). The sulfate concentrations at the dissolved oxygen concentration of 1 mg/l were anomolous and may have been due to experimental difficulties encountered due to erratic nitogen gas flow.

The majority of the sulfate was evidently generated due to iron sulfide oxidation. At the 44 mg/l dissolved oxygen concentration, the sum of the final concentrations of copper and nickel was approximately 13% that of sulfate. At the observed pH of 4.71 the majority of the copper and nickel released would be in solution, indicating that approximately 85% of the sulfate generated was due to iron sulfide dissolution.

The variation of pH indicated an increase in iron sulfide dissolution with increasing dissolved oxygen concentrations. The final pH values for dissolved oxygen concentrations of 1,5,9 and 44 mg/l were 7.6, 6.9, 5.5 and 4.7.

Nickel release increased with dissolved oxygen concentration over the range $1.0 \leq [O_2] \leq 9.3$ mg/l as is presented in Figure 3.36. The nickel rate constant was proportional to $[O_2]^{0.65}$ over this range but was independent of oxygen concentrations greater than 9.3 mg/l (Figure 3.37).

Copper release also increased with dissolved oxygen concentration as is presented in Figure 3.38. The decrease in pH with increasing dissolved oxygen most likely was a factor in the observed increase in copper release.

Figure 3.35. Sulfate concentrations vs Time: Effect of dissolved oxygen concentrations.

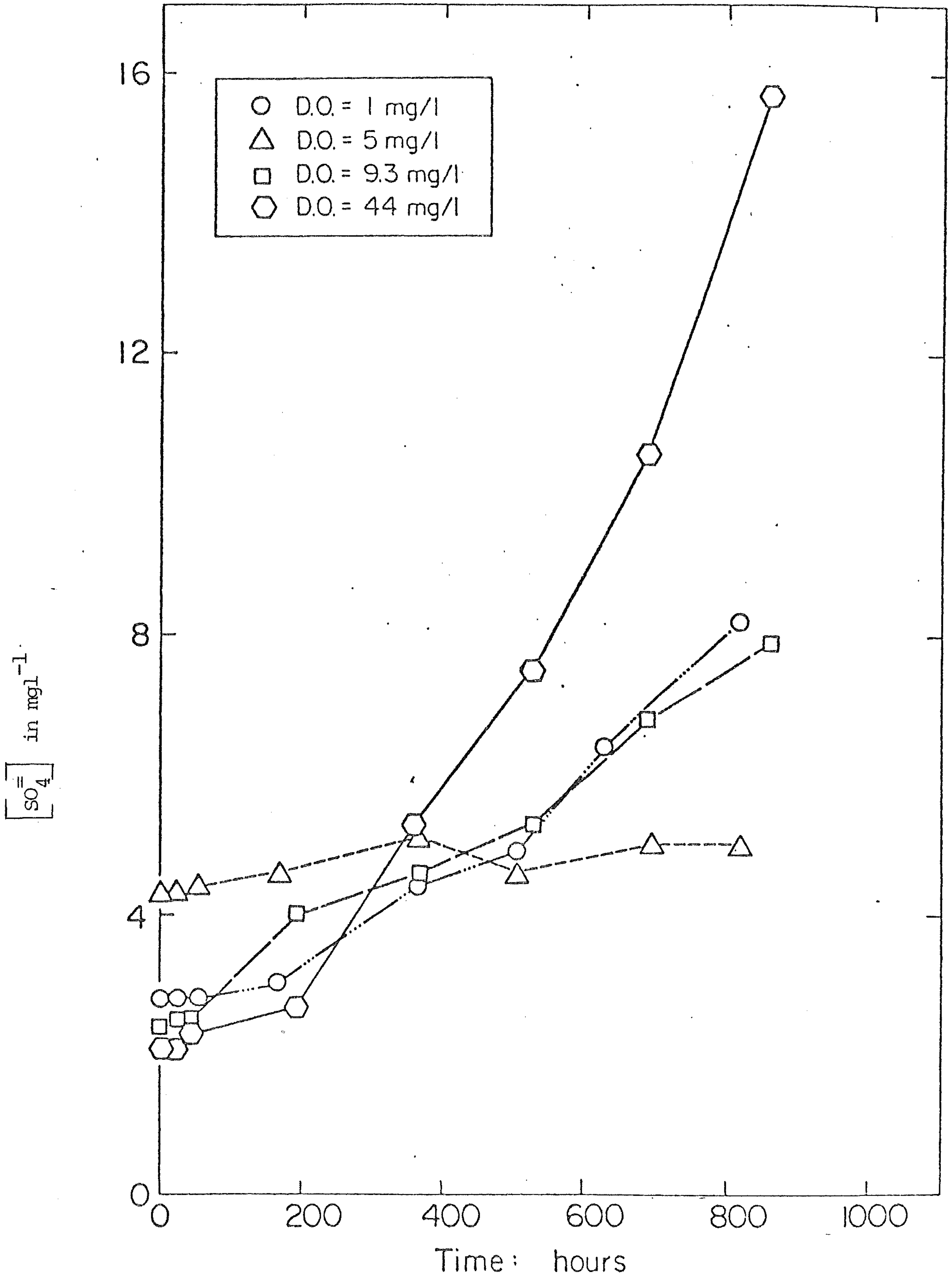


Figure 3.36. Nickel Concentration vs Time: Effect of dissolved oxygen concentration

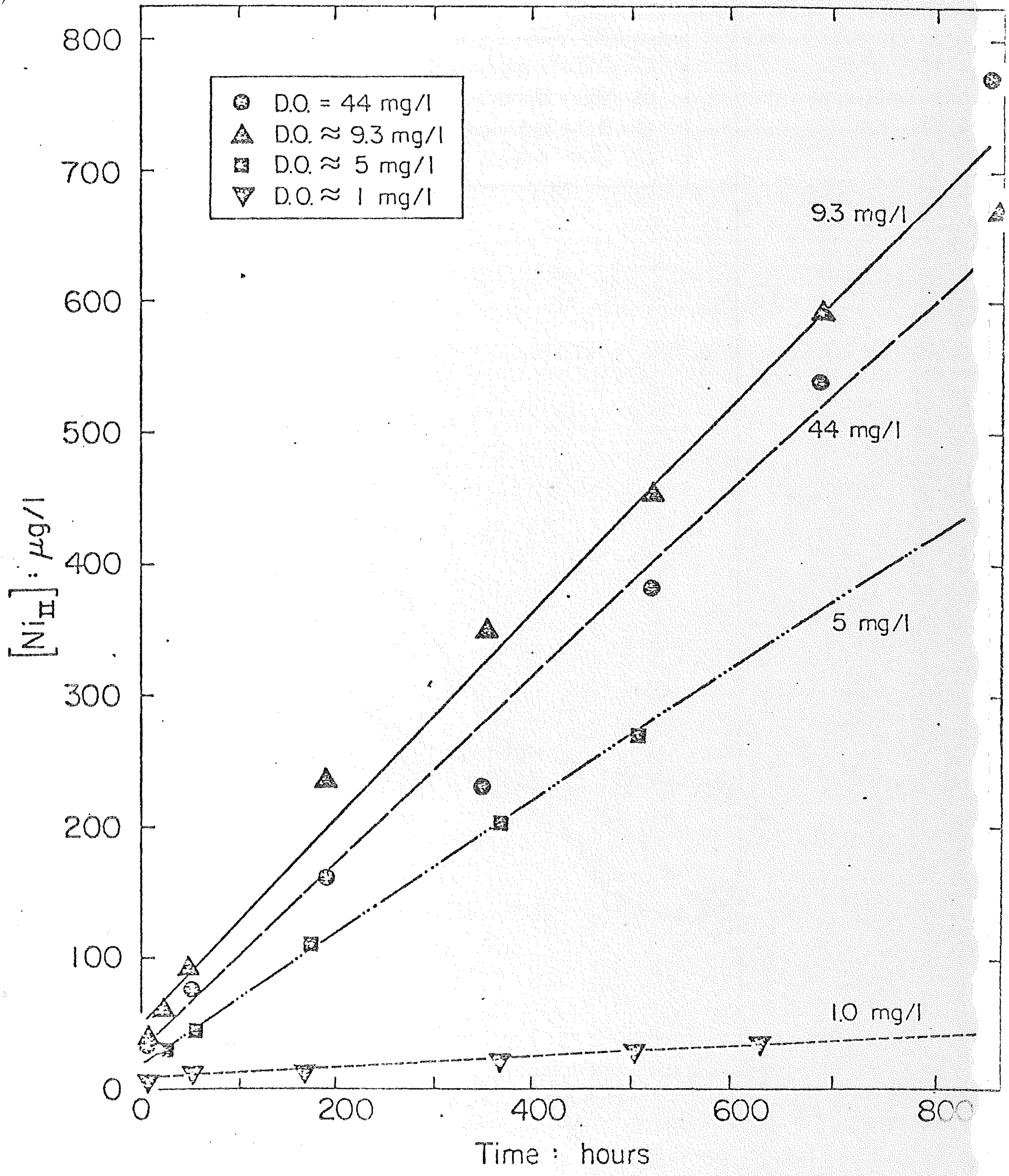


Figure 3.37

K_{Ni} VS $[O_2]$

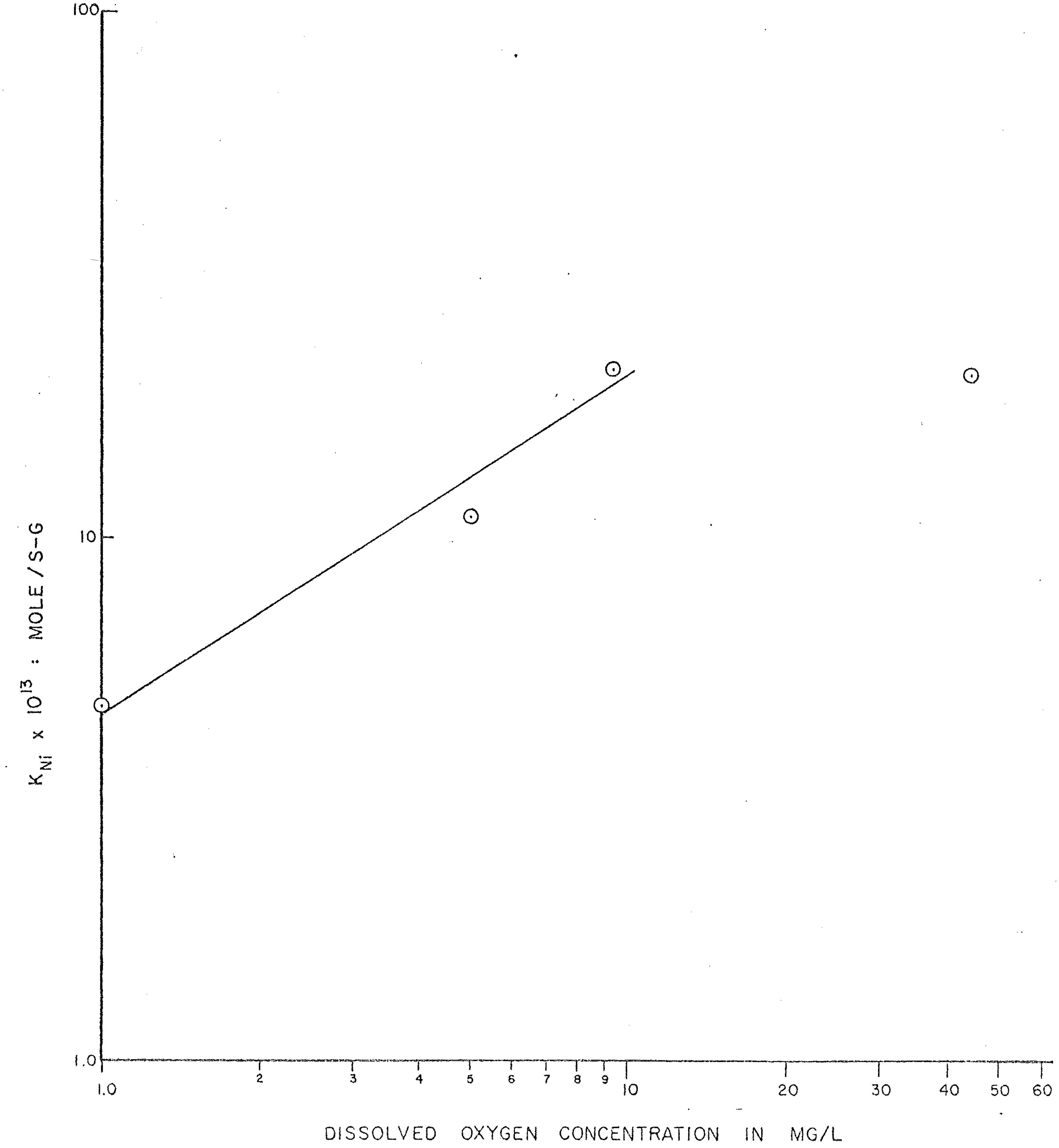
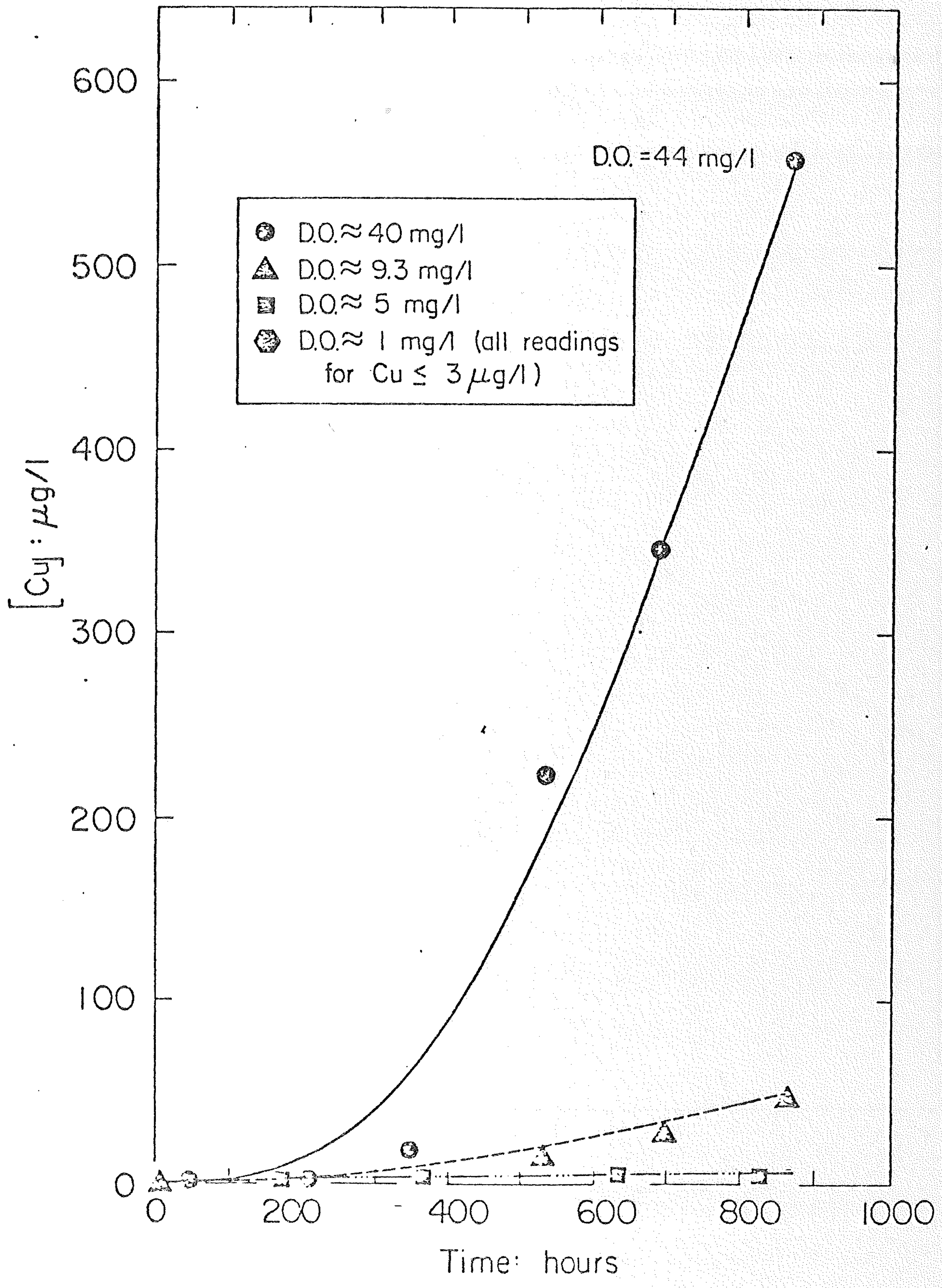
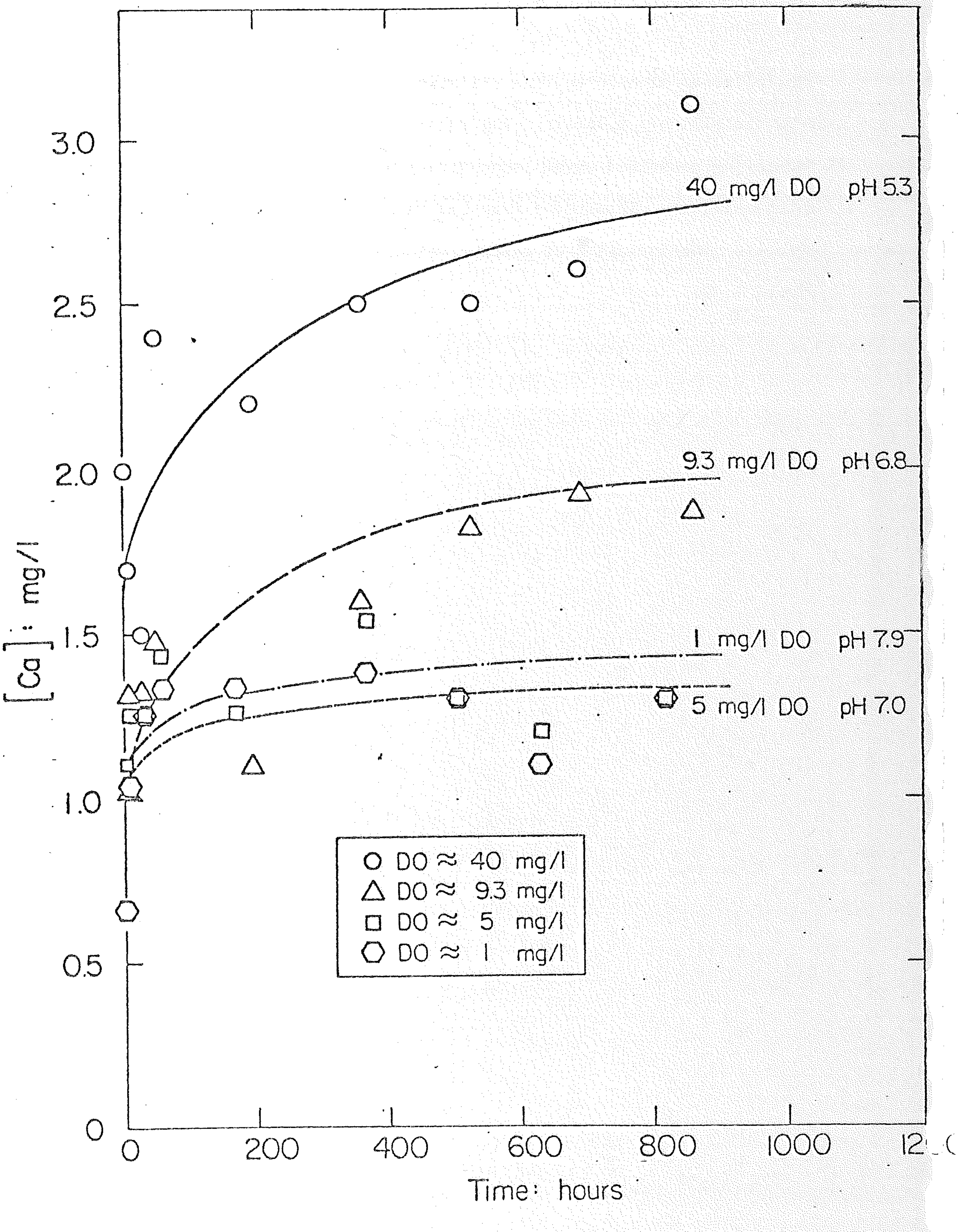


Figure 3.38. Copper Concentration vs Time: Effect of dissolved oxygen concentration



The influence of iron sulfide oxidation on pH also affected release of metals from the silicate minerals. The release of calcium and magnesium increased with increasing dissolved oxygen concentrations. Since oxygen does not participate in the silicate dissolution reaction the increase must be attributed to pH effects. The variation of calcium release with dissolved oxygen is presented in Figure 3.39.

Figure 3.39 Calcium concentration vs Time: Effect of dissolved oxygen concentration



3.5.6

Effects of Ionic Strength

Increasing ionic strength increases solubility, thereby enhancing dissolution reactions and inhibiting precipitation reactions. Batch reactor data depict the effects of sodium chloride additions in concentration of 0, $5 * 10^{-3}$ and $5 * 10^{-2}$ M. The solution pH was 7 in all cases and mineralized gabbro was used.

Observed sulfate concentrations increased slightly with increasing ionic strength as is presented in Figure 3.40, indicating an increase in metal sulfide dissolution. Nickel data support this contention as is illustrated in Figure 3.41. Copper leaching was not detectably affected by the variation in ionic strength, further evidence that leaching of copper was limited by its low aqueous mobility.

Calcium release was enhanced with increasing concentrations of sodium chloride (NaCl). The dominant effect on calcium leaching occurred in the initial stage of the reaction as can be seen in Figure 3.42. Sodium in solution evidently underwent an ion exchange reaction with calcium in the solid silicate phase. Throughout the remainder of the reaction little difference was detected in calcium release among the three solutions.

Figure 3.40

$[SO_4]$ VS TIME: Effect of Ionic Strength

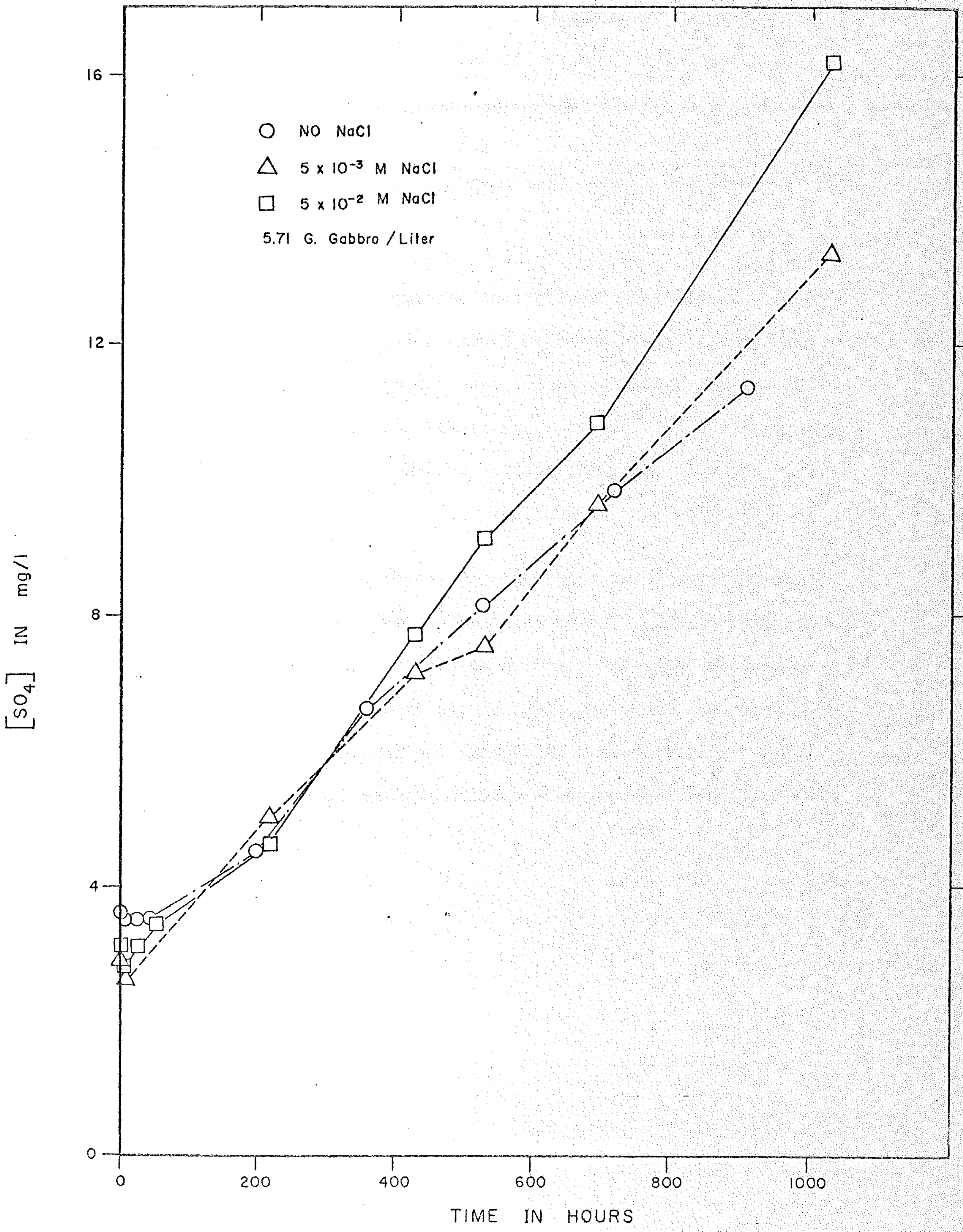


Figure 3.41. [Ni] vs Time: Effect of ionic strength.

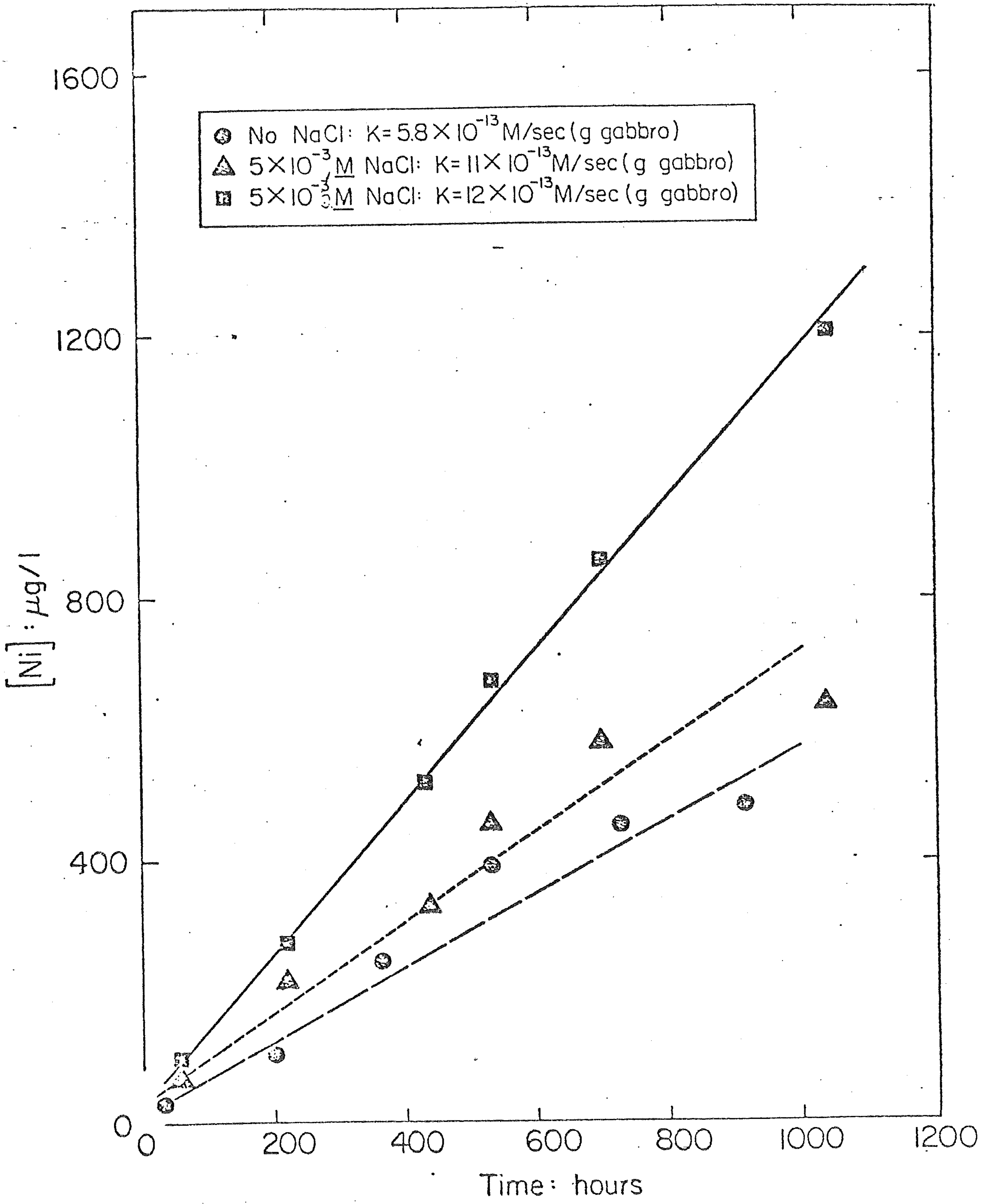
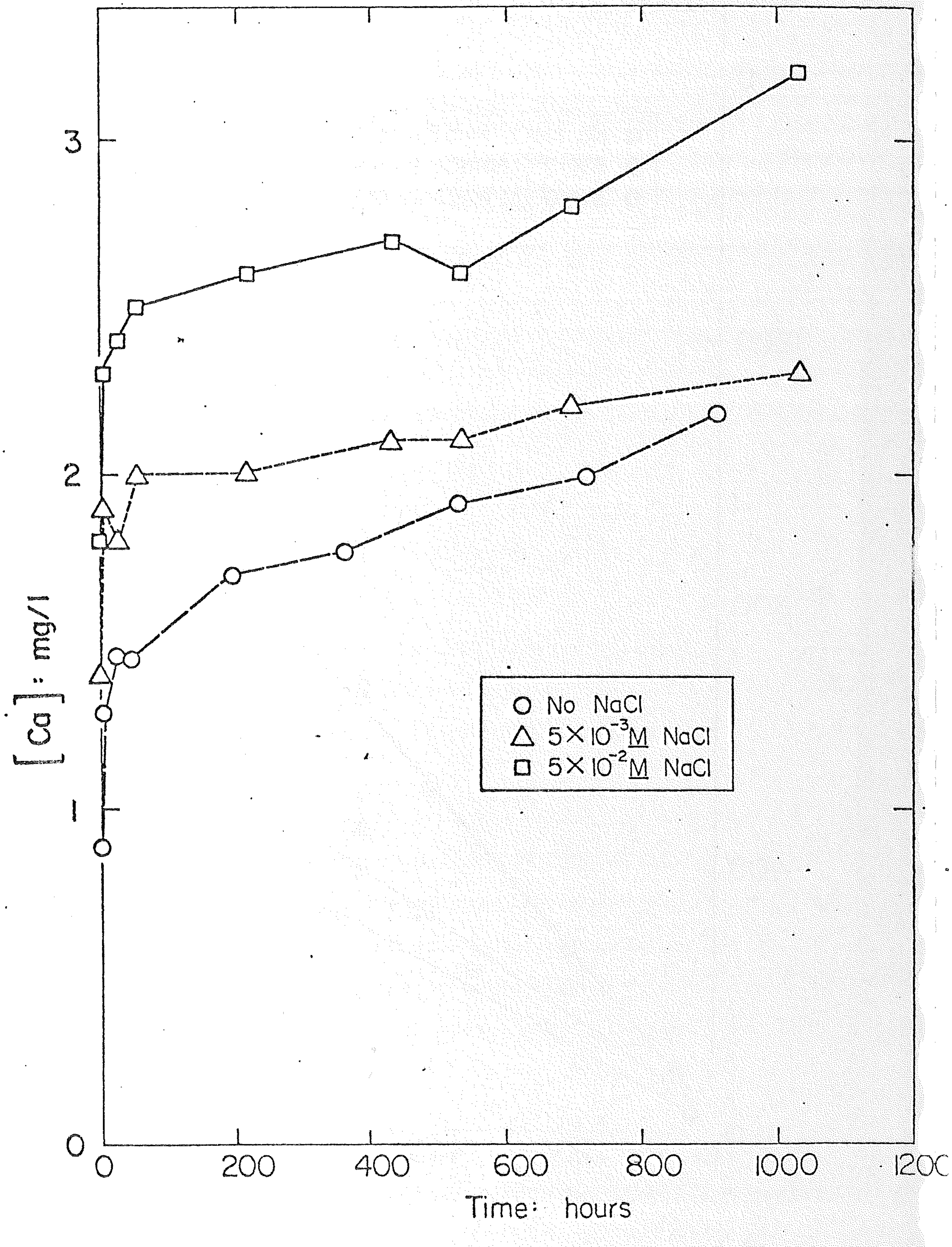


Figure 3.42. [Ca] vs Time: Effect of ionic strength.



3.5.7 Effect of Organics

3.5.7.1 Introduction

The effect of organic ligands on leaching was dependent upon the chemistry of each ligand and the individual metal leached. The model organics examined were citrate ($C_6H_5O_7^{3-}$) and phthallic acid, citrate having the greater influence on leaching.

3.5.7.2 Effect of Citrate

The presence of citrate affected both the dissolution of sulfide minerals and the phase distribution of metals released. Dissolution of sulfide minerals increased with increasing citrate concentration (Figure 3.43). Dissolution at the 1.29 * 10^{-3} M citrate concentration was four times that in the reactor without citrate, but little effect was observed at the 1.29 * 10^{-4} M concentration.

Nickel leaching increased slightly with increased concentrations of citrate (Figure 3.44). The rate of nickel release at 1.29 * 10^{-3} M citrate was 2.2 times that in the reactor without citrate. The increase was most likely due to both increased dissolution and enhanced mobility. Data from the pH experiment indicated that approximately 20% of the nickel released at pH 7 was adsorbed or precipitated in the absence of organic ligands. This fraction of the nickel would be apt to form an organic complex with citrate at the given concentrations. The increase due to complexation is not sufficient to account for the nickel concentrations observed, however, indicating that nickel sulfide dissolution must also be enhanced. The decreasing nickel concentration at the 1.29 * 10^{-4} M citrate concentration after t = 400 hours was evidently due to the breakdown of citrate, which proceeds more rapidly when complexes are in equilibrium than when they are not (Lehrman and Childs, 1973). The similar behavior of copper and iron at the 1.29 * 10^{-4} M

Figure 3.43. Sulfate concentrations vs Time: Effect of citrate

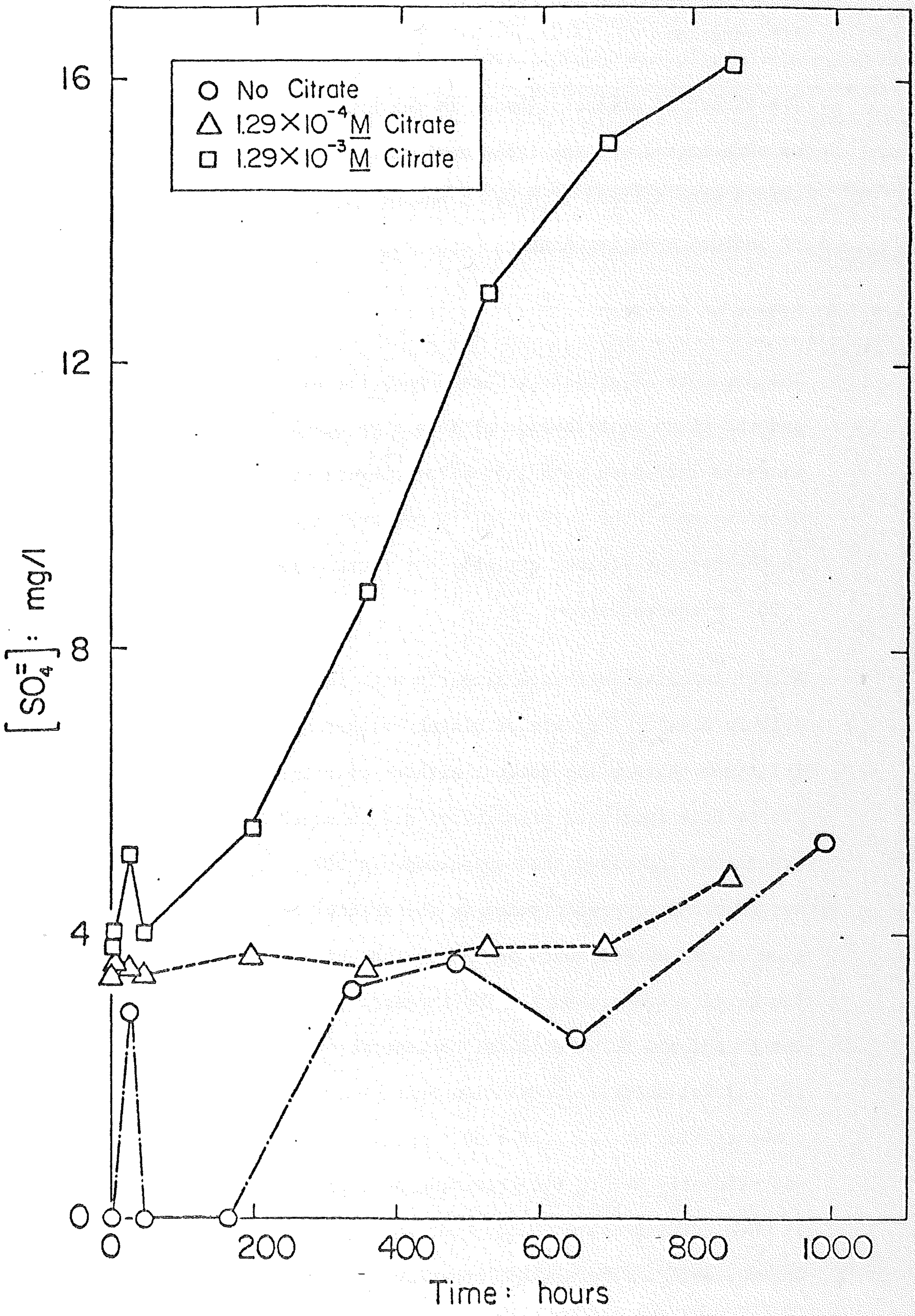
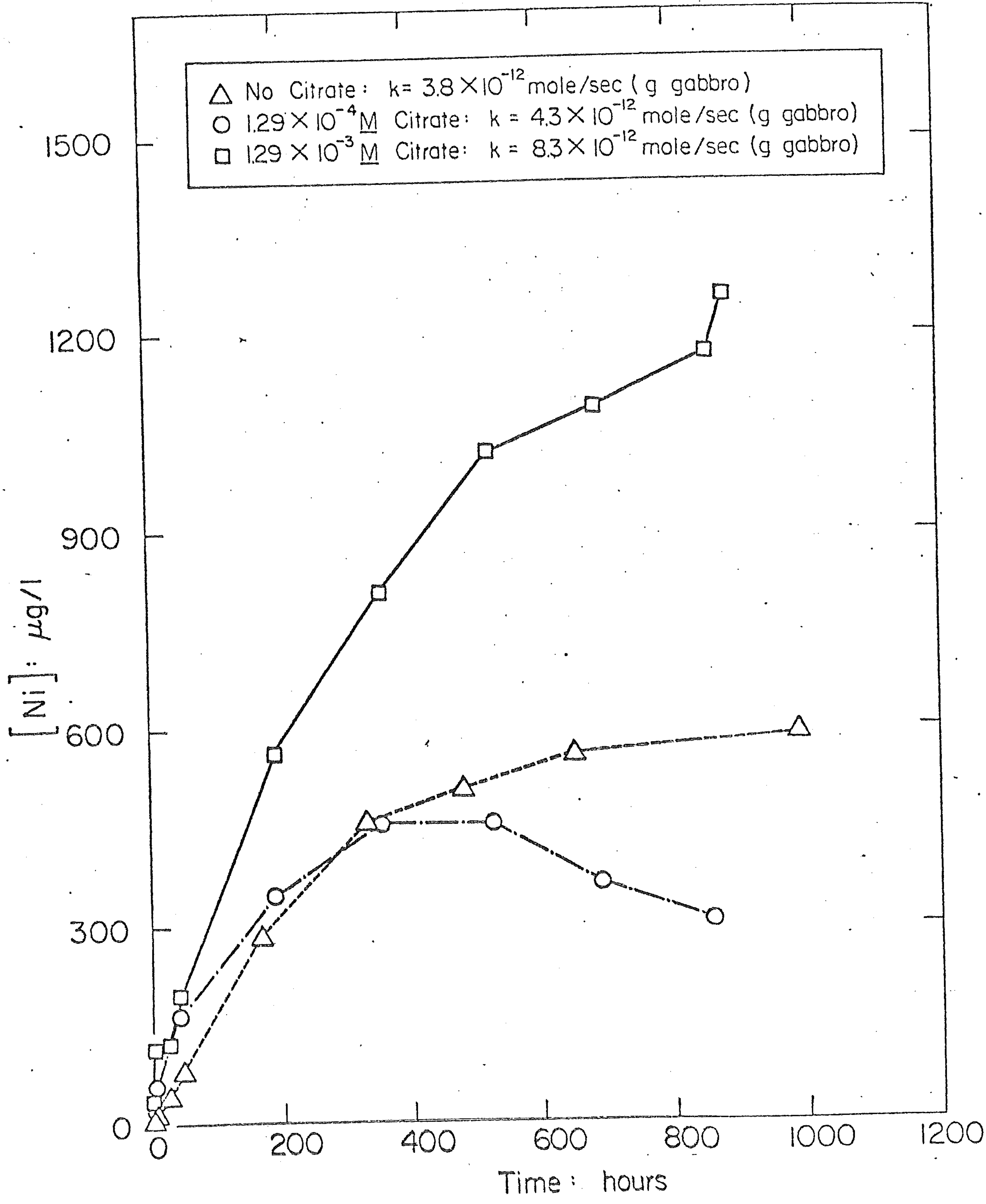


Figure 3.44 [Ni] vs Time: Effect of citrate.



citrate concentration supports this contention (Figures 3.45, 3.46).

The detection of amorphous precipitate in conjunction with previous research indicates that nickel removal may have resulted from reaction with iron or possibly silica. Hem (1977) used thermodynamic data to calculate the solubilities of solids of the form $MeFe_2O_4$ and concluded that aqueous concentrations of copper, nickel and zinc could be substantially reduced due to formation of these solids. The experimental results of Inouye et al. (1976) indicated that α -FeOOH was able to incorporate up to 50 atom percent Cu substitution for Fe. The atomic radii of Fe^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} are 0.83, 0.72, 0.68, 0.82 and 0.69 A^{o}, respectively (Cotton and Wilkinson, 1972), indicating that other trace metals may also react in this manner. Results from Theis and Richter (1979) and Vuceta and Morgan (1978) indicate that adsorption onto iron oxides or silicate surfaces can also significantly reduce trace metal concentrations.

Trace metal scavenging by iron seems more likely than by silica due to solubility considerations. Based on results from REDEQL 2 and research by Nelson (1978), the formation of iron oxide would be expected. Formation of amorphous silica would be expected only if concentrations of silicic acid exceeded $2.0 * 10^{-3}$ $\underline{M}$. An estimate of the maximum silicic acid release can be made assuming a ratio of 2:1 for the release of iron to silicic acid. Using this approximation, the solubility of silicic acid would be exceeded when the iron concentration reached 220 mg/1, which is 50 times the observed iron concentration at the $1.29 * 10^{-4}$ $\underline{M}$ citrate concentration and 8 times the observed iron concentration with the $1.29 * 10^{-3}$ $\underline{M}$ citrate.

Copper leaching was significantly enhanced by the presence of citrate (Figure 3.45). Copper concentrations in the reactors containing citrate exceeded those in the reactor without citrate by nearly two orders of magni-

Figure 3.45 [Cu] vs Time: Effect of citrate

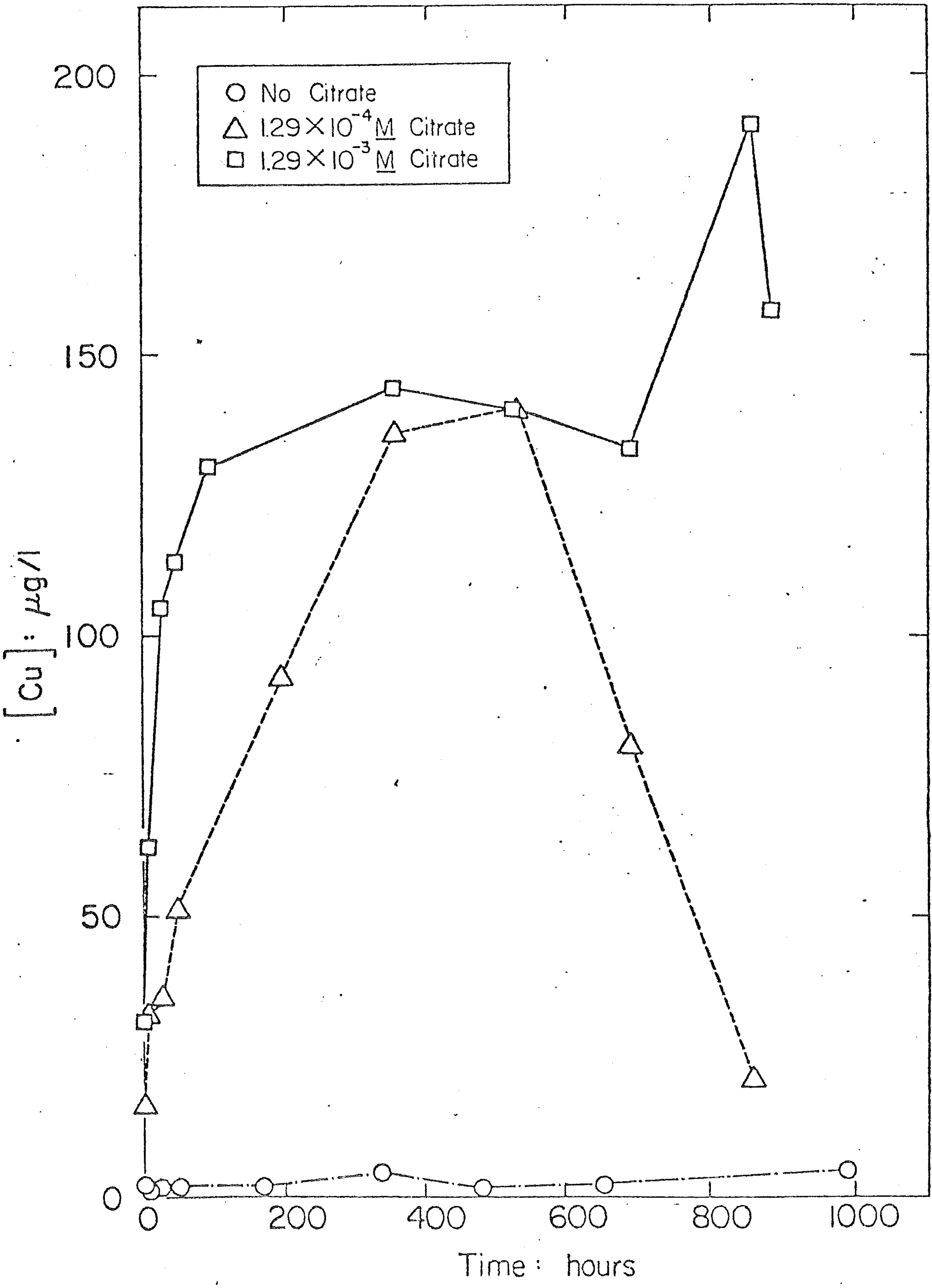
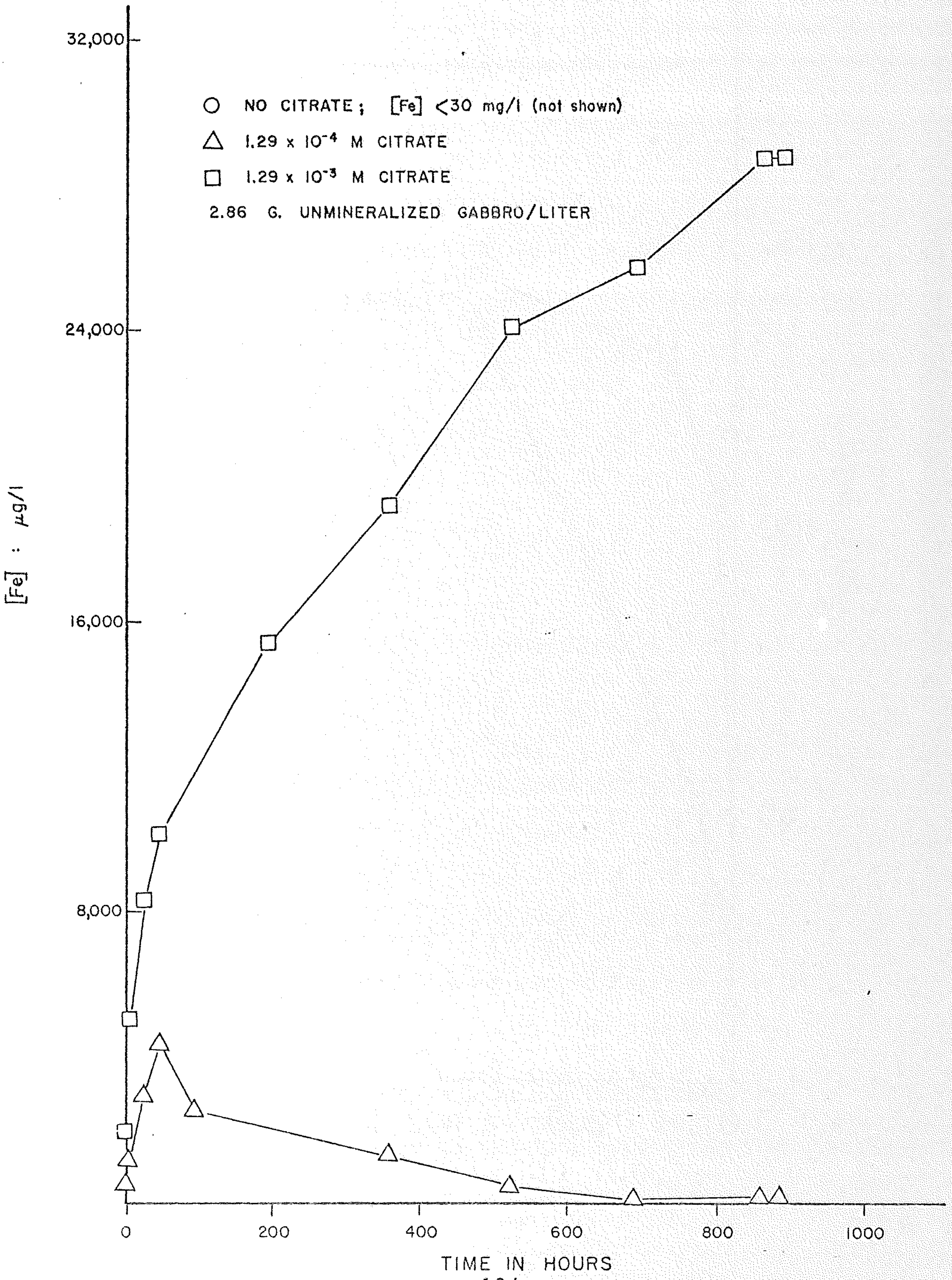


Figure 3.46

[Fe] VS Time: Effect of Citrate



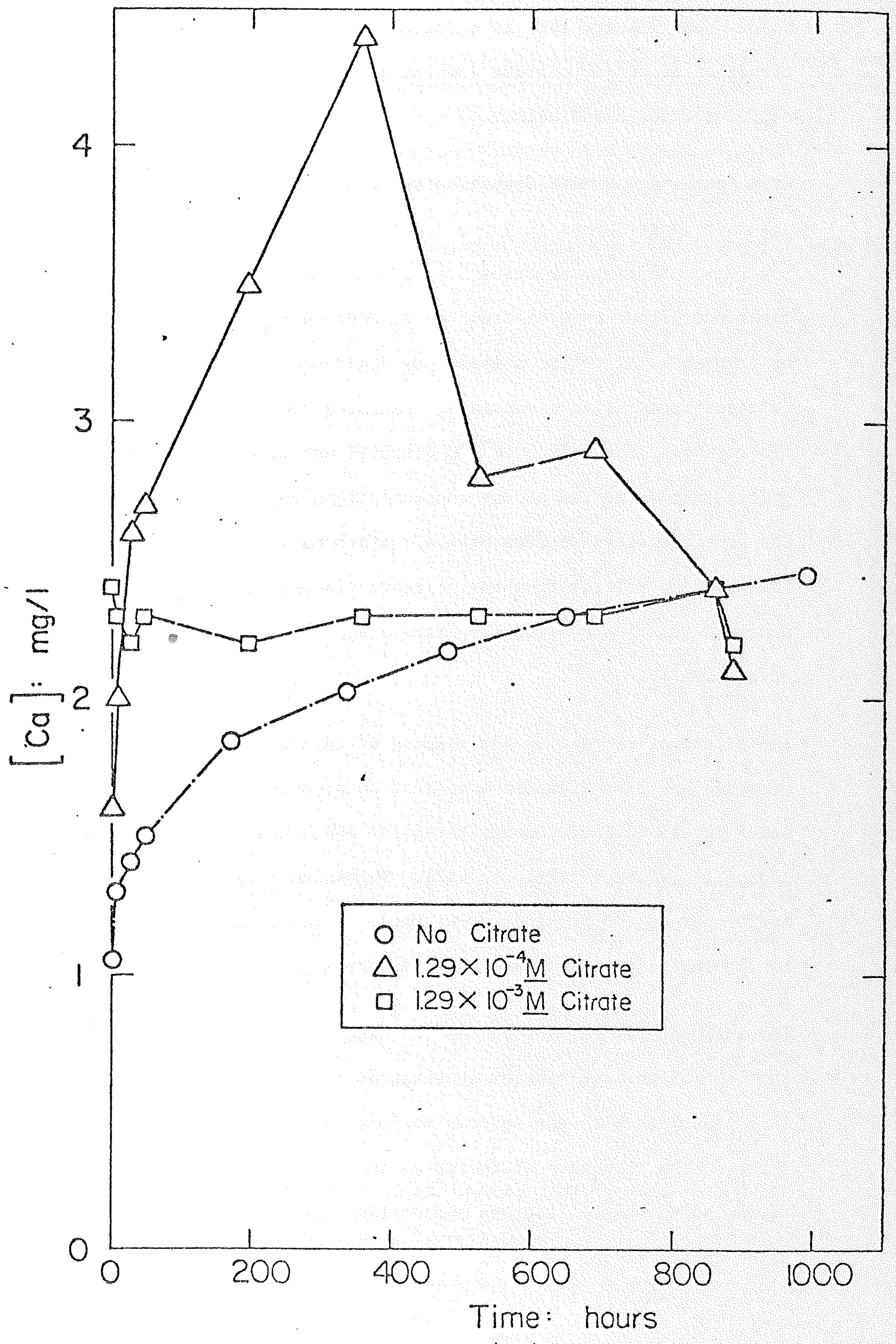
tude. Most likely, this is a result of increased aqueous mobility due to formation of copper citrate complexes rather than a drastic increase in copper sulfide dissolution.

Iron leaching was more dramatically affected by citrate than the leaching of other constituents (Figures 3.43 to 3.47). Iron concentrations in the reactor containing the higher citrate concentrations were 3 orders of magnitude higher than the reactor without citrate. When the concentrations of iron and sulfate are compared is apparent that the majority of iron was released from silicate minerals. Assuming the iron released from sulfide minerals (for the 1.29 * 10^{-3} M citrate) was equal to the sulfate concentration minus the sum of the concentrations of copper and nickel, 70% of the iron released was from minerals other than sulfides (i.e. silicates). The enhanced release from the silicate minerals was evidently the result of a direct reaction between the citrate and the mineral surface (Schalscha et al. 1967).

The effect of citrate on the release of calcium and magnesium from silicate minerals was less dramatic than that on nickel, copper and iron. Calcium leaching was enhanced during the first 400 hours of reaction but was subsequently inhibited (Figure 3.47). Magnesium release was more strongly influenced by the presence of citrate. Release may have been enhanced due to the increased iron leaching from ferromagnesian minerals.

The influence of citrate on the leaching of a given metal is evidently a function of the equilibrium constant of the specific metal-citrate complex in conjunction with the aqueous mobility of the metal in the absence of citrate, the abundance of the metal in the solid phase and the mineral form of the solid phase. Lehrman and Childs (1973) list the log of the formation constants for Cu^{2+}, Ni^{2+}, Fe^{2+} and Mg^{2+}, with $C_6H_5O_7^{3-}$, as 5.9, 5.4,

Figure 3.47. [Ca] vs Time: Effect of citrate



3.1 and 3.4, respectively. Calcium generally forms less stable organometallic complexes than iron (Schalscha et al. 1967) which is most probably the reason that calcium leaching was not as greatly affected by the presence of citrate. The leaching of copper was enhanced to a greater degree than that of nickel since the mobility of copper in the absence of citrate was quite low in comparison to that of nickel.

The effect of citrate on iron leaching can not be explained solely on the basis of the stability of iron citrate complexes, since copper and nickel citrate complexes are more stable. The fact that the iron concentration in the solid phase was two orders of magnitude higher than that of copper or nickel contributed to the relatively high degree of iron leaching. It also appears that iron was leached more readily from the silicate minerals than from the sulfides.

3.5.7.3 Effect of phthallic acid

Phthallic acid had a less pronounced effect on leaching than citrate. Metal sulfide dissolution decreased slightly as phthallic acid concentration increased, (Figure 3.48). Leaching of nickel (Figure 3.49), copper and calcium (Figure 3.50) was inhibited by the presence of phthallic acid, but observed iron concentrations increased with increasing concentrations of phthallic acid.

A possible explanation for this behavior is the adsorption of phthallic acid onto the rock surface. The decrease in sulfide oxidation could then be attributed to a decrease in oxygen transport. The removal of copper and nickel form solution may have increased due to the presence of the adsorbed ligand at the surface as was demonstrated in the research of Davis and Leckie (1978). The inhibition of calcium and magnesium release may have been due to the hinderance of diffusion of H^+ or cations at the solid surface.

Figure 3.48. Sulfate concentrations vs time: Effect of phthallic acid

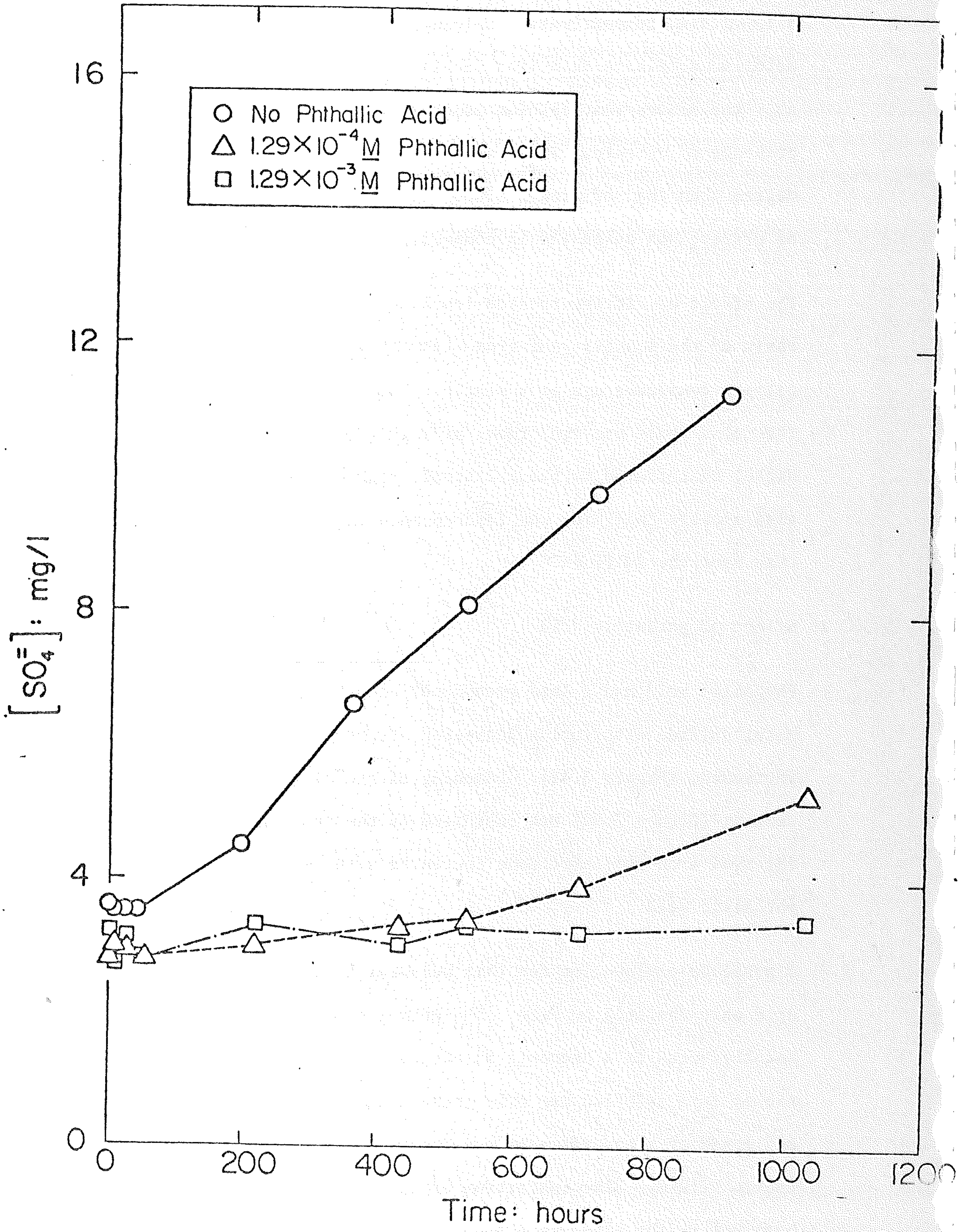


Figure 3.49. [Ni] vs Time: Effect of phthallic acid

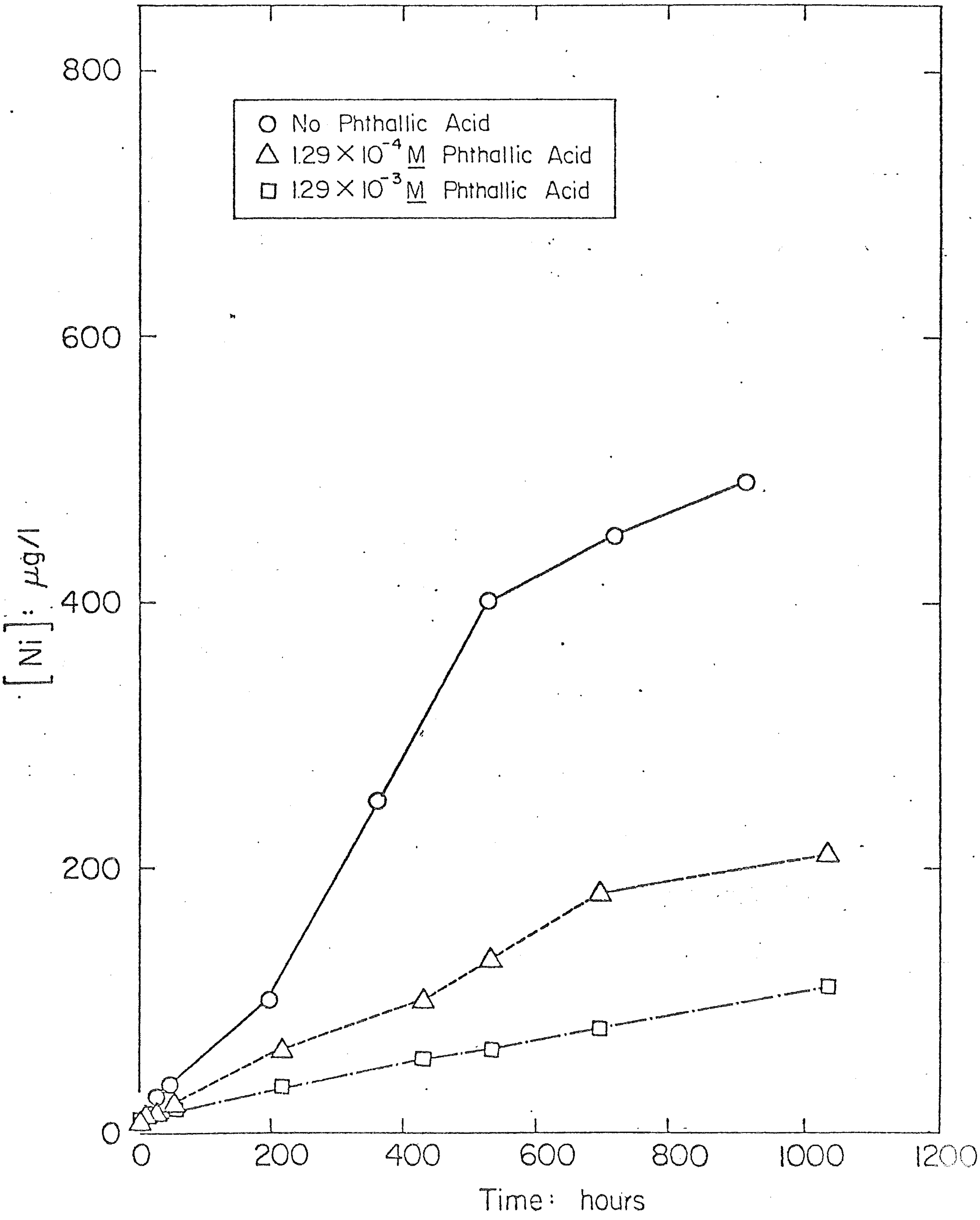
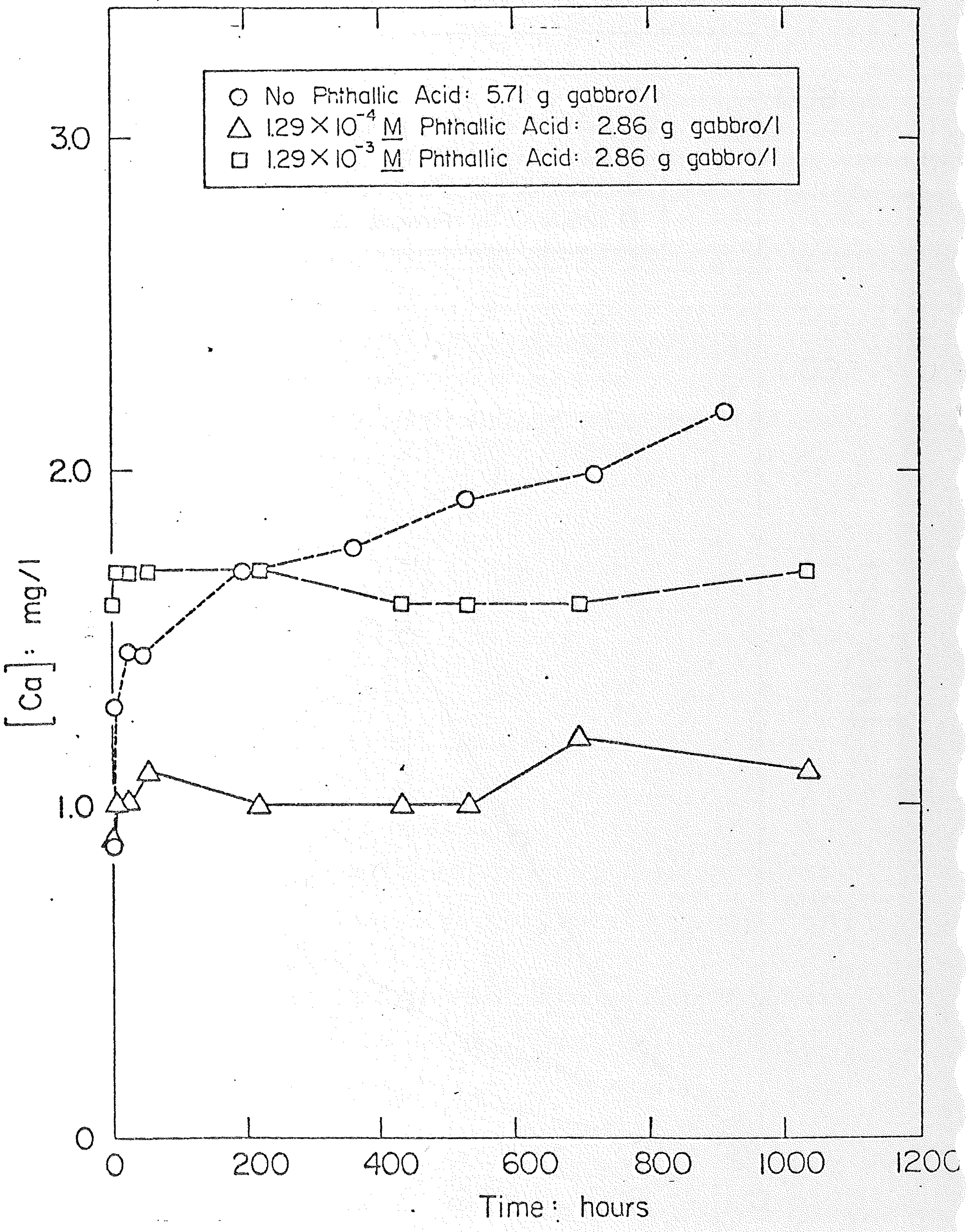


Figure 3.50. [Ca] vs time: Effect of phthallic acid



3.5.8 Natural Waters

The concentration of various components present in the natural waters collected from the study region are presented in Table 3.12. Dissolution of silicates and sulfides was not significantly affected by the natural waters although the mobility of nickel and copper was enhanced in the natural waters. This effect is presented in Figures 3.51 and 3.52 and reflects the capability of metals complexation by naturally occurring organics, thus enhancing leaching.

Calcium release in the natural waters was less than in megapure water (Figure 3.53). The initial calcium concentrations in the bog water and surface water were 7.8 and 18.9 mg/l respectively.

3.5.9 Summary of Batch Reactor Kinetic Data

3.5.9.1 Introduction

The dissolution kinetics of metal sulfide and silicate minerals in batch reactors were quantitatively analyzed under conditions of variable surface area, A_s, hydrogen ion concentration, (H^+), and dissolved oxygen concentration. Qualitative observations were made on the effects of ionic strength, I, and concentration of organics on mineral dissolution.

3.5.9.2 Sulfide Oxidation

The rate of sulfide oxidation exhibited a first order dependence on surface area, A_s, and dissolved oxygen concentration, (O_2), and was proportional to $(H^+)^{0.2}$ over the range $5 \leq pH \leq 8$.

$$\frac{d\ (SO_4^{=})}{dt} = k\ A_s^{\ 1.0}\ (H^+)^{0.2}\ (O_2)^{1.0} \qquad (3.130)$$

Figure 3.51. [Ni] vs Time: Effect of natural waters

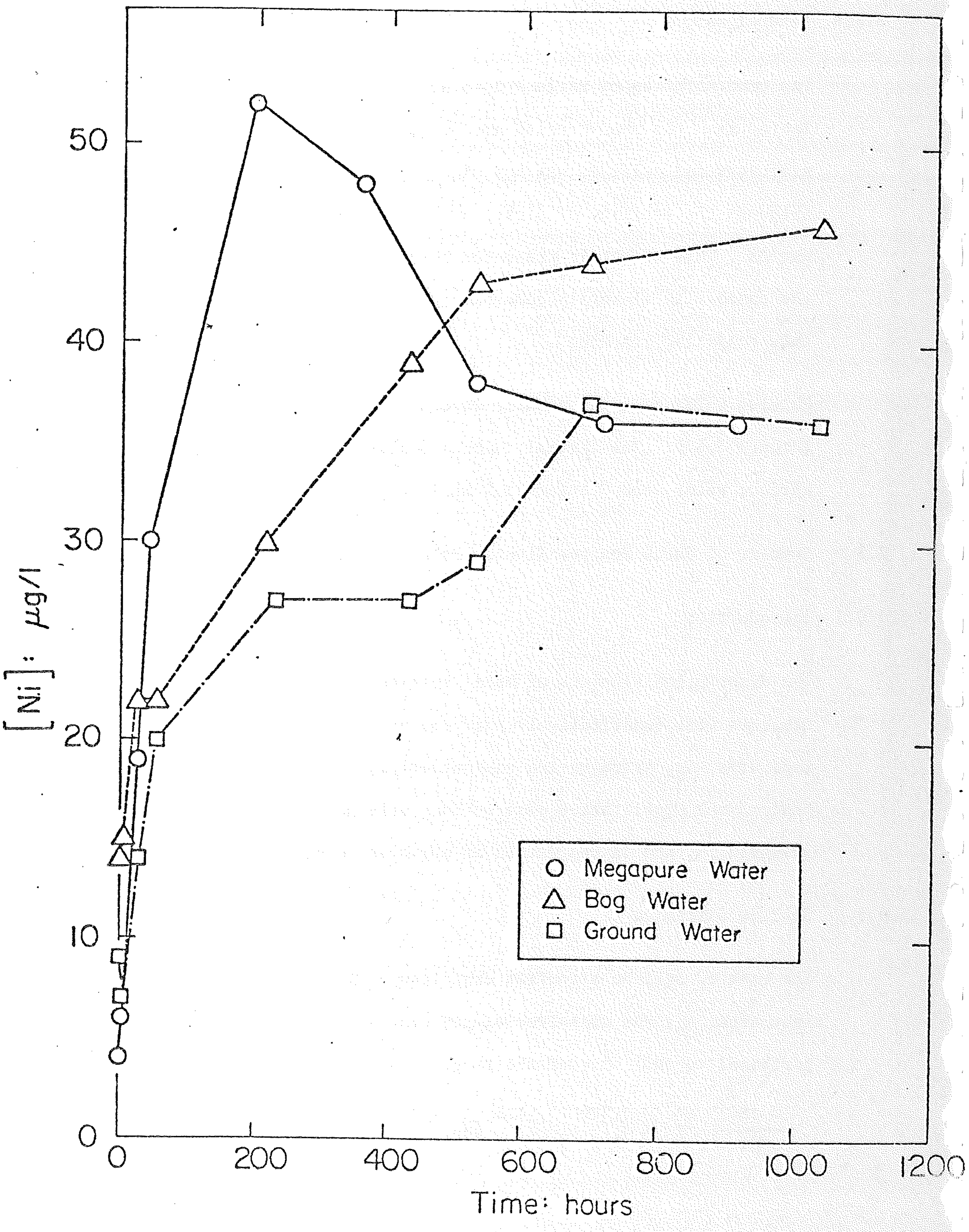


Figure 3.52 [Cu] vs Time: Effect of natural waters

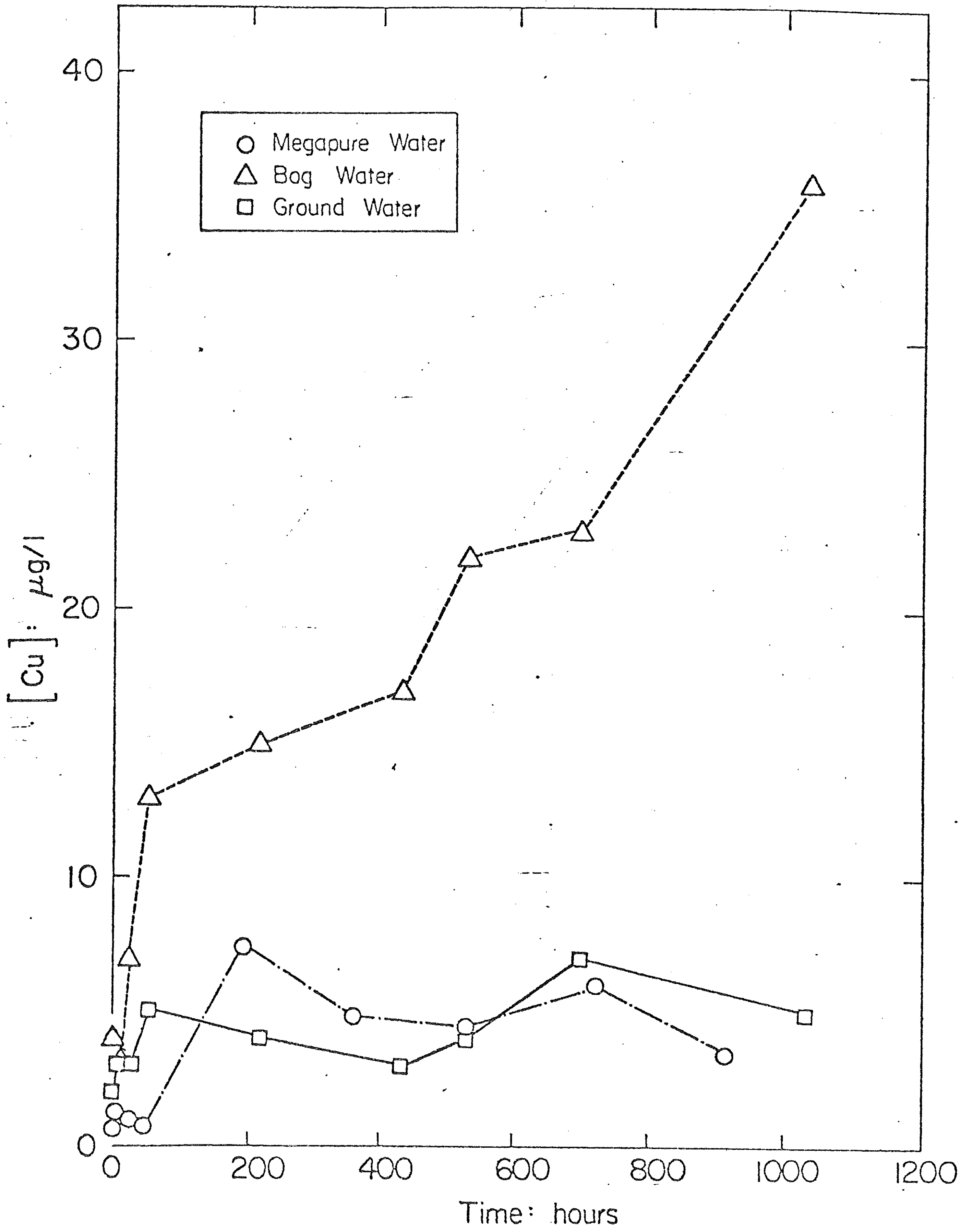
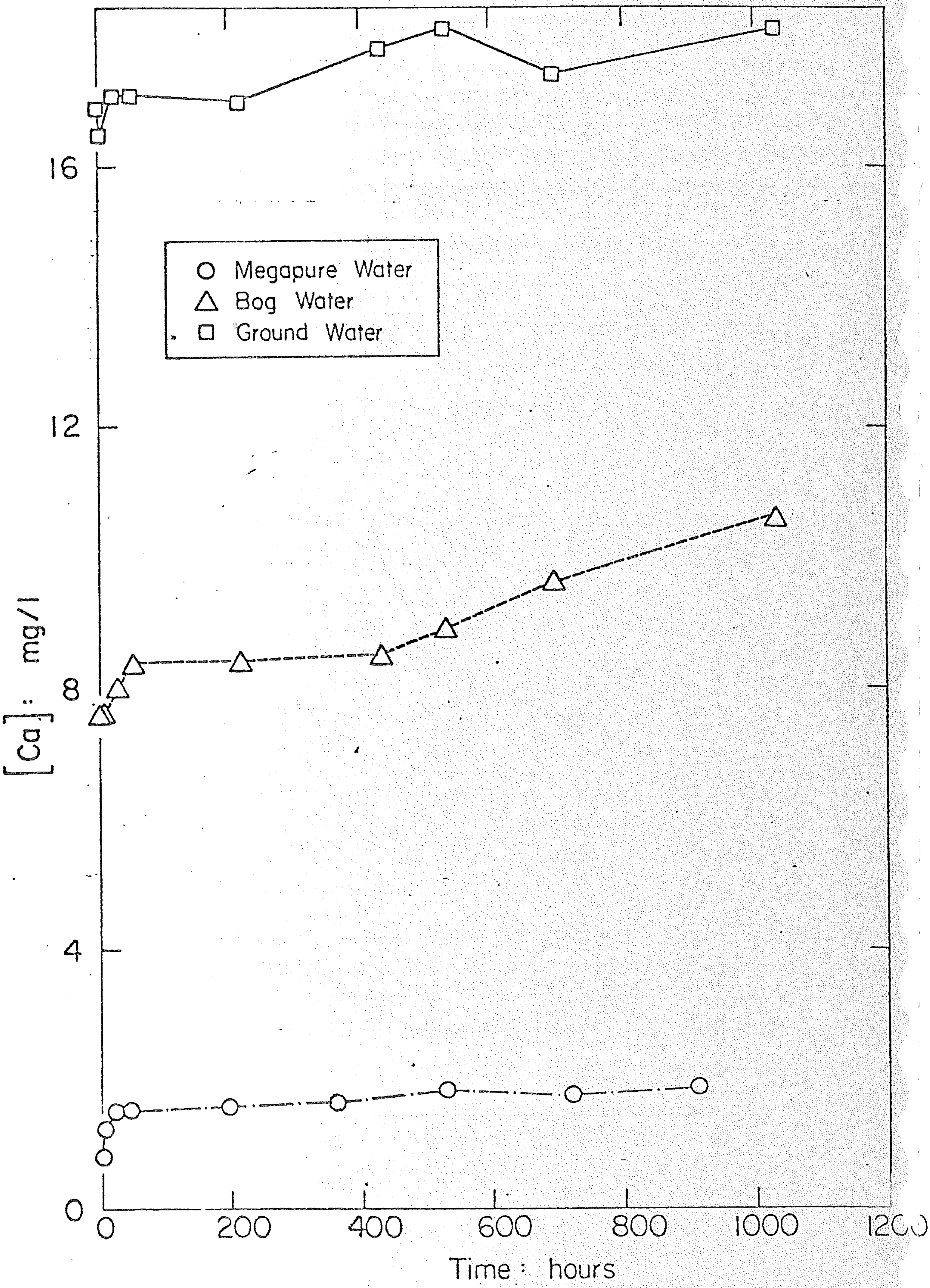


Figure 3.53. [Ca] vs Time: Effect of natural waters



Results form experiments varying the loading of unmineralized gabbro ($3400-170{,}000\ cm^2/l$) and the particle size of mineralized gabbro ($72-4900\ cm^2/l$) respectively yielded the following relations:

$$\frac{d\,(SO_4^=)}{dt} = k_1\,A_s^{1.2},\ r^2 = 0.985 \qquad (3.131)$$

$$\frac{d\,(SO_4^=)}{dt} = k_2\,A_s^{1.0},\ r^2 = 0.714 \qquad (3.132)$$

These values indicate a first order dependence on surface area which is consistent with the results of Nelson (1978).

The rate of appearance of sulfate in solution was proportional to $(H^+)^{0.2}$ over the range $5 \leq pH \leq 8$. The dependence appeared to increase as pH decreased below 6, perhaps due to additional dissolution resulting from direct attack of H^+ on the metal sulfide surface. The results of Pankow (1979) indicated that this mechanism is dominant in the dissolution of FeS at $pH < 4.3$.

Data from reactors having dissolved oxygen concentrations of 5, 9 and 44 mg/l were used to determine the dependence of sulfide oxidation on dissolved oxygen. The reactor having 1 mg/l dissolved oxygen was omitted due to the anomalous behavior of sulfate. The resultant equation was

$$\frac{d\,(SO_4^=)}{dt} = k_3\,(O_2)^{1.1} \qquad (3.133)$$

The rate of sulfide oxidation increased with ionic strength, evidently due to the effect of ionic strength on solubility. Quantification of the relationship of rate and ionic strength is tenuous due to the limited data and the conceptual problem of relating reaction rates to solubility constants. The extended Debye-Huckel law yields the equation

$$\log K_{so} = \log {}^{c}K_{so} - (nz_M^2 + mz_N^2)\,\frac{0.5\sqrt{I}}{1+\sqrt{I}} \qquad (3.134)$$

for the reaction $M_nN_m(s) = nM + mN$.

The relationship between sulfide oxidation rate and $M = \frac{0.5\sqrt{I}}{1+\sqrt{I}}$ is presented in Figure 3.54. A linear regression analysis of the data yielded the equation

$$k_{SO_4} * 10^{10} = 15M + 2.7, \quad r^2 = 0.966 \tag{3.135}$$

Using the data points at I = 0.005 and I = 0.05 in a log-log analysis the following equation was determined.

$$k_{SO_4} = k_5 \, I^{0.1} \tag{3.136}$$

Sulfide oxidation rates for reactors containing 0, $1.29 * 10^{-4}$ and $1.29 * 10^{-3}$ <u>M</u> citrate were (3.1, 0.91 and 10 mole) $* 10^{-10}$/g-min. Quantification of a relationship between the rate and citrate concentration is impractical due to the erratic variation. Sulfide oxidation was enhanced at the $1.29 * 10^{-3}$ <u>M</u> citrate concentration but was inhibited at the lower concentration. Rate inhibition was also observed in the presence of phthallic acid and natural waters.

3.5.9.3 Nickel and Copper Kinetics

Nickel release was quantified as a function of mineralized gabbro surface area, A_s, the concentration of hydrogen ions, (H^+), and dissolved oxygen concentration (0_2); the result expressed:

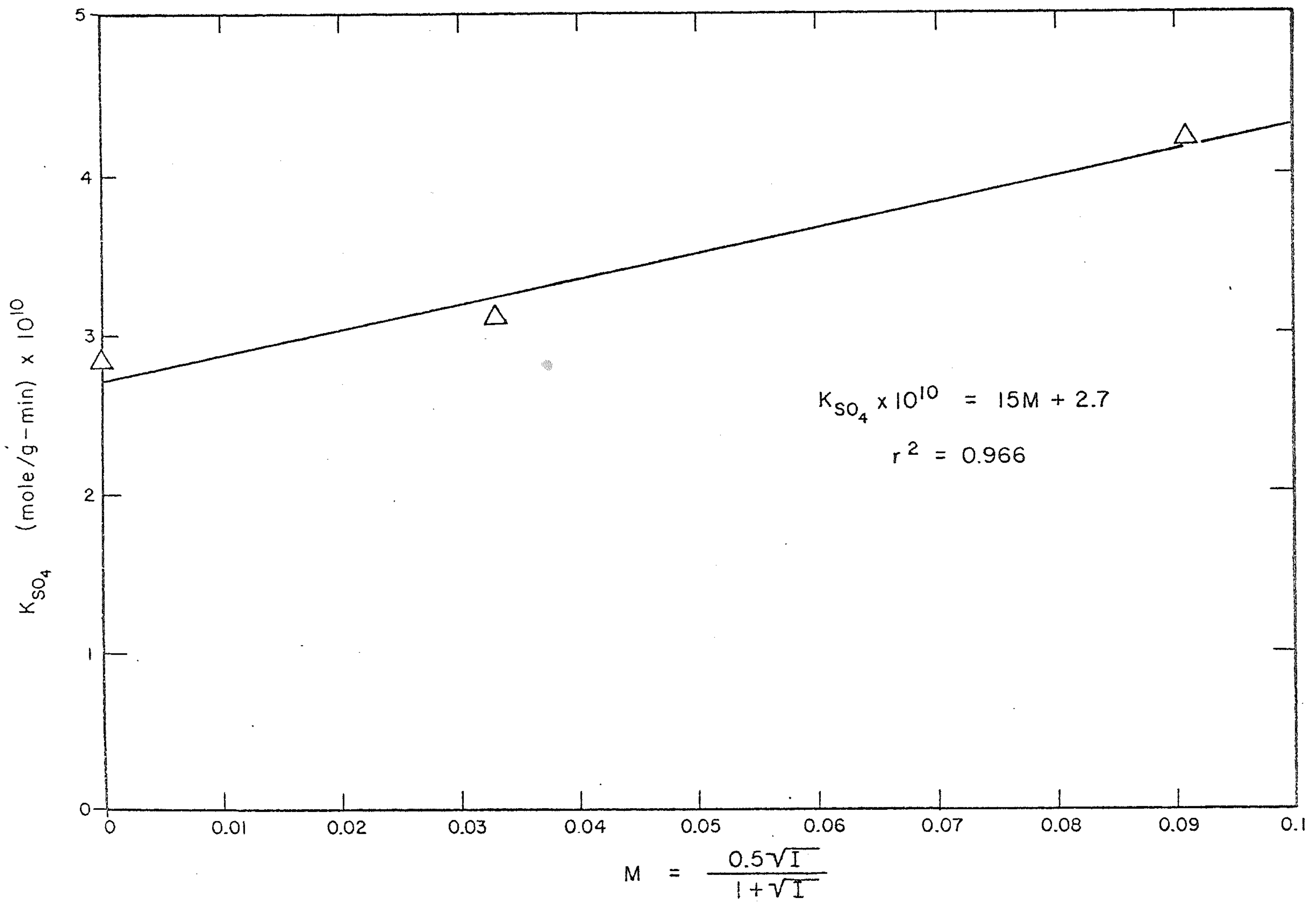
$$\frac{d\,(Ni^{2+})}{dt} = k\, A_s^{0.4}\, (H^+)^{0.13}\, (0_2)^{0.7} . \tag{3.137}$$

A 0.12 order dependence on hydrogen ion concentration was determined by Corrans and Scholtz (1976) for the leaching of pentlandite in acidified (1.8 < pH < 4) ferric sulfate.

The observed nickel release rate varied with $(0_2)^{0.7}$ over the range $1 \leq (0_2) \leq 9.3$ mg/1 but was independent of dissolved oxygen concentration

Figure 3.54

EFFECT OF IONIC STRENGTH ON K_{SO_4}



at higher levels. Schneerson et al. (1966) reported a rate proportional to $(P_{O_2})^{0.5}$ in the autoclave leaching of pentlandite.

The effect of ionic strength on nickel release was similar to that on sulfate release. Using the data at ionic strengths of 0.005 and 0.05 M the relationship of nickel release and ionic strength was determined as

$$\frac{d\,(Ni^{2+})}{dt} = k_7\, I^{0.1} \ . \qquad (3.139)$$

The rates of nickel appearance in solution for citrate concentrations of 0, $1.29 * 10^{-4}$ and $1.29 * 10^{-3}$ M were (1.8, 3.0 and 3.4 mole) $* 10^{-10}$/g-min, demonstrating a slight rate increase with increasing citrate concentration. The presence of phthallic acid and natural waters exhibited an inhibitive effect on nickel release as was the case for sulfate release.

Copper Kinetics

The rate of appearance of copper in solution was quantified with respect to hydrogen ion concentration, the resultant equation being

$$\frac{d\,(Cu^{2+})}{dt} = k_8\, (H^+)^{0.6} \ , \quad r^2 = 0.991 \qquad (3.140)$$

In general the leaching of copper appeared to be limited by its low aqueous mobility. As a result leaching was enhanced under conditions of low pH and the presence of complexing organics. The effect of organics was most pronounced for citrate. At concentrations of 0, $1.29 * 10^{-4}$ and $1.29 * 10^{-3}$ M citrate the copper release rates were (0.005, 0.61 and 1.5 moles) $* 10^{-12}$/g-min.

3.5.9.4 Comparison of Metal Sulfide Leaching Rates with Other Reported Rates

The expression of rates as a function of total surface area is not entirely correct due to the large number of chemical constituents present in the solid phase. To adjust for this discrepancy an adjusted solid surface area was computed for sulfide, copper and nickel.

Metal sulfide minerals composed 4.8 volume percent of the DP 9002 sample (Stevenson et al., 1979). Using this figure as the percentage of surface area composed of metal sulfide minerals is reasonable since the mineralogical composition was determined by thin section analysis.

The fraction of surface area composed of each individual metal sulfide was determined using the chemical compositional analysis and assuming a 1:1 molar ratio of metal to sulfide. The calculation of adjusted surface area is presented in Table 3.20 and the resultant rates in Table 3.21.

The calculated rates are slower by an order of magnitude, than the $1.14*10^{-10}$ to $4.03*10^{-10}$ mole/cm^2-min rates reported by Nelson (1978) for FeS dissolution. This discrepancy does not appear to be major, since the sample used by Nelson (1978) was a pure synthetically prepared sample as opposed to the highly complex host rock used in the batch reactors. Koch (1975) mentioned that the presence of copper in a sulfide such as chalcopyrite stabilizes the ferric iron present. Similar effects may occur with other complex sulfides.

Table 3.20 Calculation of surface area adjustment factor, f_{as}

ELEMENT	Wt %	$\frac{\text{Wt }\%}{\text{At.Wt.}} = F_x$	(F_x/F_s)	$f_{as} = \frac{F_x}{F_s} * 0.048$
S	3.92	$0.122(F_s)$	1.0	0.048
Cu	0.85	0.013	0.11	0.0052
Ni	0.23	0.0039	0.032	0.00154
Fe(as FeS)	5.8	0.10	0.86	0.042

Volume % metal sulfide = 4.8
Co + Zn < 0.6 Wt %

Table 3.21 Adjusted metal sulfide release rates

Rates in mole / cm^2-min.

pH	SO_4*10^{12}	$Cu*10^{12}$	$Ni*10^{12}$	$Fe*10^{12}$[a]
5	10	1.8	27	10
6	4.4	0.35	21	b
7	3.5	0.13	13	b
8	2.9	0.021	12	b

[a] Assuming $\frac{d(SO_4^{=})}{dt} = \frac{d(Cu^{2+})}{dt} + \frac{d(Ni^{2+})}{dt} + \frac{d(Fe^{2+})}{dt}$ at pH 5

[b] Not calculated since copper and nickel were removed from solution at pH $\geq$ 6, thereby making the calculation in "a" infeasible.

3.5.9.5 Mechanistic Interpretations of Metal Sulfide Leaching

Both metal sulfide dissolution and secondary reactions of metals in solution must be considered in evaluation of trace metal leaching. At least three mechanisms appear to operate in the dissolution of metal sulfides present in the Duluth gabbro. The reaction products of the metal sulfide dissolution and secondary reactions can be hypothesized based on equilibrium considerations and previous research.

Three mechanisms of metal sulfide dissolution reported in the literature are:

$$\mathrm{MeS} = \mathrm{Me}^{2+} + \mathrm{S}^{=} \qquad (3.141)$$

$$\mathrm{MeS} + \tfrac{1}{2}\mathrm{O}_2 + 2\mathrm{H}^+ = \mathrm{Me}^{2+} + \mathrm{S}^{\mathrm{o}} + \mathrm{H}_2\mathrm{O} \qquad (3.142)$$

$$\mathrm{MeS} + 2\mathrm{H}^+ = \mathrm{Me}^{2+} + \mathrm{H}_2\mathrm{S} \qquad (3.143)$$

Pankow (1979) concluded that the first reaction, resulting from normal thermal vibrations and H_2O solvation effects, was dominant at pH 5.6 in the anoxic dissolution of mackinawite (FeS). Pankow (1979) noted that dissolution in an oxic medium would take place oxidatively but that dissolution via reaction 3.141 would also occur to a lesser extent (personal communication, 1979). Aqueous sulfide generated by this reaction would subsequently react to form sulfate under oxidizing conditions.

The second mechanism was proposed by Sato (1960b) and Nelson (1978) for metal sulfide oxidation under environmental conditions. The effect of dissolved oxygen concentration on the rate of leaching in batch reactors supports the operation of this mechanism. The elemental sulfur generated was subsequently oxidized to sulfate as was suggested by Sato (1960b) and further supported by Nelson (1978) in the case of iron sulfide.

The third mechanism was reported by Locker and deBruyn (1969) in the dissolution of cadmium and zinc sulfides and by Pankow (1979) for the dissolution of mackinawite (FeS). Pankow (1979) determined that this mechanism was dominant for pH < 4.3. The detection of the odor of H_2S from a reactor (pH ~ 3.7) strongly suggests the action of this mechanism in lower pH ranges.

Exchange reactions may also affect trace metal release from metal sulfides as is suggested by the results of Gaudin et al. (1957), Gaudin et al. (1959) and Furstenau and Metzger (1960). The net effect of these reactions would be the enhancement of release of metals of higher solubility with respect to sulfide while inhibiting the release of metals of lower solubility. The magnitude of this effect may be small since it occurs to a minimal depth in the solid.

Based on experimental results and the results of Sato (1960b) and Nelson (1978) the dominant reaction mechanism appears to be that represented by reaction 3.142. The reaction kinetics of the individual metal sulfides vary, pentlandite leaching more readily than the copper sulfides.

The results from the pH experiment leaching unmineralized gabbro suggest that the oxidation of copper and nickel sulfides may be inhibited at lower pH. This effect has been reported for lower pH ranges in the leaching of metal sulfides by ferric sulfate (Corrans and Scholtz (1976), Dutrizac and MacDonald (1974), Arai and Majima (1977)).

The observation of this effect in higher pH ranges (4-5) may be due to the fact that oxygen, at the concentrations employed, is a less effective oxidizing agent than the high concentrations of ferric ion used in other studies.

The ultimate fate of the metals associated with sulfide depended upon the chemistry of the individual metal and the solution composition. In the pH ranges employed in batch reactor tests the iron released evidently reacted to form lepidocrocite (γ-FeOOH), the sole reaction product identified by Nelson (1978) in the oxidative dissolution of ferrous sulfide. Copper speciation, as predicted by REDEQL 2, was more diverse as is presented in Figure 3.55. For pH < 6 the predominant form was Cu^{2+} and as pH increased (6.8-7.8) malachite ($Cu_2(OH)_2CO_3$) was the major reaction product predicted. Copper removal by adsorption was also predicted. The majority of nickel remained as a free metal with some removal by adsorption predicted (Figure 3.56).

The rates determined in column leaching tests were consistent with these observations. Sulfate leaching rates in the column were more rapid than in batch reactors, evidently due to more efficient oxygen transport to reactive sites. Nickel leaching rates were also slightly faster in columns, possibly a result of the increased sulfide oxidation. Copper leaching rates were slower in the columns, apparently due to transport limitation.

3.5.9.6 Silicate Dissolution

Silicate dissolution was monitored based on observed concentrations of calcium and magnesium. The major mineral forms of these metals were plagioclase ($Na_x\, Ca_{(1-x)}\, Al_{(2+x)}\, Si_{(2+x)}\, O_8$) and olivene ($(Mg,Fe)SiO_4$), respectively. The rates of release of calcium and magnesium were dependent upon the time

Figure 3.55

COPPER SPECIATION AS A FUNCTION OF pH

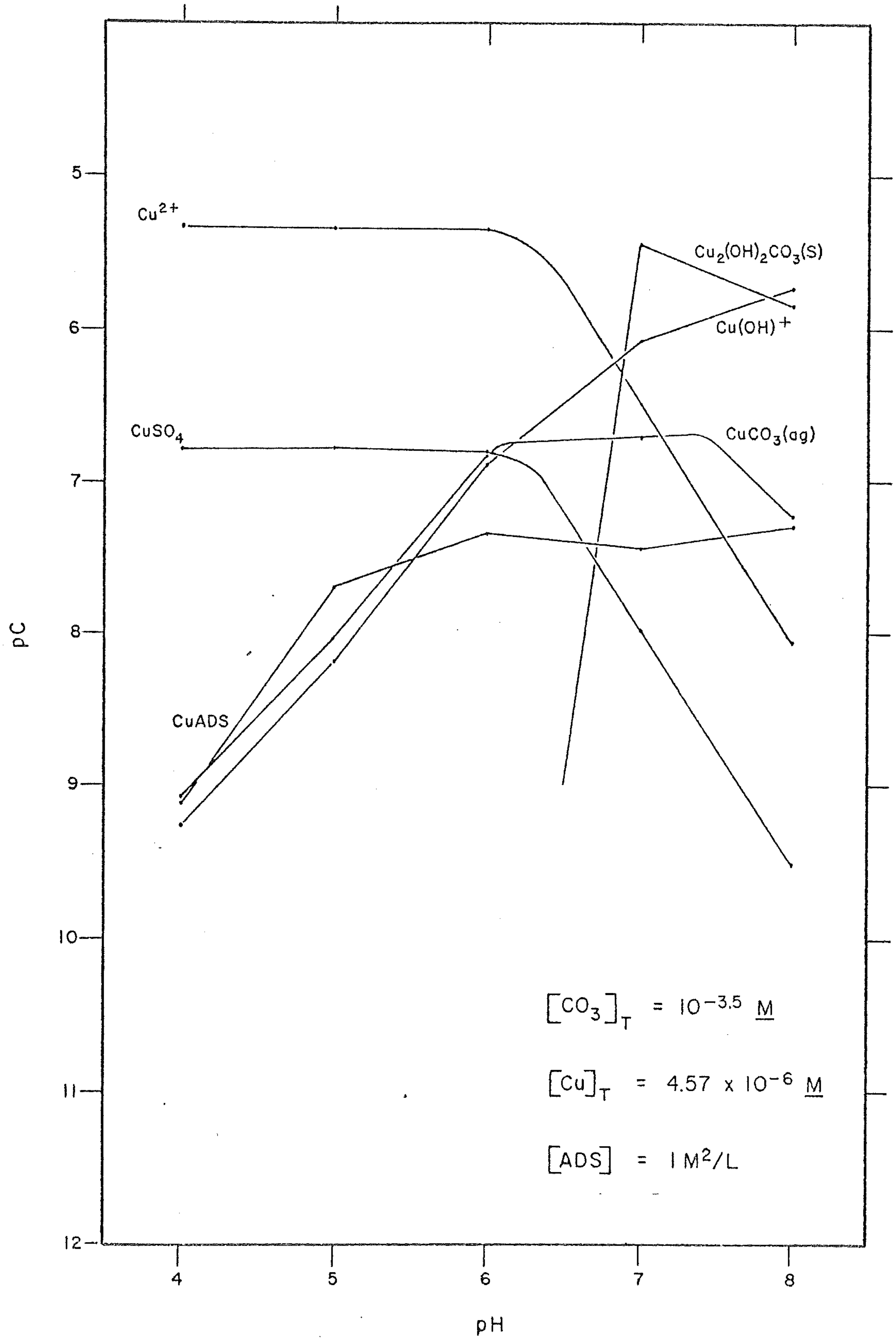
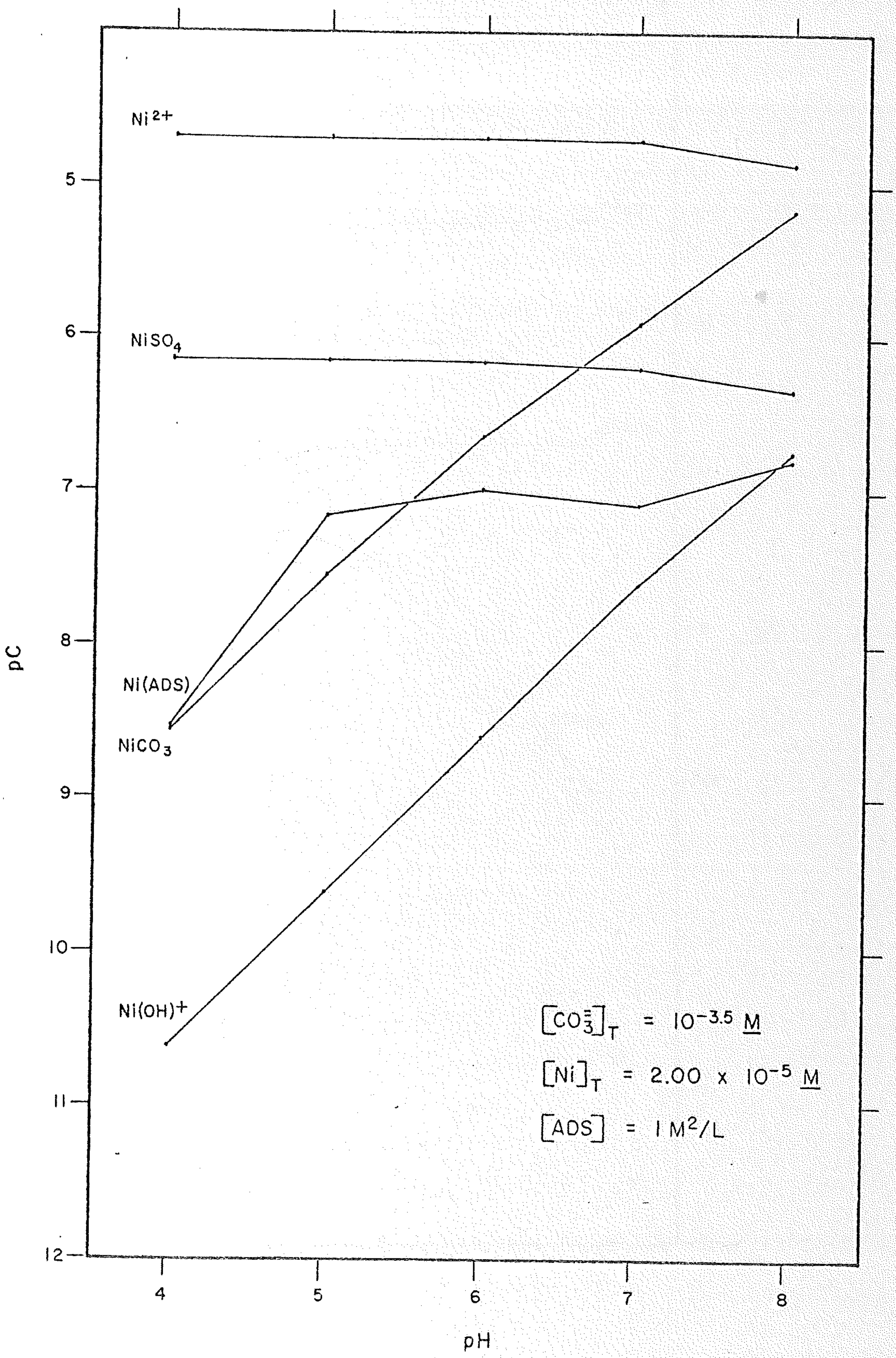


Figure 3.56

NICKEL SPECIATION AS A FUNCTION OF pH



of reaction. The following discussion is based on release rates at t = 1 hour and t = 500 hours.

The rate of release of calcium and magnesium obeyed the following functions

$$\frac{d(Ca)}{dt}_{1\ hr} = k_1 A_s^{0.8} (H^+)^{0.08} \tag{3.144}$$

$$\frac{d(Mg)}{dt}_{1\ hr} = k_2 A_s^{0.4} (H^+)^{0.07} \tag{3.145}$$

$$\frac{d(Ca)}{dt}_{500\ hr} = k_3 A_s^{1.2} (H^+)^{0.1} \tag{3.146}$$

$$\frac{d(Mg)}{dt}_{500\ hr} = k_4 A_s^{0.7} (H^+)^{0.1} \tag{3.147}$$

The dependence on surface area is based on results from the mass loading experiment in which surface area was varied from 3400-170,000 cm^2/l. In the experiment varying particle size the dependence of release of both calcium and magnesium obeyed the relations

$$\frac{d(Me)}{dt}_{1\ hr} = kA_s^{0.3} \tag{3.148}$$

$$\frac{d(Me)}{dt}_{500\ hr} = kA_s^{0.4} \tag{3.149}$$

The lesser dependence may have been due to the alteration of physical characteristics of the solid. In the larger particles diffusion of calcium and magnesium per unit surface area may have been enhanced due to larger pores in the solid. The occurrence of large pores in the smaller particles may have been less frequent due to the cleavage of particles along pores during the grinding process.

The pH dependence resulted from the exchange of H^+ from solution with calcium and magnesium ions in the silicate matrix. Busenberg (1979) indicated that although reaction products may form in patches on the surface, diffusion through the silicate skeleton is the rate limiting process in feldspar dissolution. Luce et al. (1972) suggested a similar occurrence in the dissolution of forsterite (Mg_2SiO_4), noting that "diffusion coefficients for the exchange of Mg^{2+} and H^+ will depend on the concentrations of these ions in the solid, at the solution/solid interface and the diffusion mechanism."

The dependence of release of calcium and magensium on dissolved oxygen concentration varied from -0.02 to 0.2 but the values for r^2 in all cases were less than 0.4. Since oxygen does not participate in the reactions involving release of calcium and magnesium a zero order dependence on oxygen concentration would be expected. The enhancing effect of oxygen on iron sulfide oxidation, and therefore acid production, indirectly affected the release of calcium and magnesium. Due to the low correlation observed between release and dissolved oxygen concentration, quantification of this effect is infeasible.

Increases in ionic strength enhanced the release of calcium and magnesium in the initial stage of reaction only. This effect was evidently the result of the exchange of Na^+ ions in solution for Me^{2+} ions in the mineral phase. Once this exchange was completed little effect on the release rates was detected.

The presence of citrate enhanced calcium leaching only during the initial stage of reaction. Magnesium release increased with increasing citrate concentration. This was possibly due to the strong effect of citrate on iron release. Removal of iron from the olivene matrix may have enhanced the release of magnesium. Phthallic acid enhanced the release of calcium and magnesium only in the initial stage of reaction ($t < 1$ hr). Following the initial stage release of both metals was inhibited by the presence of phthallic acid.

3.5.9.7 Comparison of Calcium and Magnesium Release Rates with Other Reported Rates

The rates observed for the release of calcium and magnesium compare closely with those reported by Busenberg and Clemency (1976) and Luce et al. (1972). The calcium release rate at pH 5 and t = 500 hours from the batch reactors was 5.3 * 10^{-16} moles/cm^2-sec for the linear calcium release stage from anorthite at approximately the same pH. The loading used by Busenberg and Clemency (1967) was two orders of magnitude higher than that used in batch reactors and the calcium content approximately 3.8 times higher.

Luce et al. (1972) reported values ranging from 2.3 * 10^{-13} to 6.7 * 10^{-13} for the release of magnesium from forsterite at a loading approximately half that in the batch reactors. The value determined in batch reactors was 2.5 * 10^{-14} mole/cm^2-sec, approximately an order of magnitude slower. This discrepancy may be due to compositional differences since the solid phase used by Luce et al. (1972) contained 15 times the magnesium present in the gabbro used in the batch experiments.

3.6 Column Leaching Experiments

3.6.1 Introduction

In the column leaching experiments the effects of variable solid phase and solution composition on the leaching process were investigated. Detectable leaching occurred in all cases with solid phase variation being the dominant factor for sulfide, nickel and cobalt leaching while solution composition was more influential in leaching of copper and iron. No significant pH trends were detected as pH generally remained between 7 and 8 in all solutions. A summary of experimental results is presented in Table 3.22 and the observed rates in Table 3.23

Table 3.22 Summary of results from column leaching experiment
Particle size: $0.25<d<0.64$ cm

VARIABLE	EFFECT on pH	SULFATE LEACHED (Sulfide dissolution)	COPPER LEACHED	NICKEL LEACHED	COBALT LEACHED
Composition: Min vs Unmin	none	greater leaching with mineralized	little effect	significantly greater with mineralized	
Water: rain, surface and groundwater (RW,SW,GW)	none	GW>RW>SW	SW>GW >RW	GW>SW >RW	GW>SW >RW

3.6.2 Effect of Rock Composition

The data indicate that with each leaching solution metal sulfide dissolution increases with increased sulfide mineralization, as reflected by the sulfate leaching data presented in Figure 3.57

Nickel and cobalt leaching follow a similar trend, but the effect of increased mineralization is markedly more pronounced as is indicated in Figures 3.58 and 3.59. The ratio of mineralized to unmineralized gabbro leaching rates exceeds two orders

Table 3.23 Release rates from column leaching experiment: kg/m^2-yr

SOLUTION SOLID	GROUNDWATER		SURFACE WATER		RAIN WATER	
	Mineral	Unmin.	Mineral	Unmin.	Mineral	Unmin.
Component						
$SO_4 * 10^4$	5.4	2.5	2.5	1.9	3.8	2.0
$Ni * 10^7$	320.	8.8	200.	4.0	160.	0.25
$Cu * 10^7$	0.85	0.65	2.0	2.7	0.35	0.13
$Co * 10^7$	18.	0.40	8.5	0.19	7.9	0.023
$Fe * 10^7$	2.1	3.5	7.7	4.6	0.31	0.60
$Mn * 10^7$	38.	5.4	23.	3.1	16.	0.23

FIGURE 3.57 MASS SULFATE LEACHED VS TIME

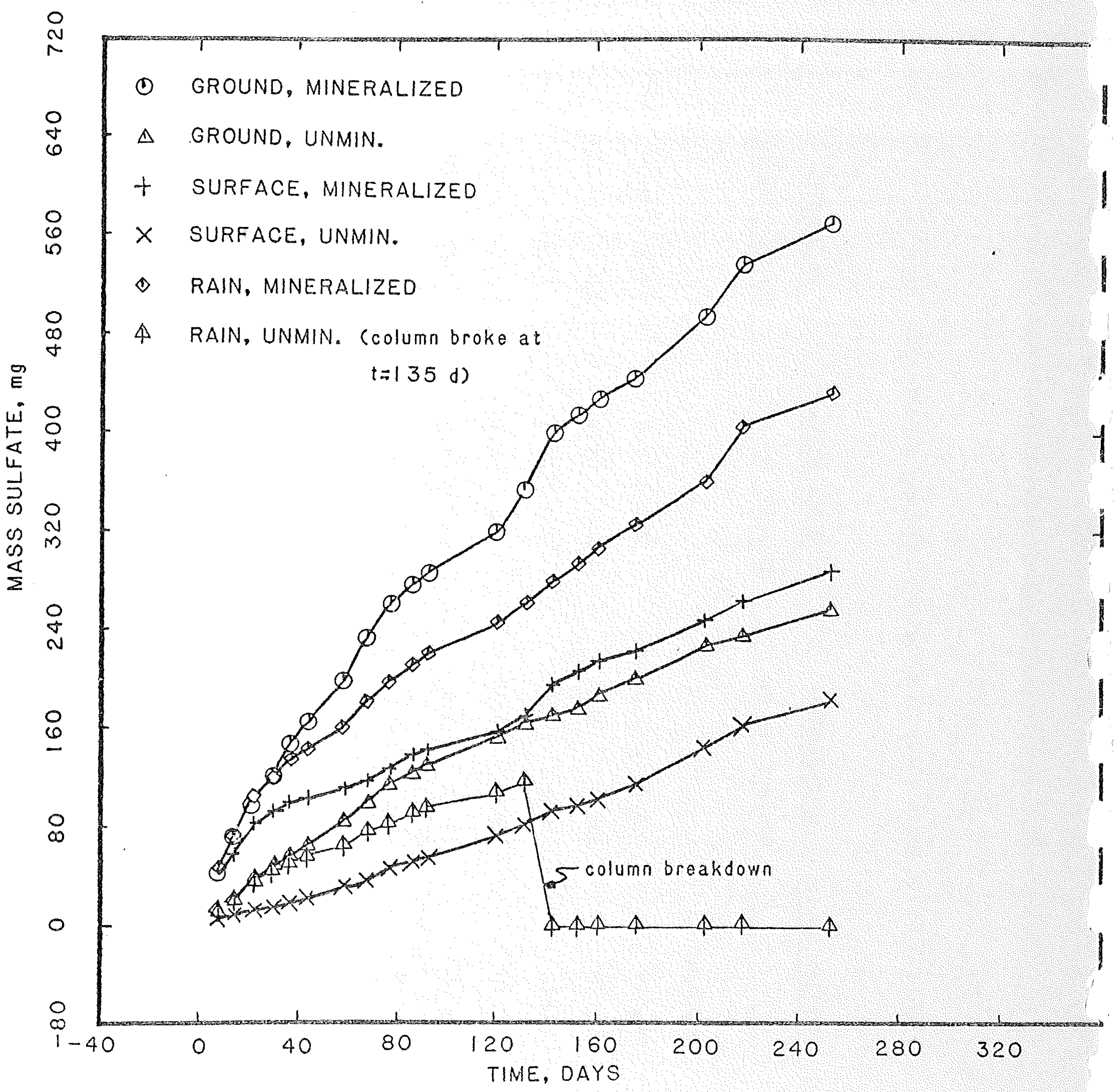
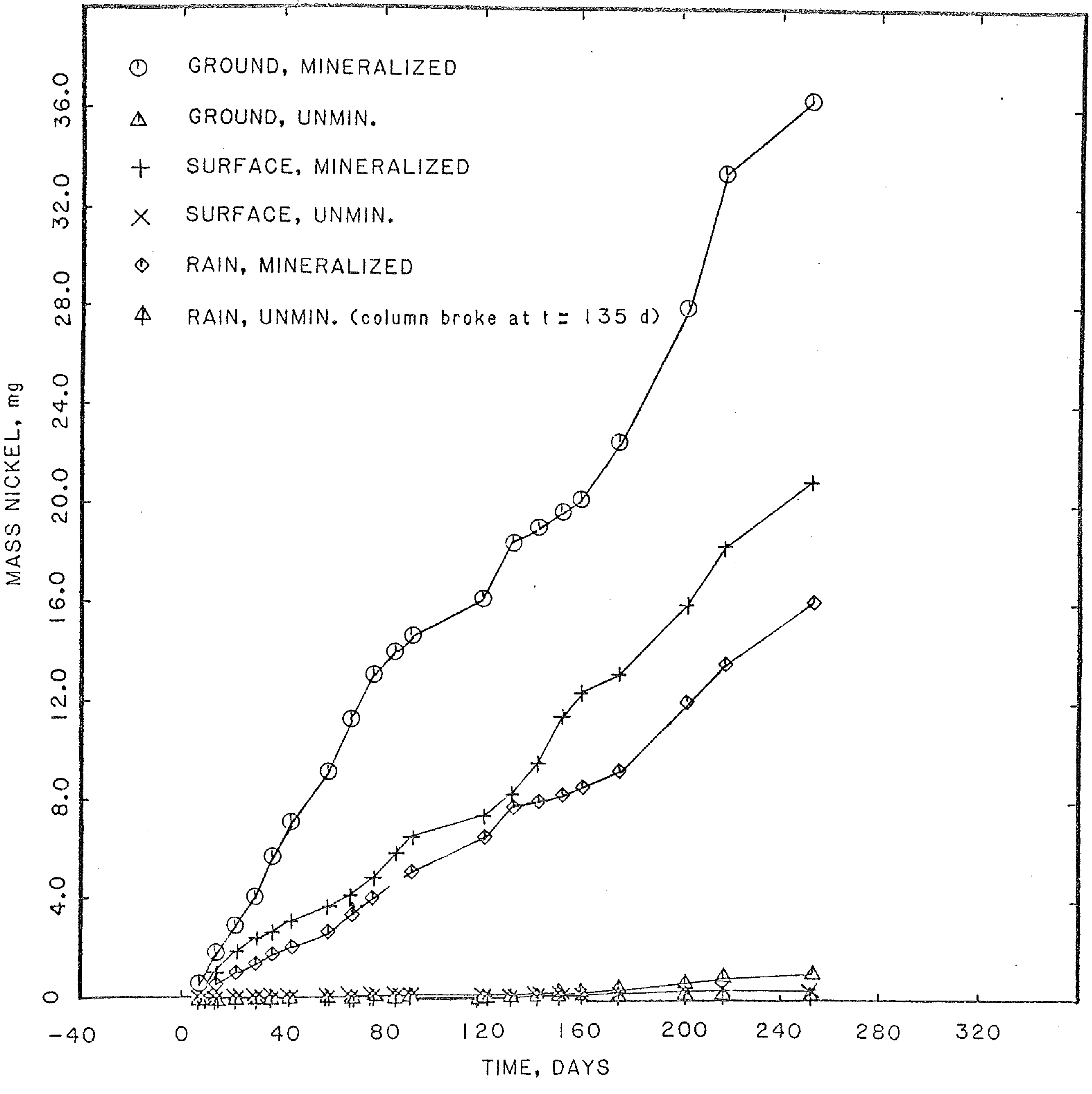


FIGURE 3.58 MASS NICKEL LEACHED VS TIME



of magnitude for both nickel and cobalt in the case of the distilled water leach solution, which appears excessive in light of the chemical compositional data. Nickel and cobalt are present jointly in pentlandite and, evidently, the surface availability of pentlandite is of major influence and is determined by mineralogical factors within the gabbro matrix.

Copper leaching rates are influenced to a lesser degree by compositional factors. In the surface water leach copper release from unmineralized gabbro exceeds that of the mineralized gabbro reflecting the importance of aqueous mobility in copper leaching as opposed to rock composition. The simulated surface water contains citrate which enhances the aqueous mobility; with the groundwater and rainwater leach solutions copper release is a function of rock composition as is illustrated in Figure 3.60. These observations indicate that rock composition is a factor in copper leaching, but that aqueous mobility considerations may be of greater influence.

3.6.3. Effect of Solution Composition

Sulfide mineral dissolution from both mineralized and unmineralized gabbro increases with respect to the leaching solution in the order surface water < < rainwater < groundwater, as indicated by sulfate release data from Figure 3.57 The behavior of metals occurring in sulfide minerals (nickel, cobalt, copper, iron) appears to be dependent upon the aqueous mobility of the individual metals. For metals of typically low aqueous mobility, such as copper and iron, surface water is the most effective leaching solution (Figure 3.60), perhaps due to the organic complexation of copper and iron by citrate and tannic acid in solution. Groundwater is the most effective solution for leaching metals of higher aqueous mobility such as cobalt and nickel (Figure 3.61, 3.62). For all metals megapure water was the least effective leaching solution.

3.59 MASS COBALT LEACHED VS TIME

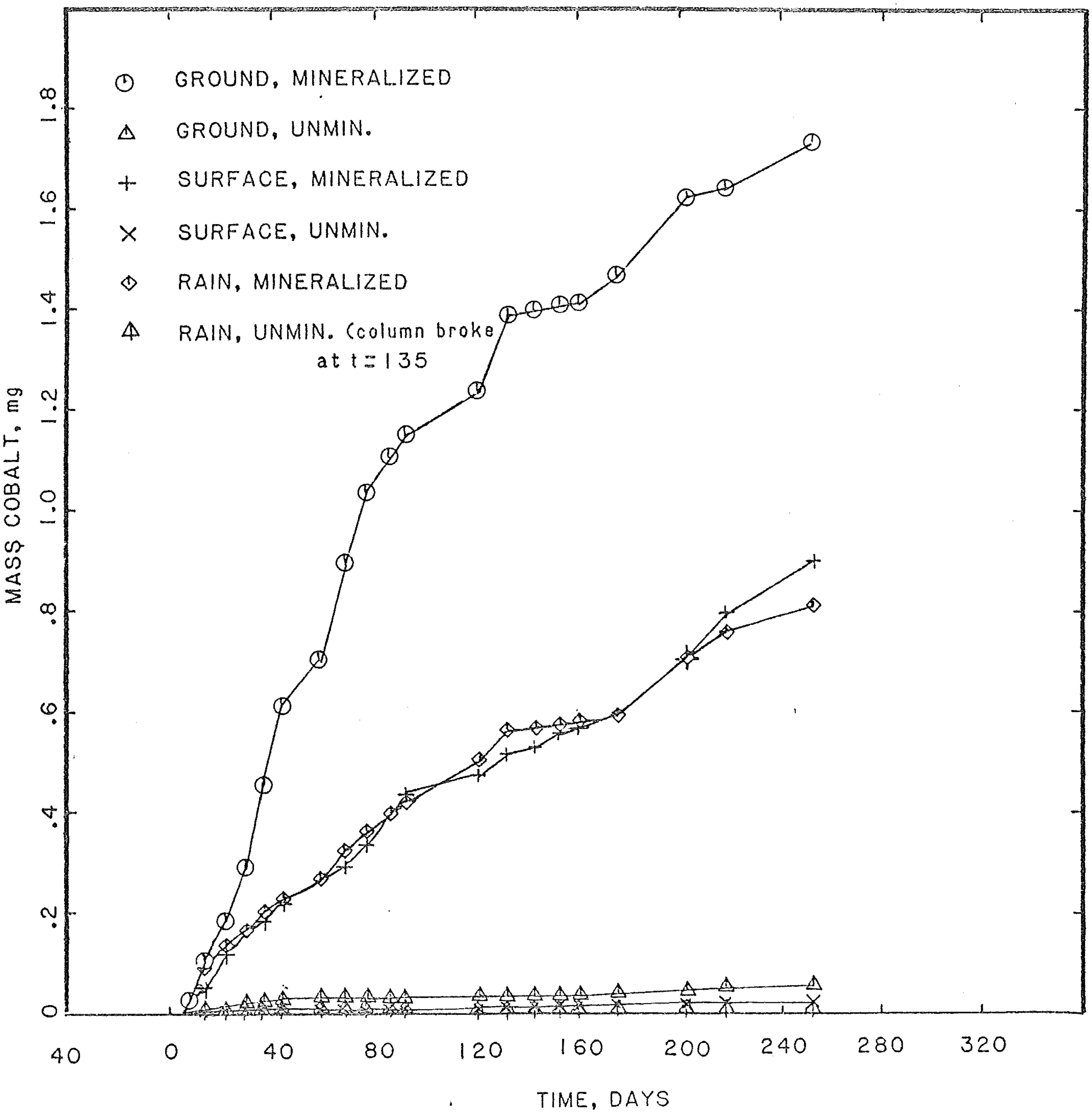


FIGURE 3.60 MASS COPPER LEACHED VS TIME

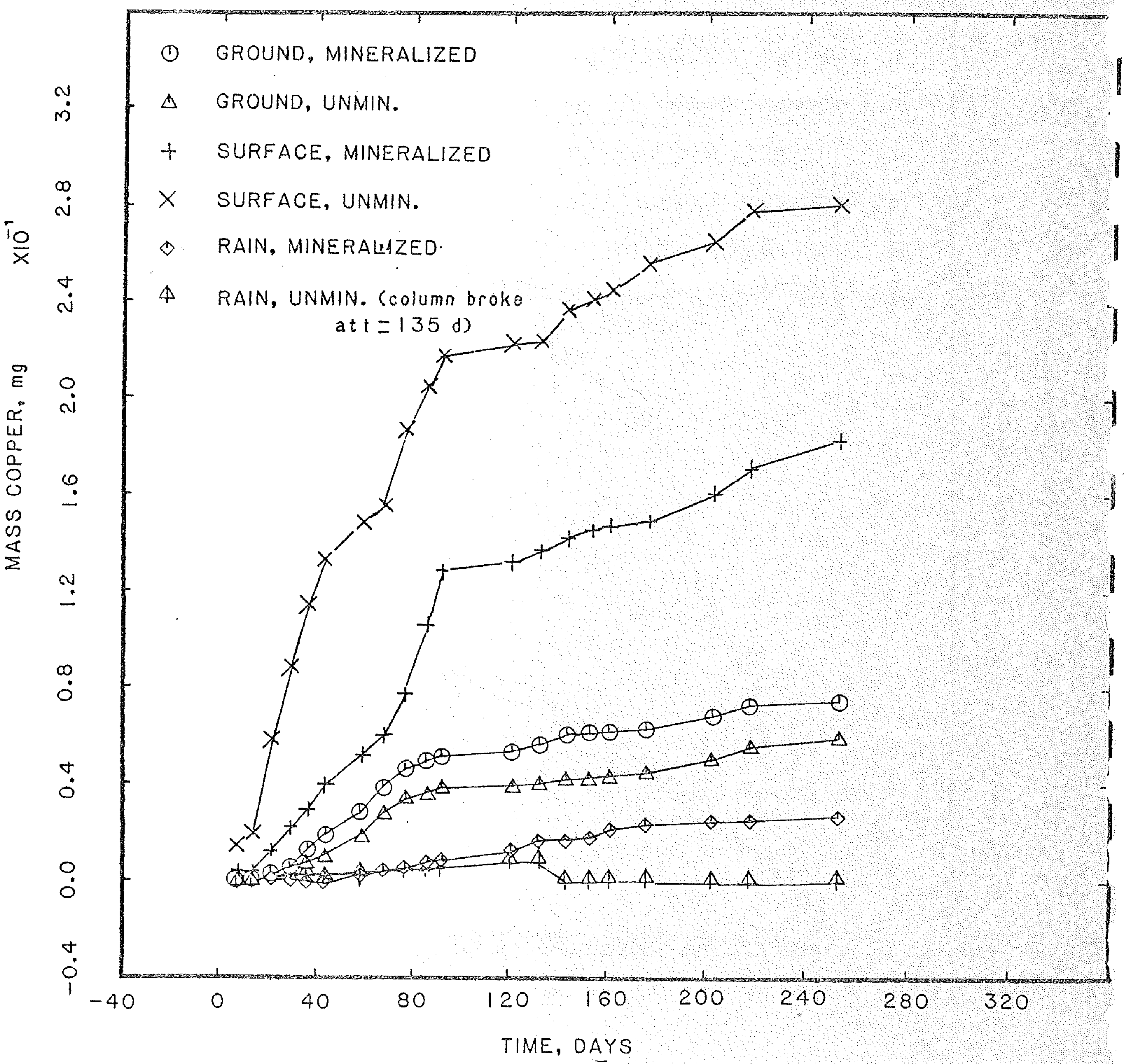


FIGURE 3.61 MASS NICKEL LEACHED VS TIME, MINERALIZED GABBRO

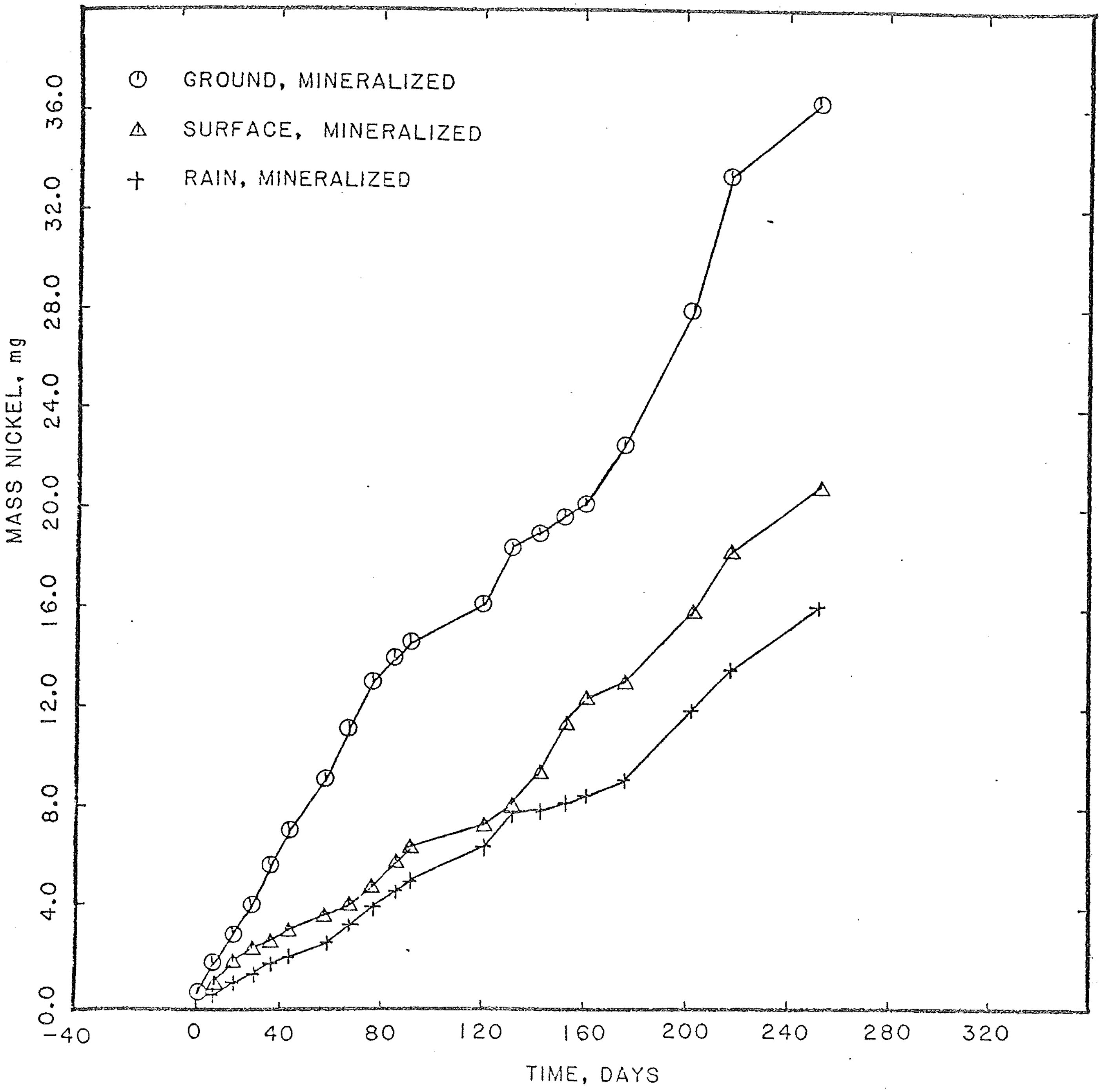
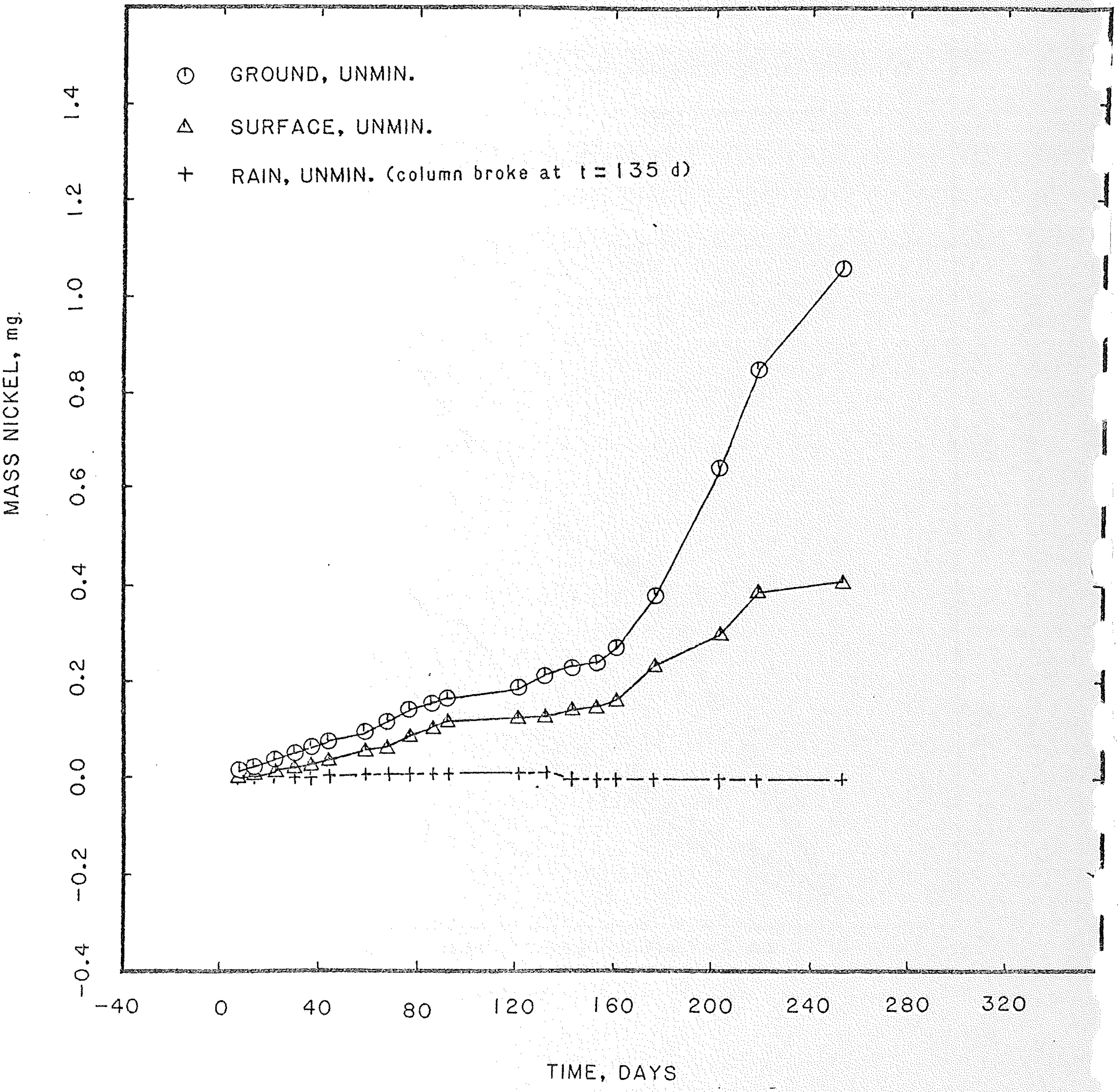


FIGURE 3.62 MASS NICKEL LEACHED VS TIME, UNMINERALIZED GABBRO



3.7 Tailings

3.7.1 Introduction

Observed aqueous concentrations of copper, nickel and sulfate in tailings leachate were significantly lower than those observed in leachate from unprocessed gabbro which is reflective of the lower metal sulfide content of the tailings. The weight percent composition of the tailings was 0.061%S, 0.051% Cu and 0.048% Ni. Elevated pH values, with respect to unmineralized gabbro, were also observed in the tailings leachate (8.1 as compared to 7.5 after 520 hours) indicative of the increased silicate to sulfide mineral ratio. When the solids were returned to the reactors after the 7 day drying period the initial pH was significantly lower than in the first stage but eventually rose to a comparable level. The initial decrease may have been partially due to the depletion of readily exchangeable silicate associated cations such as calcium, magnesium and sodium thereby limiting the initial ion exchange reaction with hydrogen ions in solutions (e.g., $CaAl_2Si_2O_8$ (s) + $2H^+ \rightleftharpoons Ca^{2+} + H_2Al_2Si_2O_8$ (s)). An additional factor may be the rapid release and subsequent hydrolysis of metals such as copper and nickel, the rapid release due to sulfide oxidation occurring during the drying stage and/or release from adsorptive sites.

3.7.2 Effect of pH

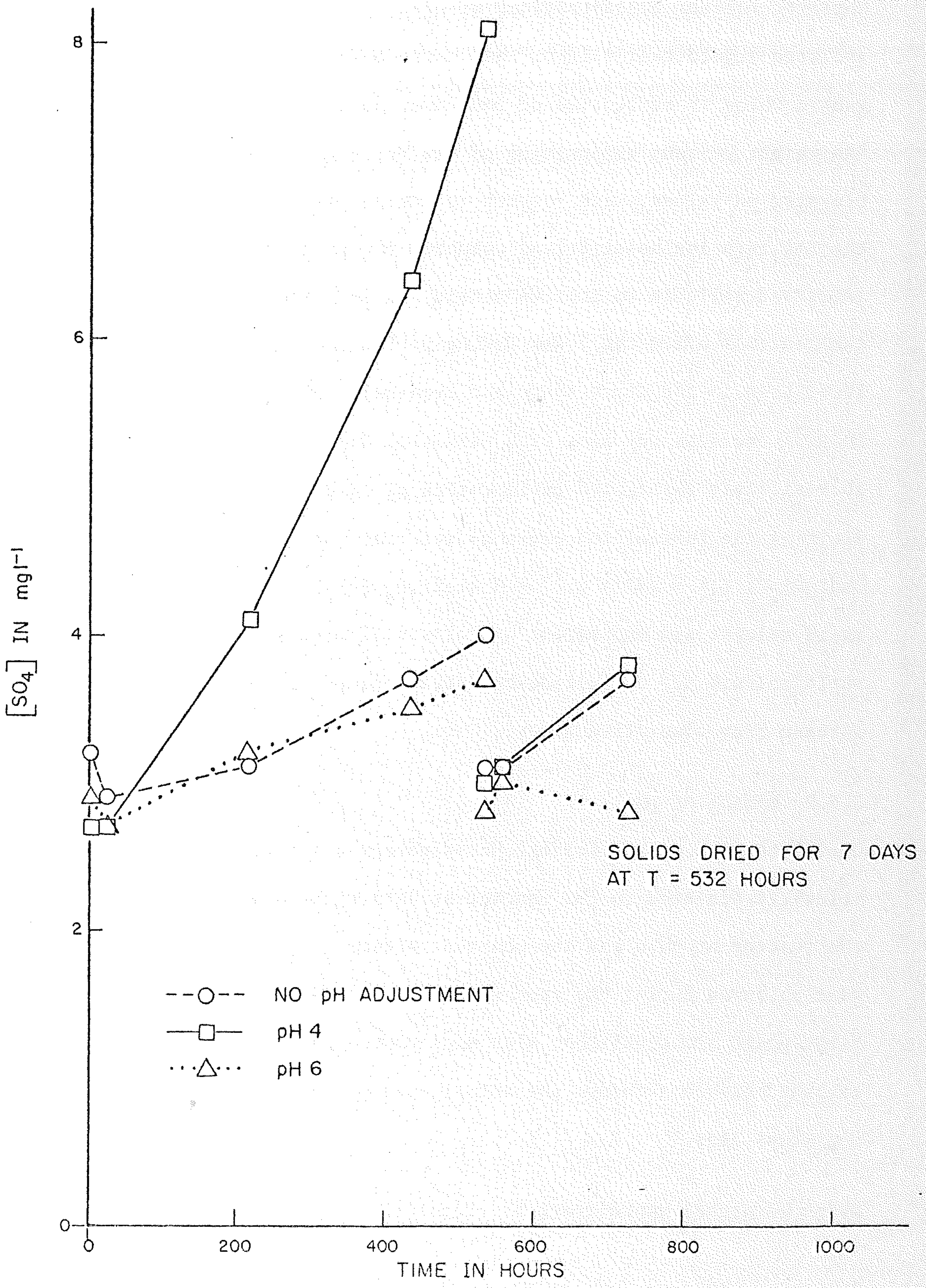
During the first experimental phase observed sulfate concentrations were significantly elevated in the reactor at pH 4 with no appreciable difference between the reactor at pH 6 and the control reactor (Figure 3.63). No significant trends were observed during the second phase. The pH dependency trends observed in the first phase are consistent with those observed for the same loading of unmineralized gabbro although the actual concentrations are approximately an order of magnitude less.

Observed nickel concentrations increased with decreasing pH (Figure 3.64) with

Figure 3.63

$[SO_4^{=}]$ VS TIME

EFFECT OF pH ON TAILINGS

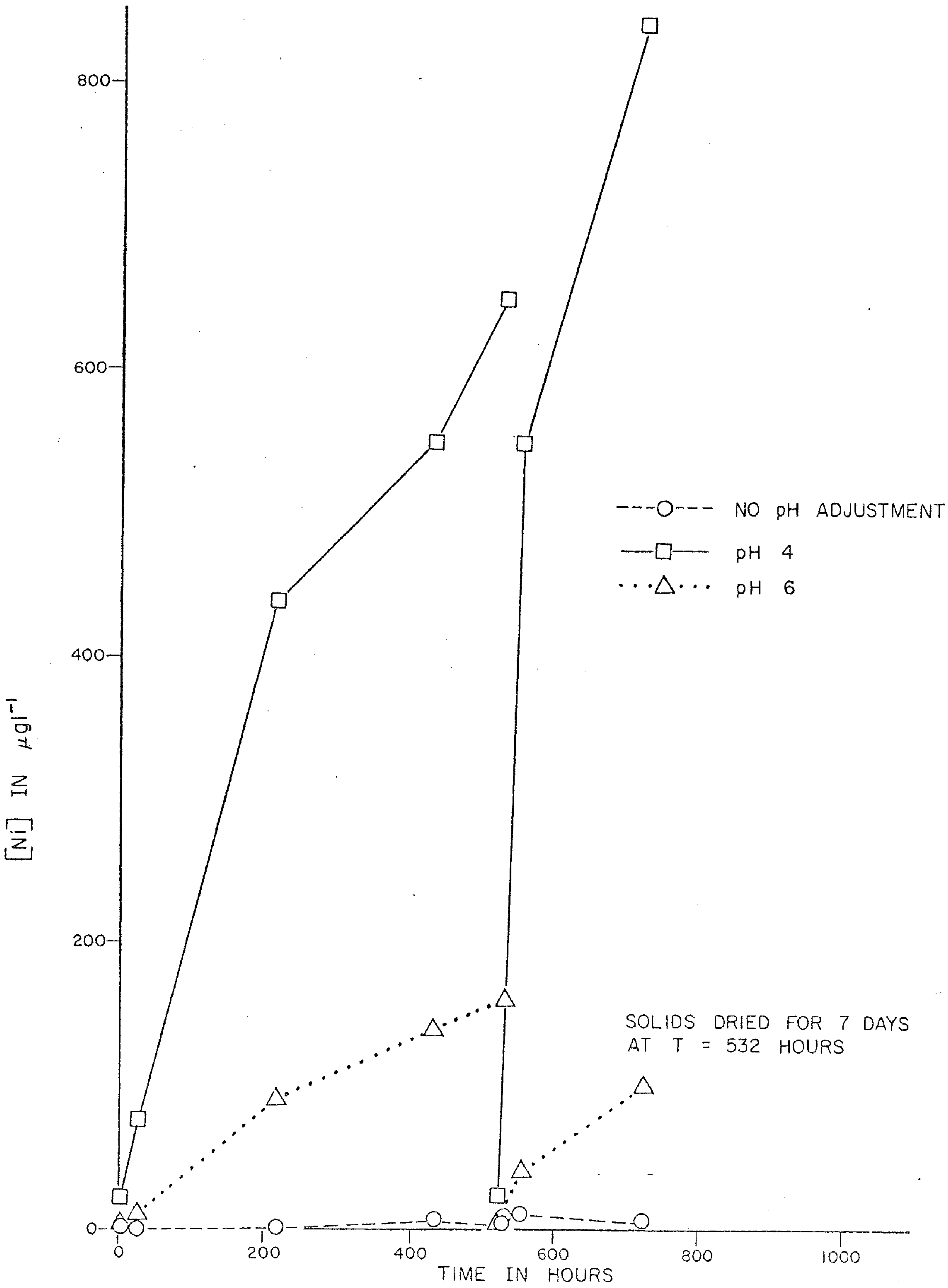


SOLIDS DRIED FOR 7 DAYS
AT T = 532 HOURS

Figure 3.64

[Ni] VS TIME

EFFECT OF pH ON TAILINGS



release in the second experimental phase being more rapid than in the first, perhaps due to oxidation of nickel sulfides during the drying phase or release of nickel adsorbed during the first phase. In the control reactor the lower pH in the second phase may have been a factor enhancing nickel release.

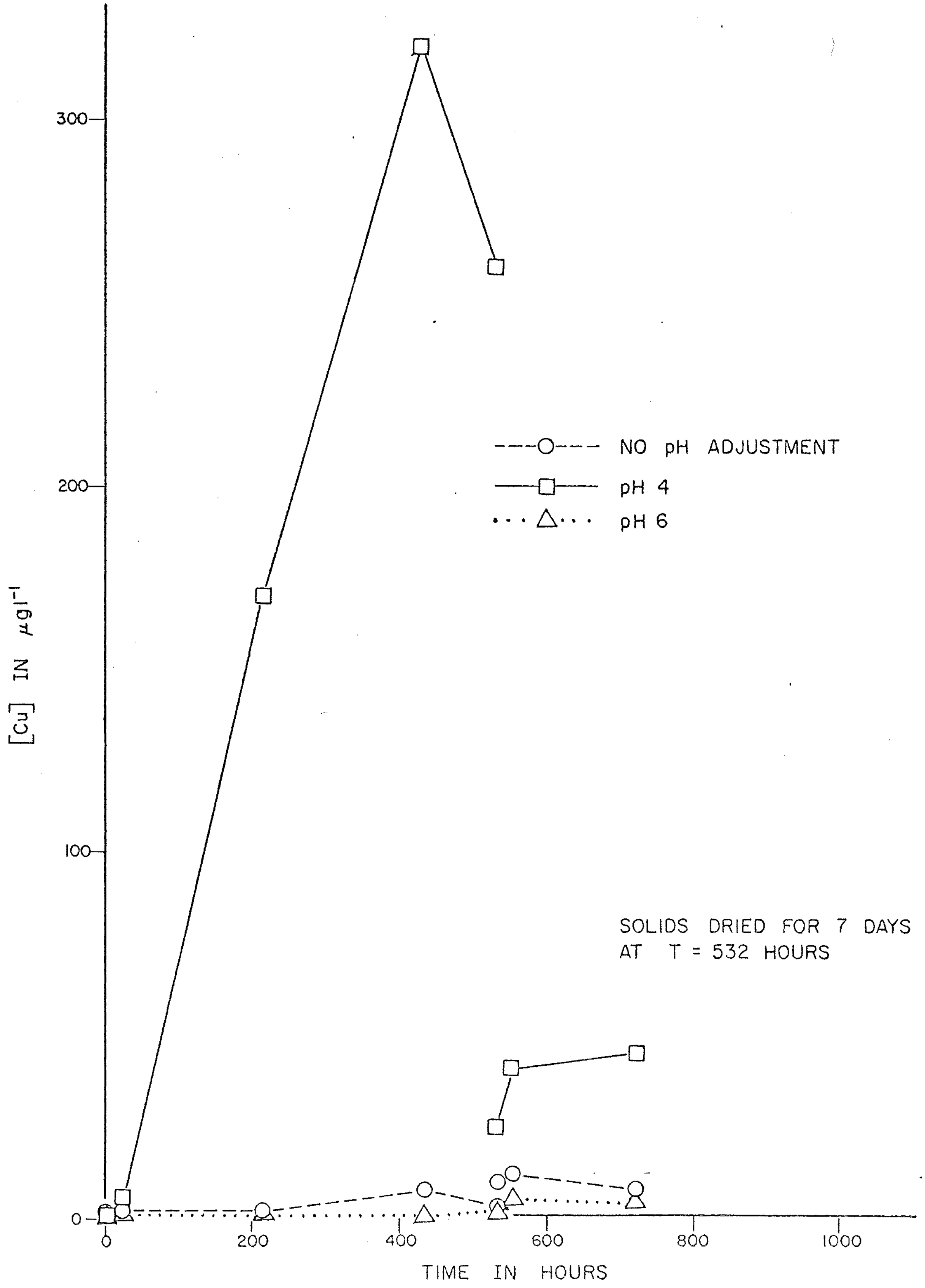
Maximum copper concentrations were observed at pH 4 with little difference between the control reactor and the reactor at pH 6 as is presented in Figure 3.65.

The effect of pH on calcium release was different in the two experimental phases. During the first phase observed calcium concentrations followed a similar pattern in the three reactors, a rapid release during the first 27 hours followed by a very gradual increase in concentration, as can be seen in Figure 3.66. During this phase release increased with decreasing pH, a trend which was reversed during the second phase in which concentrations were significantly lower. These observations are indicative of a reduction of readily exchangeable calcium ions.

Figure 3.65

[Cu] VS TIME

EFFECT OF pH ON TAILINGS



SOLIDS DRIED FOR 7 DAYS
AT T = 532 HOURS

Figure 3.66

[Ca] VS TIME

EFFECT OF pH ON TAILINGS

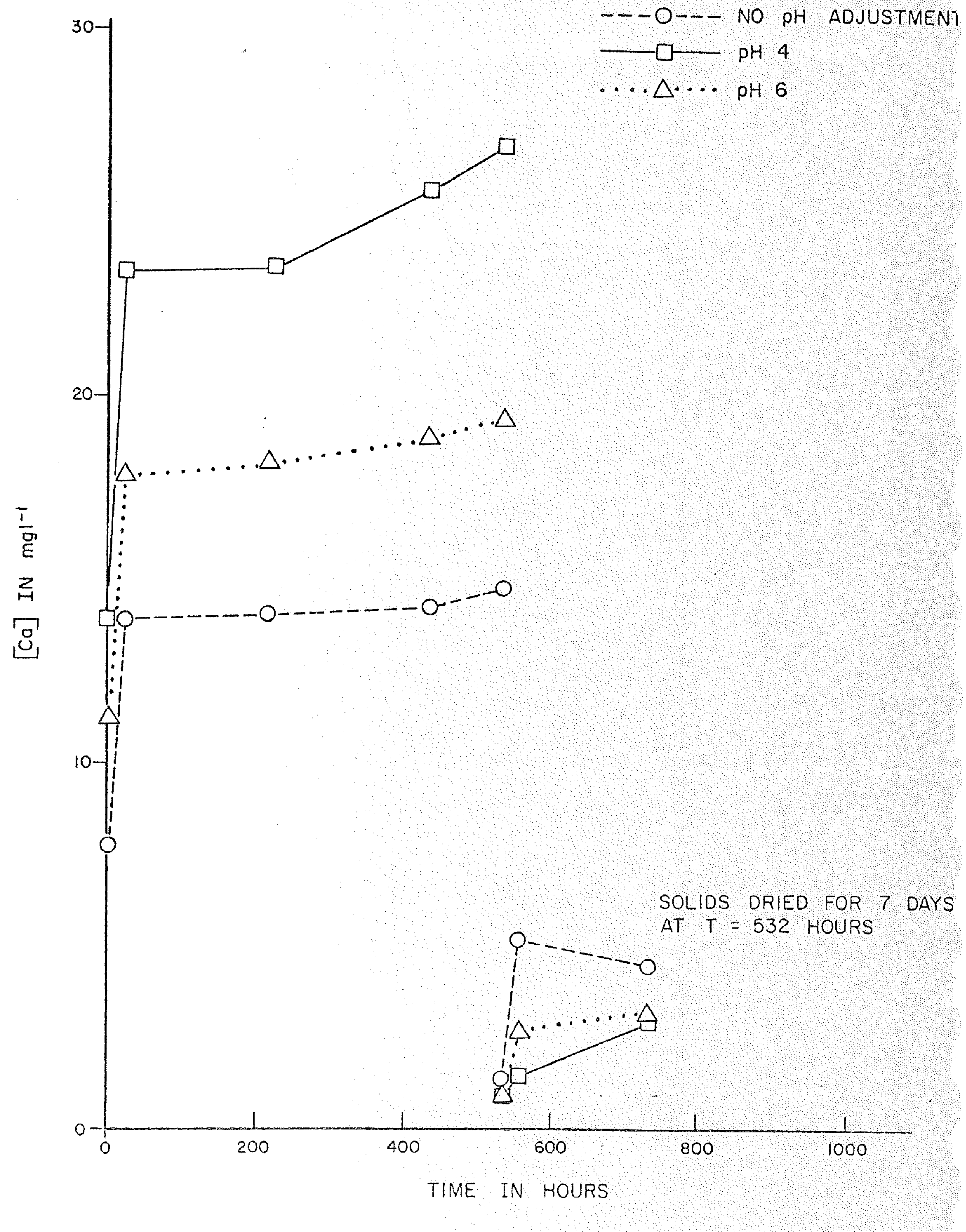
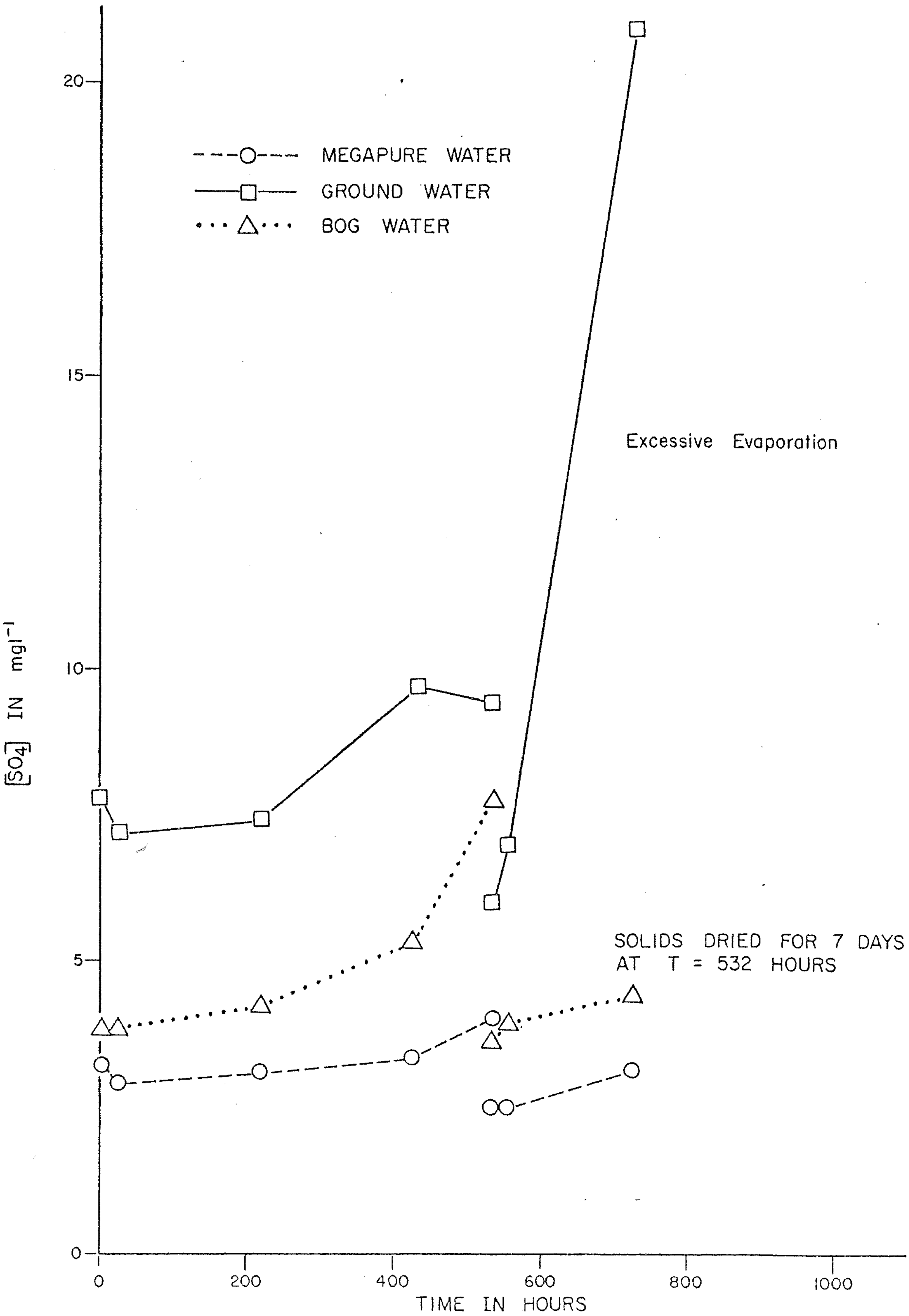


Figure 3.67

[SO4] VS TIME
EFFECT OF NATURAL WATER ON TAILINGS



3.7.3 Effect of Natural Waters

Metal sulfide dissolution in all reactors, as indicated by observed sulfate concentrations, was less than that observed for unmineralized gabbro by an order of magnitude. Although metal sulfide dissolution was evidently not enhanced by the natural waters, the aqueous concentrations of nickel and copper were (Figures 3.67, 3.68, 3.69), indicating a capacity for complexation.

Observed calcium concentrations during the first phase tended to remain fairly stable in the natural waters as can be seen in Figure 3.70. Concentrations in the groundwater were slightly lower than the natural concentrations while those in the bog water gradually increased. Concentrations generally decreased in the second phase of the experiment indicating a reduction in readily available calcium. The second phase groundwater concentrations are somewhat misleading as excessive evaporation occurred in that reactor.

Figure 3.68

[Ni] VS TIME

EFFECT OF NATURAL WATER ON TAILINGS

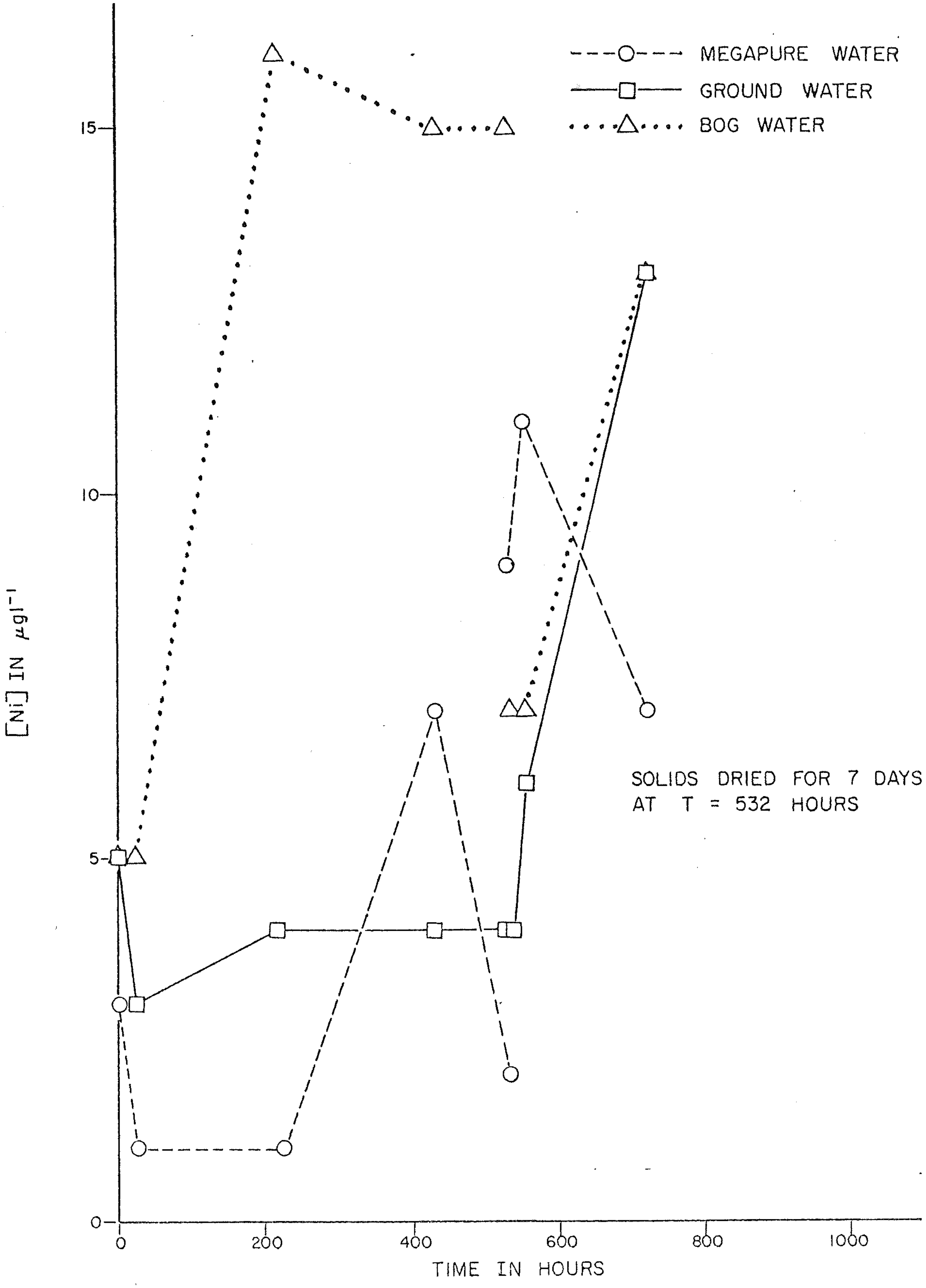
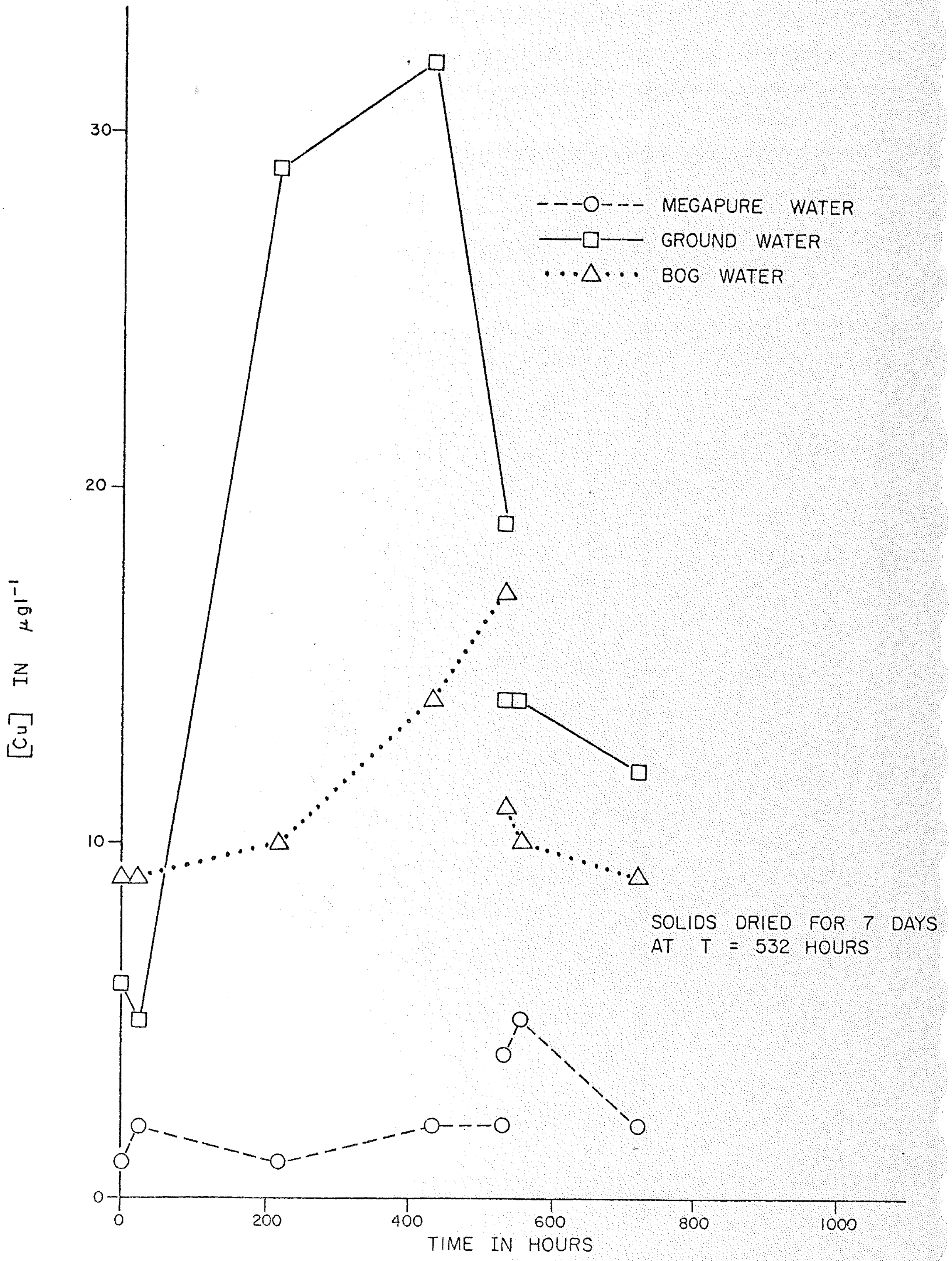


Figure 3.69

[Cu] VS TIME

EFFECT OF NATURAL WATER ON TAILINGS

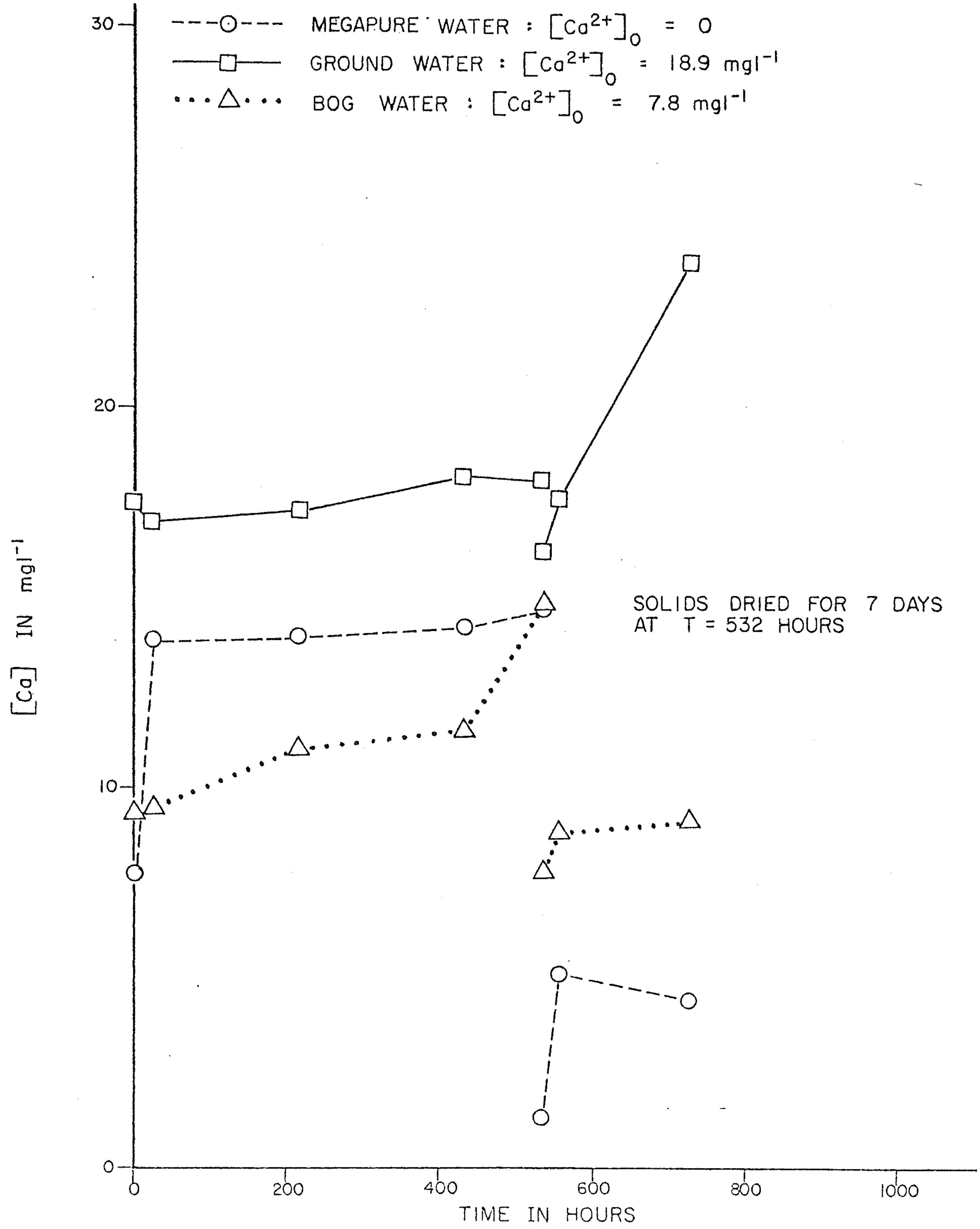


SOLIDS DRIED FOR 7 DAYS AT T = 532 HOURS

Figure 3.70

[Ca] VS TIME

EFFECT OF NATURAL WATER ON TAILINGS



3.8 Environmental leaching test

3.8.1 Introduction

The Environmental Leaching Test (ELT) consisted of leaching solids of varying composition with two types of solution, acidic and synthetic natural water. A summary of results for copper, nickel, cobalt and zinc is presented in Table 3.24 with more detailed information in Tables 3.25 and 3.26.

3.8.2 Effect of solid composition

Copper and nickel are best suited for investigation of the effect of rock composition on the leachate quality as the low cobalt and zinc content in the solid phase is subject to significant analytical error. Among the host rock samples, the acid leach indicated a trend for increased metal release with increased solid phase metal concentration (Figure 3.71).

The percent of individuals metals leached from host rock samples by the acid solution is presented in Table 3.25. The average values for copper, cobalt, nickel, and zinc were 0.7, 1.6, 3.9, and 19 percent respectively.

The leaching of copper, nickel and cobalt occurs to a lesser degeee with tailings than the ores sampled which is consistent with the fact that the chemical availability of these metals is reduced during mineral processing. Zinc release from tailings is not reduced relative to raw ore and may pose a problem of environmental concern in regard to water quality in tailings basins.

3.8.3 Effect of solution composition

In all cases the extent of leaching is greater with the acid solution than the synthetic natural water, in some cases differing by three orders of magnitude (Table 3.24). The natural water leach is most likely dominated by considerations of mobility of metals, the equilibrium pH (8) providing for effective removal

Table 3.24 Summary of ELT Results

ORE

ELEMENT	SOLID PHASE COMPOSITION (WT%)		FINAL AQUEOUS CONCENTRATION (MG/L)			
			ACID LEACH		NATURAL WATER	
	RANGE	MEDIAN	RANGE	MEDIAN	RANGE	MEDIAN
Cu	0.16 -1.2	0.59	0.28 - 3.97	3.4 (7)[1]	0.002-0.27	0.008(8)
Ni	0.073-0.42	0.14	1.63 -33.9	3.4 (7)	0.03 -0.265	0.088(8)
Co	0.010-0.036	0.012	0.050- 0.43	0.074(7)	0.05	<0.05 (8)
Zn	0.011-0.016	0.013	0.42 - 1.95	1.7 (7)	0.088-0.017	0.008(8)

TAILINGS (3 Samples)

ELEMENT	SOLID PHASE COMPOSITION (WT%)		FINAL AQUEOUS CONCENTRATION (MG/L)			
			ACID LEACH		NATURAL WATER	
	RANGE	MEDIAN	RANGE	MEDIAN	RANGE	MEDIAN
Cu	0.044-0.070	0.068	0.034-0.61	0.20	0.002-0.003	0.002
Ni	0.029-0.05	0.031	0.45 -1.01	0.54	0.008-0.013	0.010
Co	0.012-0.02	0.013	0.009-0.041	0.018	ND -0.02	0.0004
Zn	NA		0.42 -2.90	1.69	0.010-0.016	0.010

1. Numbers in parentheses represent number of samples.
NA = not available   ND = no data

Table 3.25: Elemental analysis of mineral phase[f] and environmental acid leaching test aqueous phase[a]

	(S)	(Fe)	(Cu)		(Ni)		(Co)		(Zn)		Percent Leached			
Sample	Solid	Solid	Solid	AQ	Solid	AQ	Solid	AQ	Solid	AQ	Cu	Ni	Co	Zn
Ores														
AX 9001	0.655	0.696	0.306	0.92	0.073	2.39	0.009	ND	0.016	3.93	0.30	3.3	-	25
AX 9002	0.990	1.02	0.583	0.56	0.124	1.63	0.12	NP	0.017	1.94	0.096	1.3	0.03	11
DP 9001	1.1		0.156	3.91	0.138	3.39	0.082[b]	0.30	<0.0009	0.42	2.5	2.5	0.4/3[c]	42.2
AX 9003	1.145	1.21	0.592	0.28	0.122	2.24	0.011	ND	0.019	1.40	0.047	1.8	0.04	7.4
IP 9003	1.215	1.28	0.625	4.44	0.174	13.8	0.012	0.426	0.0085	1.73	0.71	7.9	3.6	20.4
AX 9005	1.340	1.42	0.723	3.4	0.140	3.6	0.014	0.421	0.011	1.58	0.47	2.6	3.0	14.4
AX 9004	10.5	13.89	1.155	8.97	0.418	33.9	0.036	0.074	0.0185	1.95	0.78	8.1	2.1	10.5
Tailings										AVE	0.70	3.9	1.6[d]	18.7
IP 9002	0.09		0.044	0.61	0.05	0.45	0.02	0.018		0.42				
AX 9004 SC2T	0.14		0.068	0.034	0.029	0.54	0.012	0.041		1.69				
AX 9004 ROT	2.40		0.070	0.200	0.031	1.01	0.013	0.009		2.90				

[a] - Mineral phase values in weight percent, aqueous pahse in mg/l.
[b] - 0.01 by acid digestion.
[c] - 0.4 based on solid analysis by Barringer, 3 on solid analysis by MRRC.
[d] - 0.040 = 0.8 * detection limit used for non-detectable values.
[e] - % leached = $\frac{(ME)(aq)}{(ME)(s)} * 0.1$
[f] - See Stevenson et. al. (1979).

Table 3.26: Elemental analysis of mineral phase and environmental natural water leaching test aqueous phase[a]

	(S)	(Cu)		(Ni)		(Co)		(Zn)		(Fe)
Sample -	Mineral	Mineral -	Aqueous	Mineral -	Aqueous	Mineral -	Aqueous	Mineral -	Aqueous	
AX 9002	0.990	0.583	0.008	0.124	<0.03	0.012	<0.05	0.017	0.01	
DP 9001	1.1	0.156	0.014	0.138	0.36	0.082[b]	<0.05	<0.0009	0.01	
AX 9003	1.145	0.592	0.001	0.122	0.032	0.011	<0.05	0.019	<0.01	
US 9001	1.160	0.330	0.027	0.086	0.103	0.010	<0.05	0.0133	0.003	
IP 0003	1.215	0.625	0.004	0.174	0.019	0.012	ND	0.00845	0.017	
AX 9005	1.340	0.723	0.002	0.140	0.015	0.014	ND	0.0111	0.011	
DP 9002	3.88	0.782	0.022	0.178	0.088	0.020	<0.05	0.022	<0.01	
AX 9004	10.5	1.155	0.005	0.418	0.265	0.036	0.010	.0185	0.015	
Tailings										
IP 9002	0.09	0.044	0.003	0.05	0.010	0.02	ND		0.010	
AX 9004 (SO_2T)	2.40	0.068	0.022	0.029	0.008	0.012	0.0004		0.010	
AX 9004 (R_oT)	2.40	0.070	0.002	0.031	0.013	0.013	0.002		0.016	

[a] Mineral phase values in weight percent, aqueous phase for natural water leach in mgl^{-i}

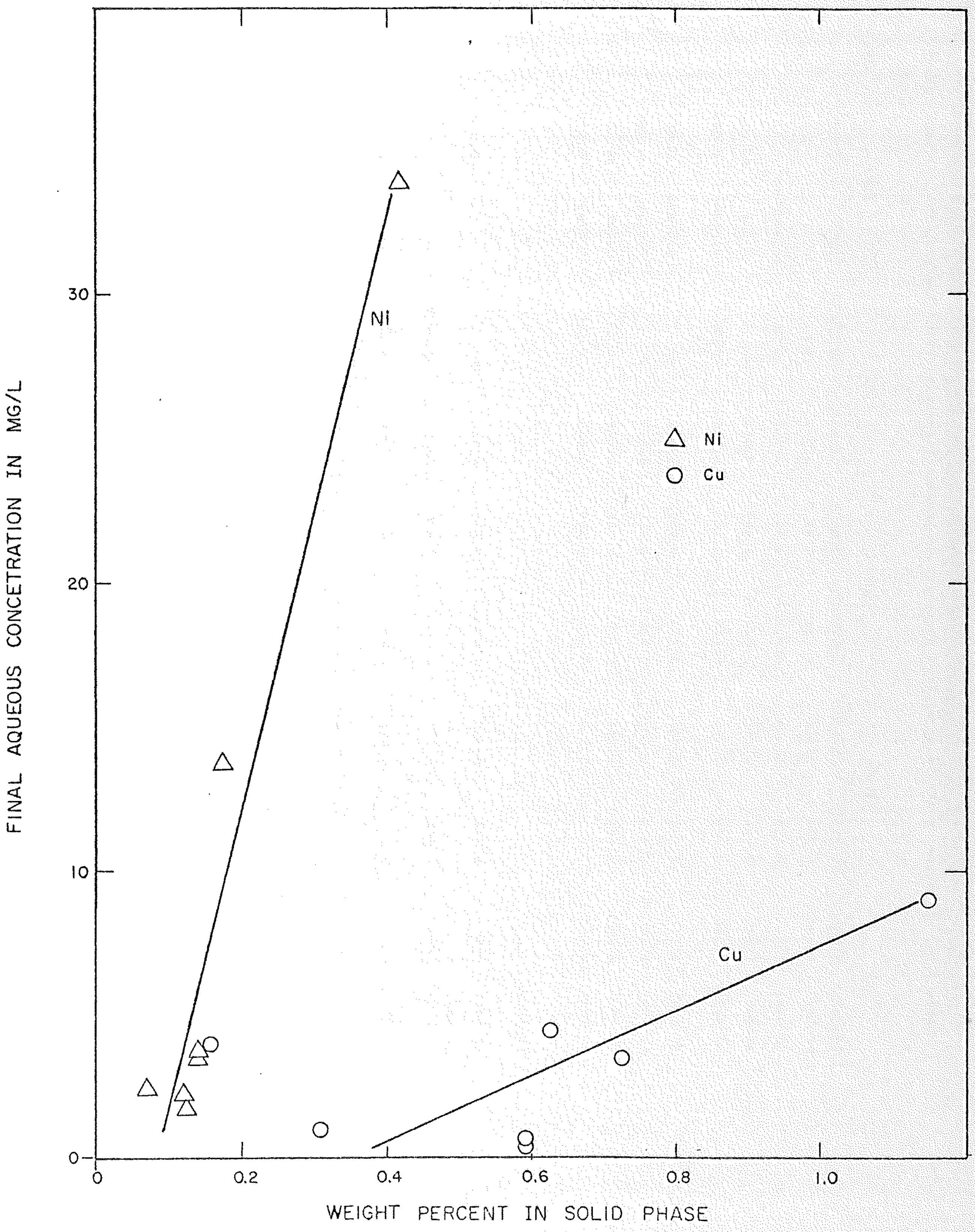
[b] 0.01 by acid digestion

[c] ND=not detectable

Figure 3.71

FINAL AQUEOUS CONCENTRATION VS WEIGHT PERCENT IN SOLID PHASE

ELT RESULTS FOR Cu and Ni



of metals due to chemical precipitation and adsorption.

INTRODUCTION

Stockpile runoff is the term given to any water which contacts stockpiled material and then is released to the environment, either by surface or ground water flow. Large amounts of waste rock and lean ore will be stockpiled in an open pit operation. For the model open pit mine, (20 x 10^6 mtpy production rate), 650 x 10^6 mt of waste rock lean ore will be removed and stockpiled over the projected 25 year mine life.

This section discusses the quality of stockpile runoff. A conceptual model for stockpile leaching, the factors affecting release and the water quality results from the field study areas are discussed. "Model" stockpile runoff is presented and the rate of metal release from stockpiles is discussed. Data presented in this section were collected by AMAX, the U.S. Forest Service and the Regional Copper-Nickel Study. Stockpile runoff is of poor quality, with observed trace metal concentrations in field samples ranging from 10-10,000 times the natural background concentrations found in the streams of the region. It appears that stockpiled material may present a significant environmental problem.

Stockpile Runoff

The quality of stockpile runoff is the result of several interacting factors. Hewett (1980) has discussed stockpile hydrology in detail and a conceptual model of the runoff components is shown in Figure 4.1. Figures 4.2 and 4.3 illustrate the quality considerations in evaluating runoff.

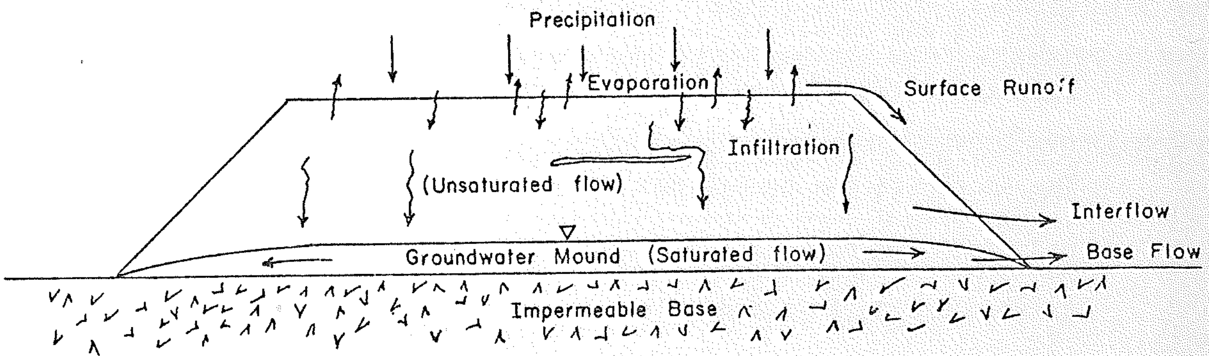
The stockpile can be divided into two zones, an unsaturated zone that comprises the bulk of the stockpile, and a saturated zone, which can exist under certain conditions at the base of the stockpile. Rocks in the unsaturated zone are exposed to water from rainfall and moist air, while those in the saturated zone are subject to long term submersion.

It has been shown that sulfide minerals do not have to be in constant contact with water but can oxidize in moist air. It has been shown by Anderson and Allman (1968) that wet-dry cycling (discussed in preceeding section) enhances the dissolution rate of copper bearing ores. The conceptual model, Figure 4.3, indicates that reaction occurs between precipitation events, and reaction products are transported from the unsaturated zone by rainfall. The amount of reaction that occurs in the unsaturated zone is determined by several factors: the chemical and mineralogical composition of the rock; the particle size; the time between precipitation events; and the temperature. The amount of product removal is determined by the amount, duration and intensity of the rainfall, the water quality of the rain, the particle size, and the construction of the pile. As intensity and duration of rainfall increase, the transport of reaction products increases. Some of the runoff will appear as direct runoff, and some may enter the saturated zone, from which it will later emerge as base flow or ground water seepage.

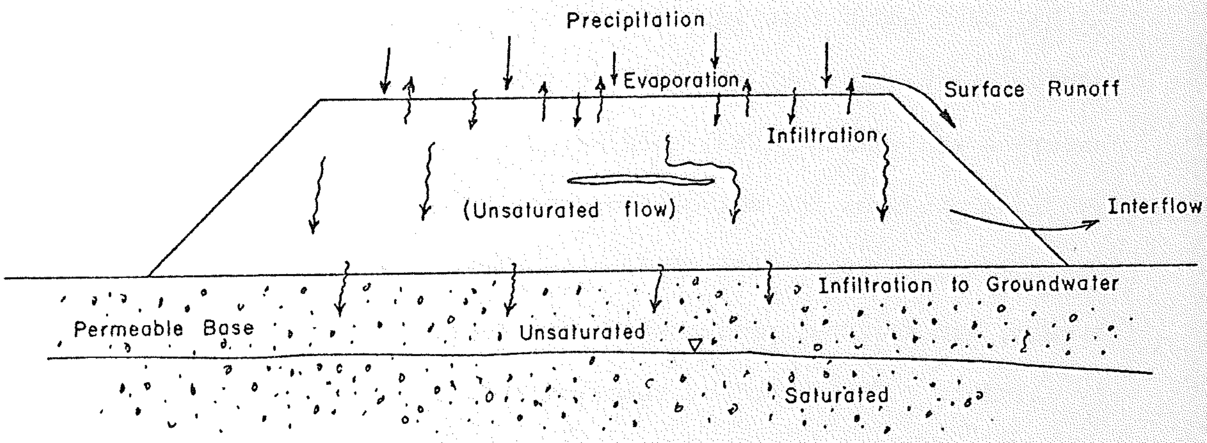
Figure 4.1

FLOW PATHS WITHIN STOCKPILES

A. STOCKPILE ON IMPERMEABLE BASE



B. STOCKPILE ON HIGHLY PERMEABLE BASE



C. STOCKPILE ON IMPERMEABLE BASE, BLOCKING SURFACE DRAINAGEWAY

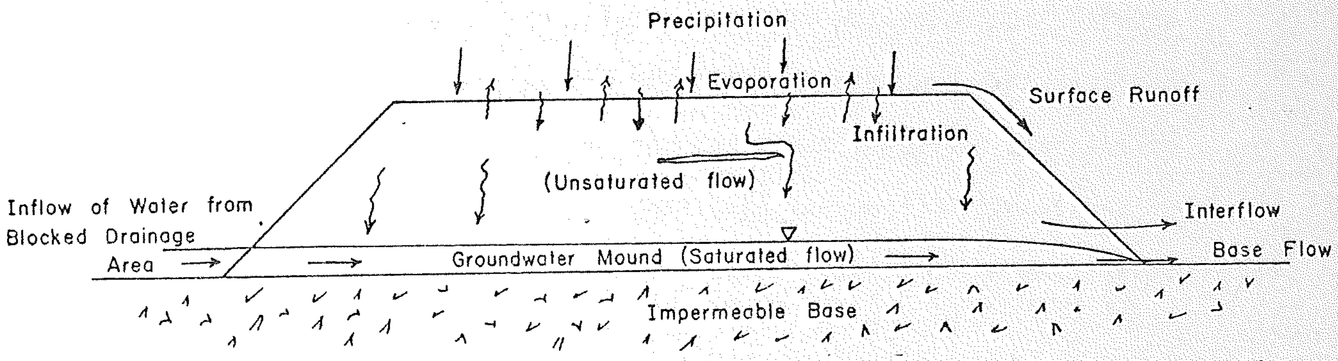


Figure 4.2

FACTORS AFFECTING THE QUALITY OF STOCKPILE RUNOFF

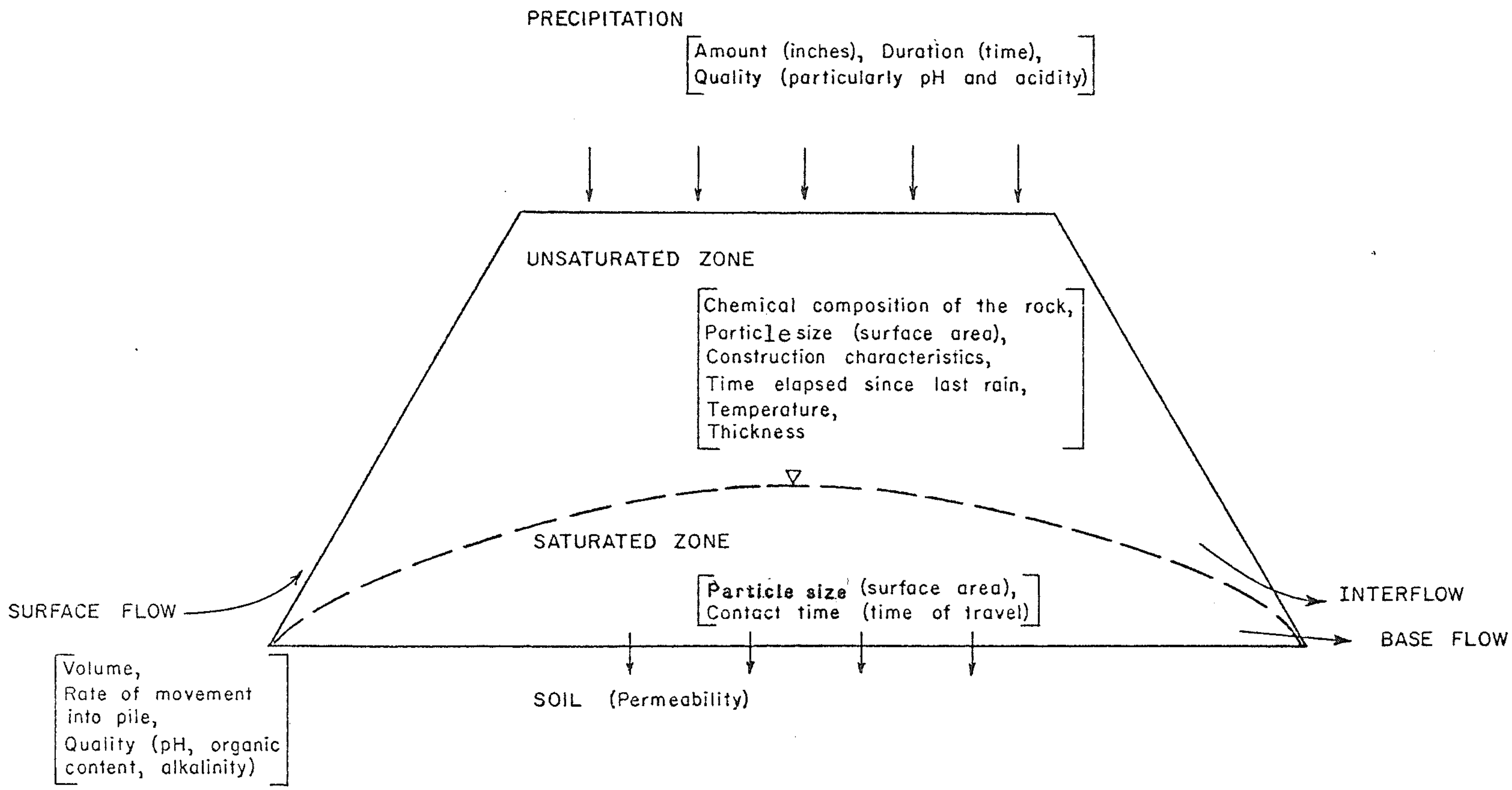


Figure 4.3
Schematic of Stockpile Leaching Process

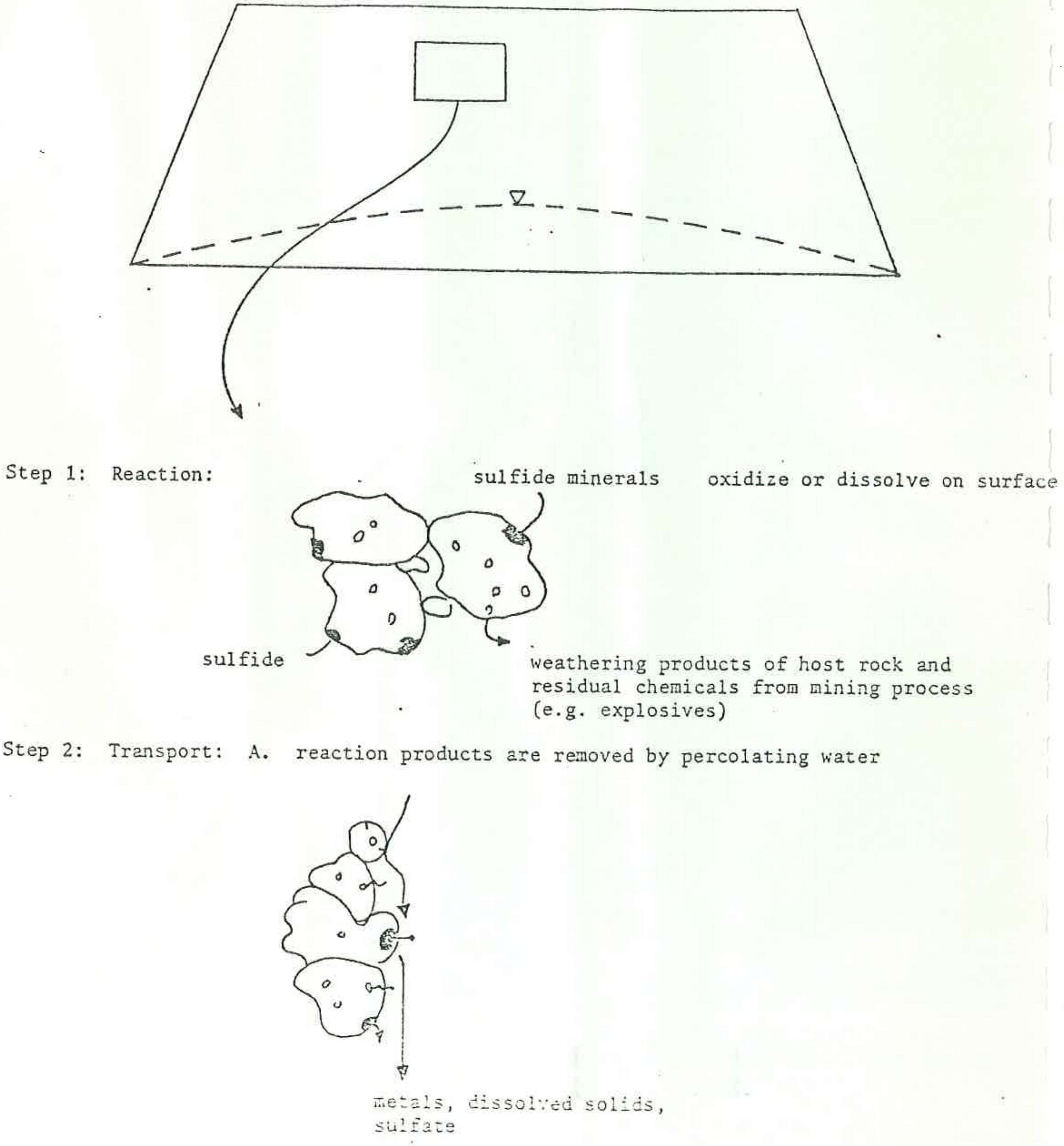
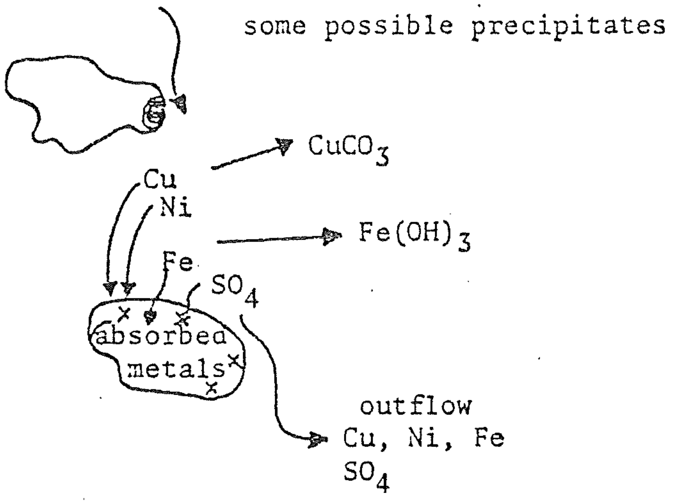


Figure 4.3 (con't.)

B. Some of the metals are readsorbed onto the silicate mineral surface or form precipitates.



(In saturated zone the processes are essentially the same, although water is always available to transport the reaction products.)

The outflow from the stockpile is composed of the weathering products of 1) the sulfide minerals (the prime source of the trace metals; copper, nickel, zinc, cobalt; and sulfate) 2) the silicate minerals (major contributors of calcium, magnesium) and the residual chemicals that were on the rocks when they were stockpiled (primary source of nitrate).

4.1.2. Conceptual Model

Conceptually, the processes in the saturated zone are much different from those that occur in the unsaturated zone. Water is continually available for transporting reaction products but reaction conditions, such as temperature, pH and dissolved oxygen may be quite different from those in the unsaturated zone above. The rate of movement through the pile will vary as a function of the permeability and hydraulic gradient, but in general the time the water remains in contact with the rock is much longer in the saturated zone than the unsaturated zone. Field data collected at the Dunka Pit indicates that the flow time through the saturated zone from waste rock pile 8011 (Figure 2.2) (Hewett 1980) is from 17 to 170 days. The flow time for rainfall through the unsaturated zone is on the order of 1 day.

Since conditions differ between these two zones, the water quality of the leachate is expected to be different. To attempt to differentiate the quality of these zones could require intensive sampling of stockpile runoff during storm events and low flows. This type of study has not been completed. Present field work (1978-1979) includes the study of concentration variations during storm events.

The data collected during 1976-77 are from a fixed time interval sampling program (every two weeks) and therefore do not adequately describe the difference in base flow and interflow. Field data therefore represent the combined effects of leaching in both zones of the stockpile runoff. The general discussion of the factors which affect the leaching process is in Chapter 3. Table 4.1 summarizes effects of the different parameters on the leachate production (The range of these parameters observed in field study areas will be discussed in a later section).

Table 4.1 Summary table, factors which affect leaching

Parameter	Effect on Leaching	
	As parameter	Release
pH	decreases	increases
temperature	increases	increases (s)[1]
dissolved oxygen	increases	increases
stockpile composition	increases	increases (s)[2]
stockpile height	increases	unknown: increases (s)[3]
alkalinity	decreases	increases
organic ligands	increases	increases
ionic strength of solution	increases	increases
surface area	increases	increases
rainfall	increases	increases

(s): speculative

[1] In general the rates of chemical reaction increase with increasing temperature.

[2] No comprehensive experiments have been conducted to study release as a function of composition.

[3] As the stockpile height increases, the solid/liquid ratio increases.

4.1.3 Site Description

The field study sites were previously described. The size and chemical composition of the stockpiles studied are summarized in Table 4.2. The compositions of model waste rock and lean ore are shown for comparison.

Subsequent analysis by Stevenson (1979) indicates that there is a possibility that much of the waste rock in future copper-nickel operations may have a very low percentage of sulfur and trace metals. One estimate is that 43% of the waste rock may have a sulfur content of $\leq .1\%$. This is based on the analysis of drill core samples selected from the study area (Figure 4.4). The average concentrations of sulfur and trace metals in the low grade material is:

		Composition (%)		
% of rock $\leq 0.1\%$	S	Cu	Ni	Co
43	.053	.027	.027	.0092

The leaching behavior of the stockpile will be influenced by its composition (A general discussion of the effect of sulfide content on sulfate and metal release is presented in the laboratory section). Present data are insufficient for determination of a release vs grade relationship. Most of the rock samples tested, both on the field and laboratory, had copper concentrations greater than .1%. More experimental work is needed to investigate the relationship between grade and release, particularly for low sulfide mineralization. It may be that waste rock should be separated based on its potential to produce environmental problems.

Table 4.2 Stockpile size and composition

	----------Erie - Dunka- Pit--------			AMAX	Inco	Models	based on(20x10^{6} mtpy open pit)
Site:	Em8	Seep 1	Seep 3	FL 1			
Mass (tons)	12.2x10^{6}	.92x10^{6}	3.0x10^{6}	1766	not known	325 x 10^{6} mt	325 x 10^{6} mt
Cu (%)	.04^{+} *	.03^{+}*	.29	.33-.35	.47	.1	.306
Ni (%)	.01^{+} *	.01 *	.08	.075	.15	.023	.073
S (%)	no data^{+}	no data^{+}	no data^{+}	.6	1.08	.207	.655
classification of material	waste rock	waste rock	lean ore	lean ore	ore	waste rock	lean ore

* These are average compositions for the entire pile. Both stockpiles are only 70% gabbro. If the assumption is made that the iron formation and Virginia formation contain no copper and nickel then the composition of the gabbro can be calculated:

$$\frac{\text{Overall composition}}{\text{fraction gabbro}} = \text{gabbro composition}$$

	Cu (%)	Ni (%)
Em8	.057	.014
Seep1	.043	.014

+ sulfur to copper ratio is generally on the order of 2-3:1

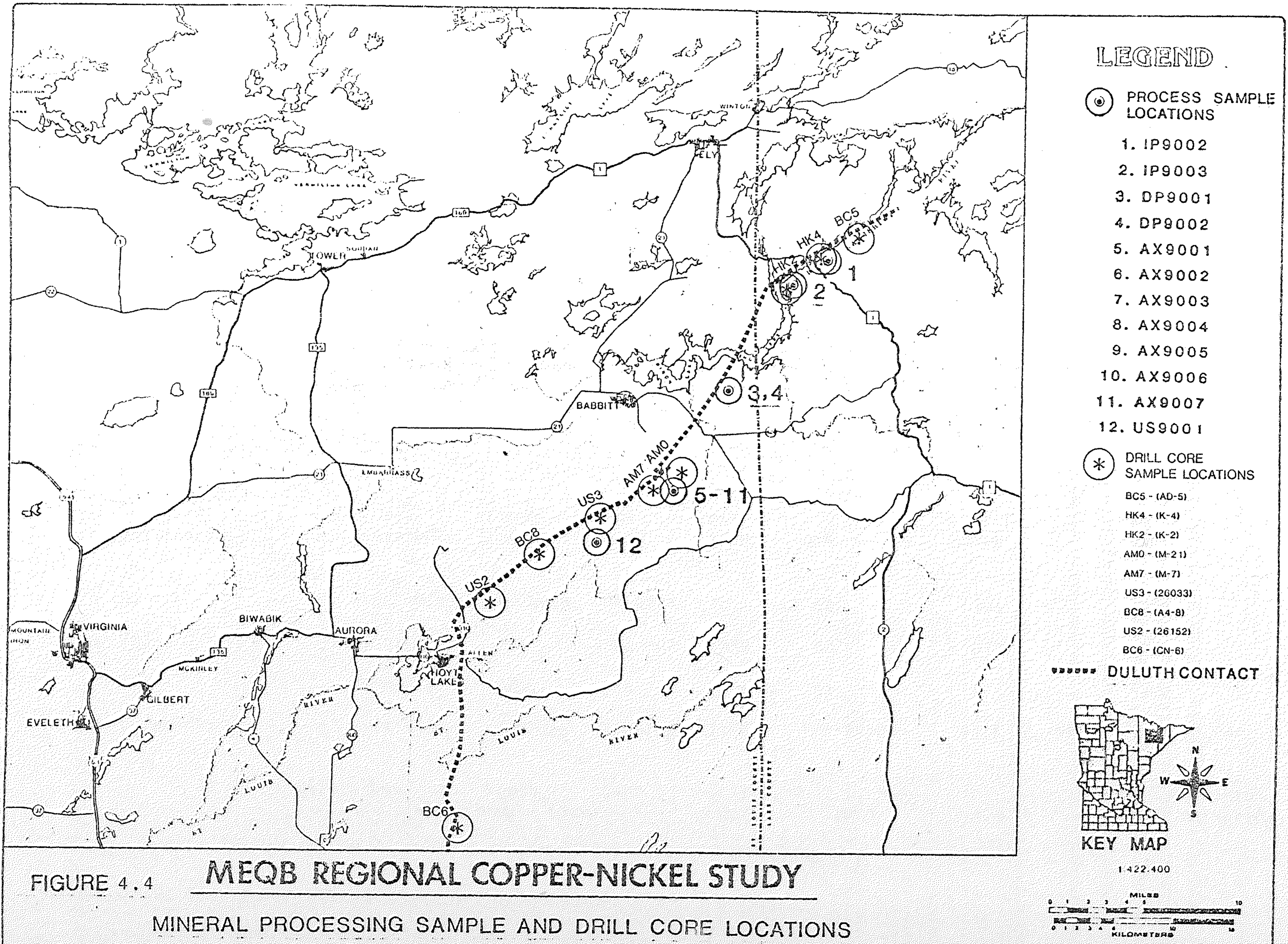


FIGURE 4.4 MEQB REGIONAL COPPER-NICKEL STUDY

MINERAL PROCESSING SAMPLE AND DRILL CORE LOCATIONS

Although the average grade of the stockpiles at Erie is comparable to the models developed by Stevenson (1979), these stockpiles may contain some high grade mineralization. Analysis of drill hole information (Listerud, 1978) indicates the occurrence of potential minerialization in the area. These stockpiles, particularly the gabbro pile, (Lean ore by overall grade) may contain material which is of ore quality. The waste rock piles also contain non-gabbro materials. Given the lack of detailed chemical composition of these piles, extension of these results to future stockpiles must be made carefully.

The mineralogy and chemistry of the Amax test piles is well known but the piles are much smaller than operational stockpiles. Intuitively concentrations would be expected to increase (at least to some degree) with stockpile size since a given amount of water traverses more rock. This assumes that the concentration is reaction controlled; if the concentration is controlled by transport considerations, it may be unaffected by size.

The Inco site is not a stockpile, but represents a seep from a reclaimed area. The main purpose for discussing it is to illustrate that although there are differences in the field study data, the general trends of gabbro reactivity are evident at all field locations. This implies that the gabbro is generally quite reactive across much of the Study Area, so that extrapolating from one site to others in the area is reasonable.

4.1.4 Water Quality Data

Select water quality data collected at these sites are summarized in Figures 4.5 through 4.13. The more important chemical parameters are discussed here. Additional information on leachate quality is available and will be included in future reports. The parameters can be divided into two categories, those which influence the release of metals from the stockpile and the major trace metals detected in the leachate.

The concentration of a given parameter in the leachate is the result of many factors: mass of material available for leaching, volume of transport water, reaction and transport conditions. Therefore, since none of the situations described are identical, variations in concentrations are expected.

Concentration values from an eighty foot stockpile may be higher than a similar stockpile ten feet high, since the water which enters the pile through rainfall contacts more rock surface area in the larger pile. Therefore when comparing stockpiles, the comparison must consider stockpile size. One method of comparison is to examine the mass of material released relative to the mass of the stockpile. A rate of release can be defined as the mass released per unit time per unit mass of stockpile. These release rates are presented in a later section.

Alkalinity, pH and dissolved organic carbon (DOC) are three key parameters which influence the rate of leaching and the mobility of metals in the aqueous environment. (The effect of pH and specific organic compounds on leaching was studied in the laboratory. Laboratory results are discussed in Chapter 3). Mobility of a given component refers to its tendency to remain in solution as opposed to being removed by chemical precipitation or adsorption.

The mobility of a metal influences the amount of that metal which leaves the stockpile as well as its transport in the streams and lakes of the area. Precipitation and adsorption reactions remove the metal from solution and produce a solid phase. In general, metals produce the most environmental problems when they are in solution (D. Lind, 1978).

Variation in pH affects both the leaching process and the mobility of components in solution. Decreasing pH (increasing acid) tends to enhance both rock dissolution and metals mobility, although both dissolution and metals transport do occur in the neutral pH range. Historically, one of the major problems in the sulfide mining industry has been the generation of acid mine water (acid leachate). As has been discussed previously, when iron sulfide minerals oxidize, acid is produced. For the Duluth gabbro it appears that in most instances, the silicate minerals are able to neutralize the acid that is produced. Figure 4.6 shows that the pH of the various seeps is in general above 6.5. This indicates that there is not a great tendency for generating acid conditions. Recent data indicate that in one of the AMAX test piles pH has fallen below 6, suggesting that although acid conditions are not prevalent, they may occur.

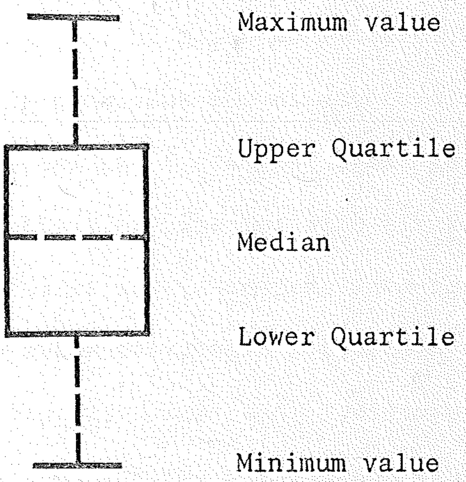
When acid conditions occur high concentrations of metals may occur in the leachate solution. For example the quality of leachate from Amax test pile FL5 is shown below: (additional data are available in Eger et al., 1979).

Figure 4.5 Box plot construction

Figures 4.6 through 4.13

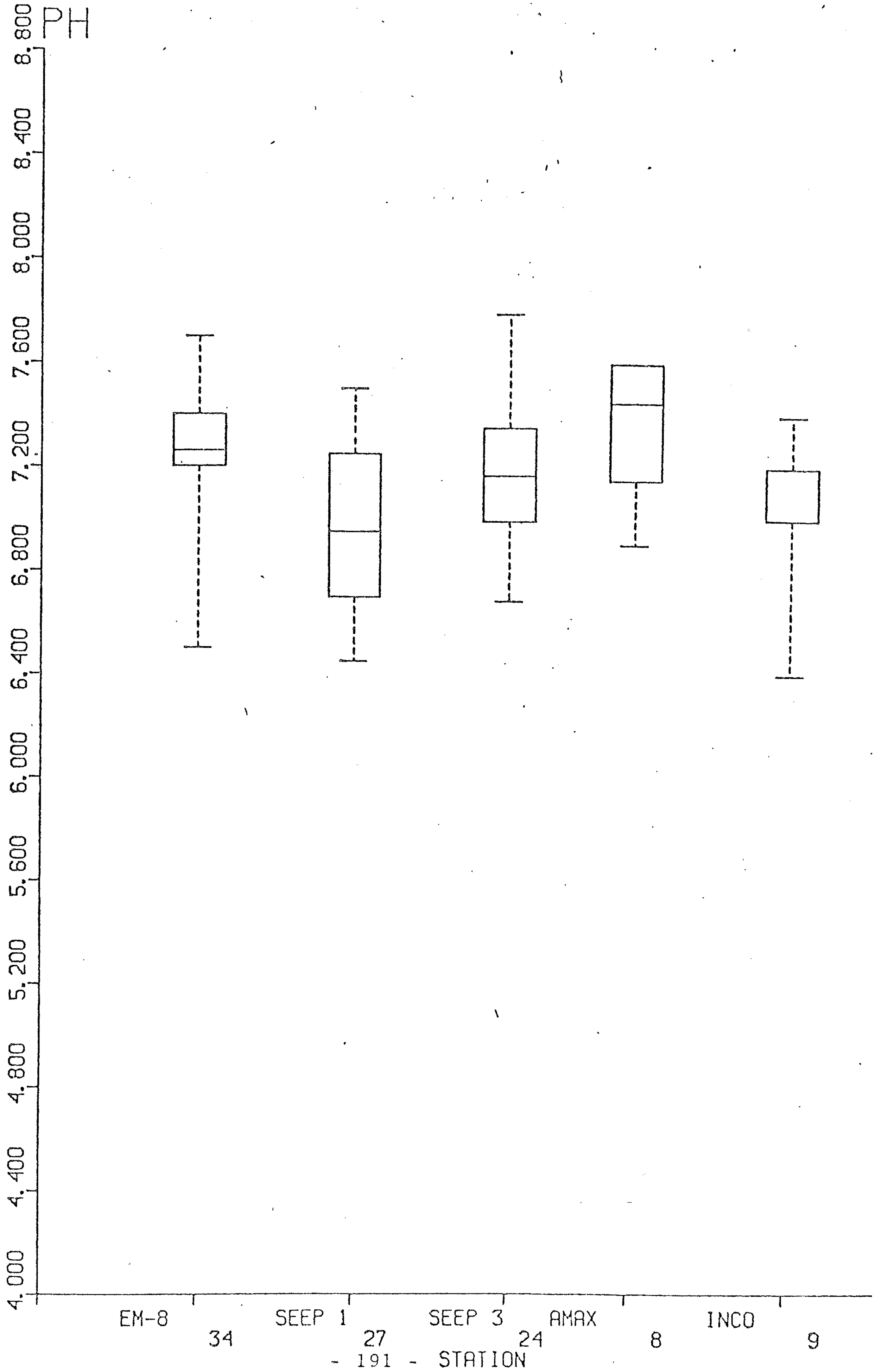
Water quality data collected by the Regional Copper Nickel Study during the period July 1976 to August 1977; the data is presented from leachate sources, identified in the introduction.

The general format is the box plot diagram which is described below:



n number of samples

Figure 4.6 pH, Box Plot Summary



		Filtered metals mg/1			
Date of sample	pH	Ni	Cu	Co	Zn
5/25/78	7.6	.780	.021	.136	.096
7/5/78	7.05	5.1	.90	.195	.257
8/16/78	5.8	24.1	1.3	4.05	.66
9/13/78	3.62	83.0	10.42	6.25	2.47

The reason for the acidification is being investigated. More work is needed to develop the criteria for acid producing conditions. It may be necessary to separate stockpiles by the percent sulfur in the rock.

Alkalinity is a measure of the ability of a solution to neutralize acid and resist change in pH. As alkalinity increases the pH buffering capacity increases. At low values of alkalinity, pH is subject to greater fluctuations due to additions of small quantities of acid or base. The higher the alkalinity the more acid must be added to lower the pH. At high values of alkalinity, copper and cobalt tend to form insoluble precipitates and are less readily removed from the stockpile. Figure 4.7 shows that the alkalinity observed for Erie seeps are much higher than typical background concentrations of 15 to 25 mg/1 as $CaCO3$.

Many types of dissolved organic compounds are capable of complexing metals and causing increased mobility. These organics can also increase the rate of leaching. Dissolved organic concentrations observed from seeps are presented in Figure 4.8. These concentrations are higher than the 12-15 mg/1 background concentrations typical of streams in the region.

Figure 4.7 Alkalinity, Box Plot Summary

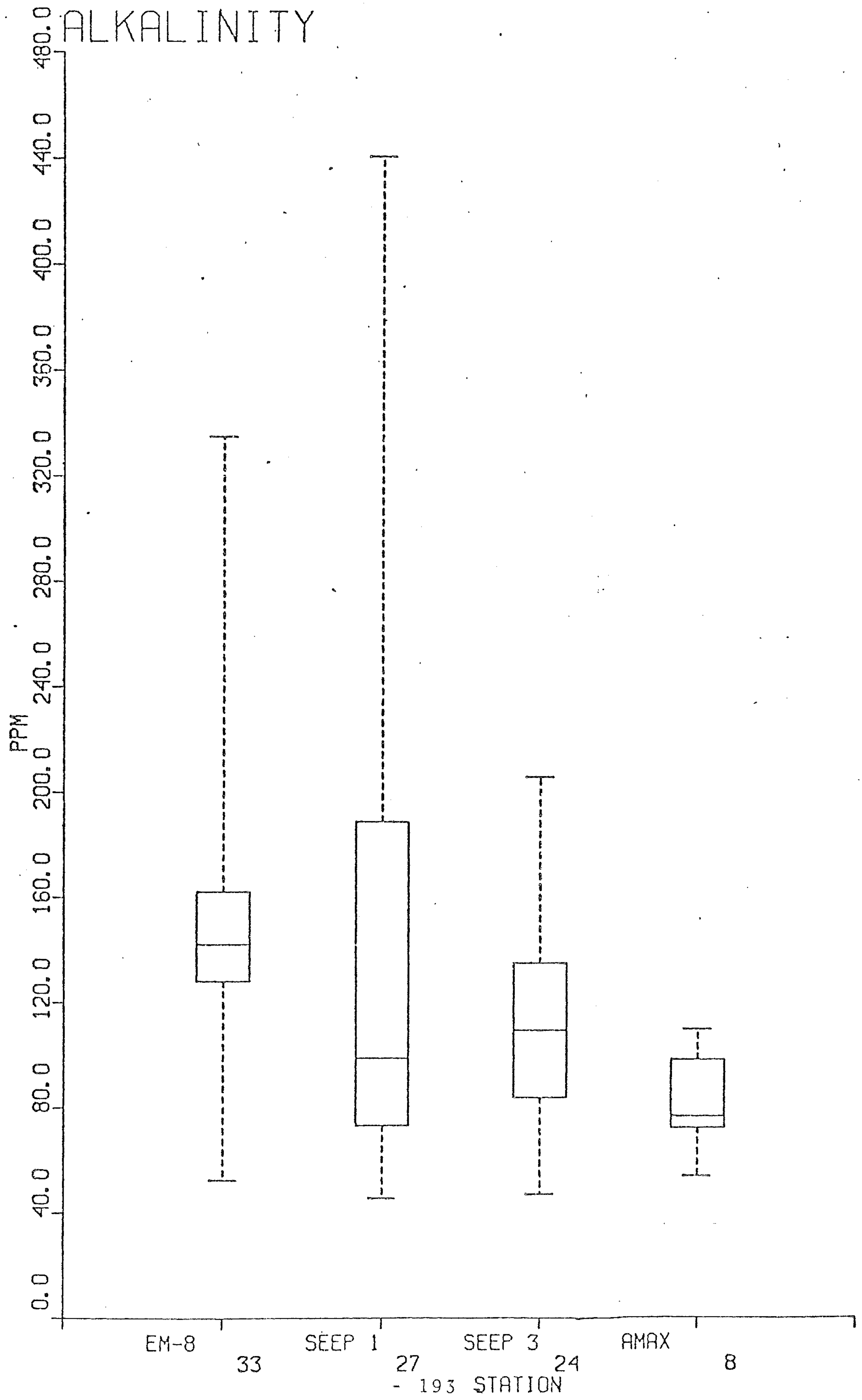
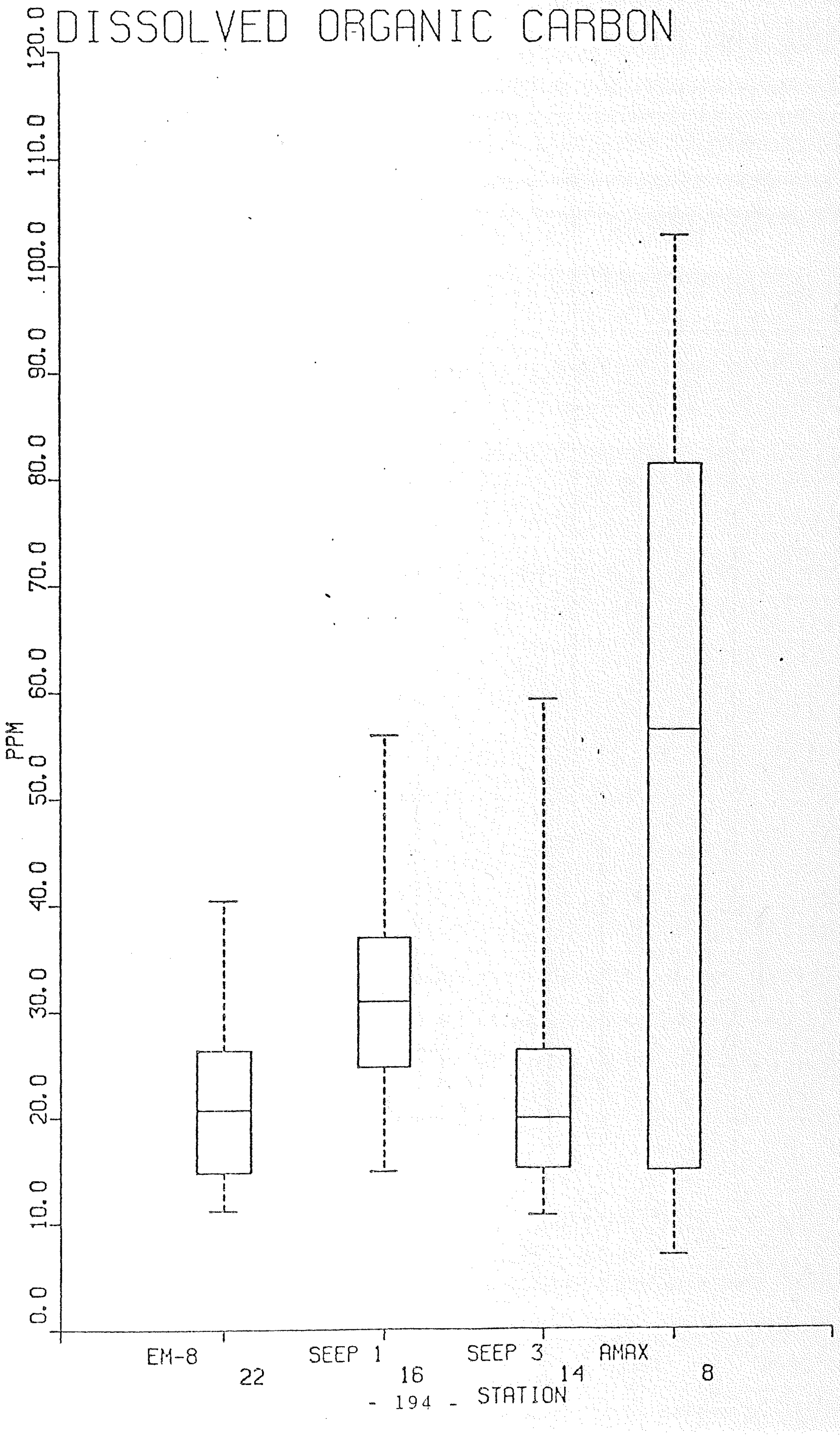


Figure 4.8 Dissolved Organic Carbon, Box Plot Summary



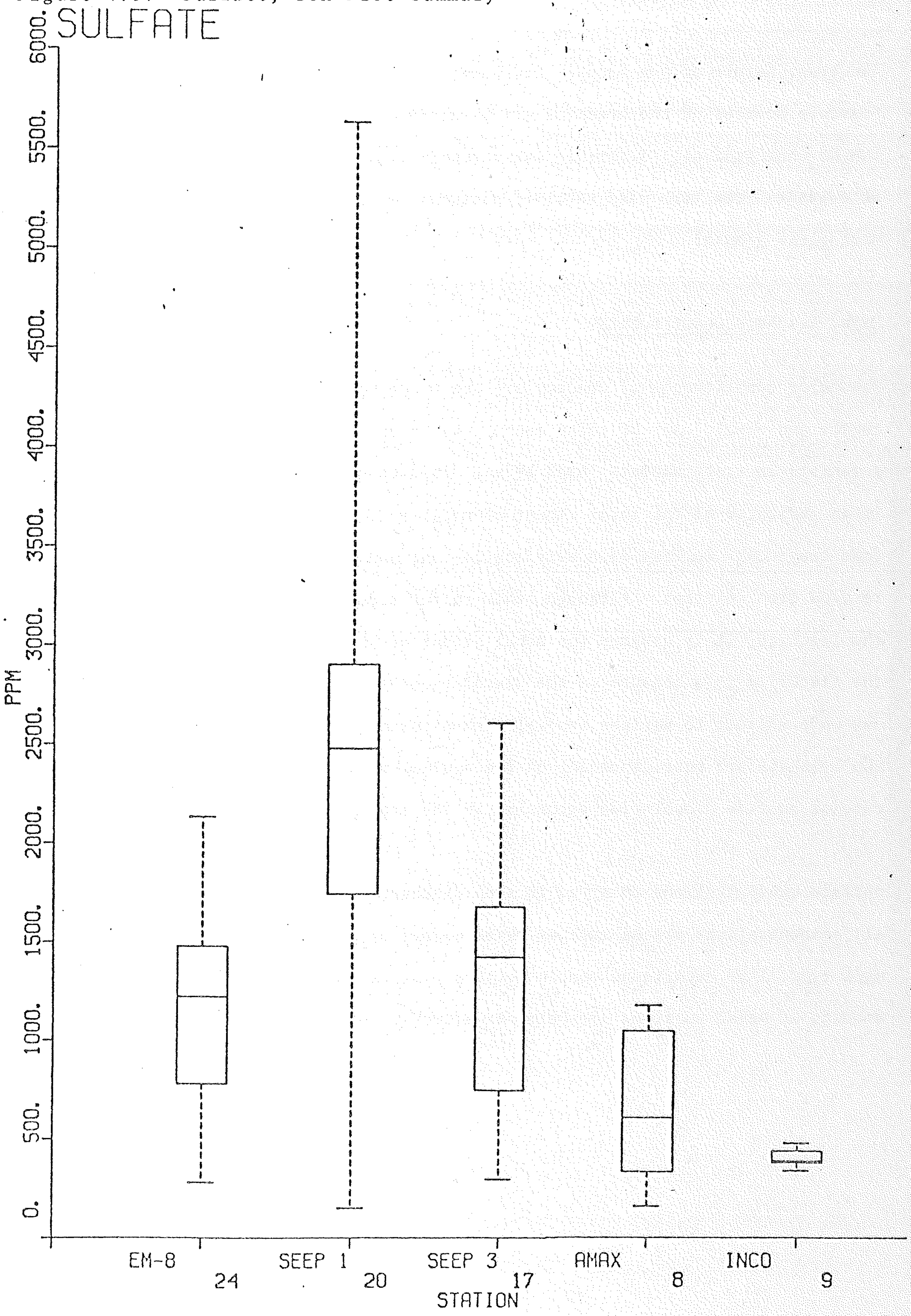
The exact nature of the organic compounds in the leachate is not known. Possible sources of the organics are 1-rainfall, 2-residuals from explosives (NH_4NO_3 and fuel oil) 3-surface water runoff from non stockpile areas 4-removal of organics from till used to cover portions of the stockpiles 5-products of biological growth.

Major Leachate Constituents

The major constituents of concern are the trace metals (copper, nickel, cobalt and zinc). All of these metals have been shown to be toxic to aquatic organisms in trace amounts (Lind 1979). Sulfate has been included since it is an indicator of the total amount of metal sulfide that has been dissolved from the rock. Sulfate is a very mobile ion; and it is unlikely to be removed from solution. Although other sulfur species are probably present in the leachate, it is assumed the total amount of sulfate transported out of the stockpile is a measure of the dissolution of metal sulfides. The metals are more subject to various removal mechanisms and their concentrations in the leachate are more dependent on the aqueous mobility of the metal than the rate of sulfide dissolution occurring in the stockpile.

Sulfate concentrations observed in seep discharges are presented in Figure 4.9. All concentrations are as much as three orders of magnitude greater than 5-10 mg/l typical of background concentrations. It is clear that substantial amounts of metal sulfides are being oxidized in the stockpiles.

Figure 4.9. Sulfate, Box Plot Summary



Seepage concentrations for copper, nickel, cobalt and zinc are presented in Figures 4.10 to 4.13. A rather wide range of concentration was observed for each of the metals. As previously discussed some of the concentration range is the result of site differences. The box plots include all the data that was collected during the study, June 1976 to August 1977. This time period includes some early spring samples collected prior to actual seepage and therefore contained low concentrations.

1 - Metal concentrations range from 10 to 10,000 times the background concentrations found in the streams and lakes of the study area.

Although flow rates in these seepages are not shown, the volume of leachate produced at the Erie sites is substantial. Maximum discharge observed at site EM8 during the period June 1976 to August 1977 was 142 liters/sec (5 cfs). Estimates of the total mass of nickel removed from the stockpiles over this period are

Site	Kg Nickel
Seep 3	1800
Em8	150
Seep 1	110

2 - Concentrations are above levels at which detrimental effects on biological organisms have been observed. Bioassay tests performed on leachate samples have demonstrated toxicity (Lind 1979).

Figure 4.10 Copper, Box Plot Summary

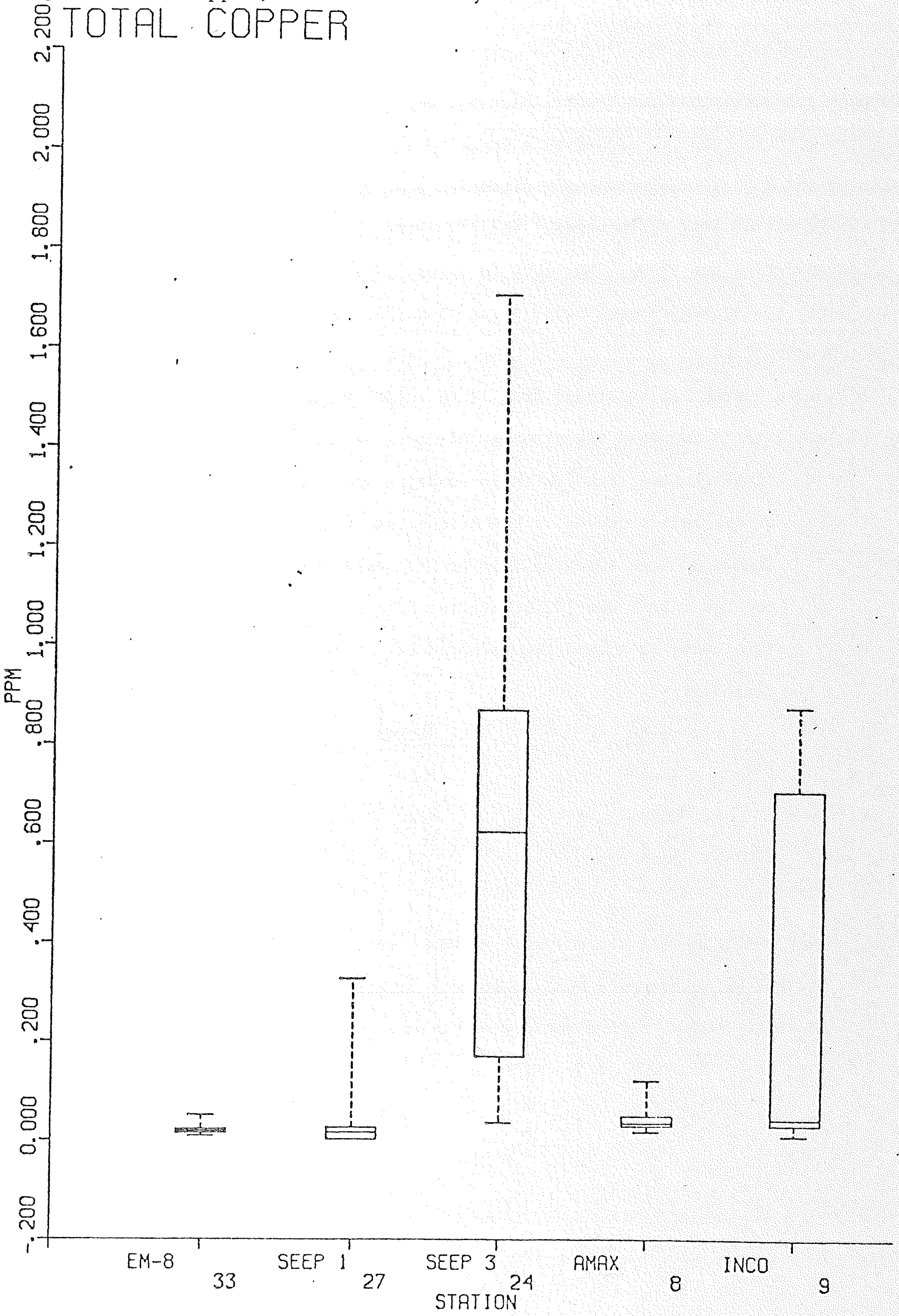


Figure 4.11 Nickel, Box Plot Summary

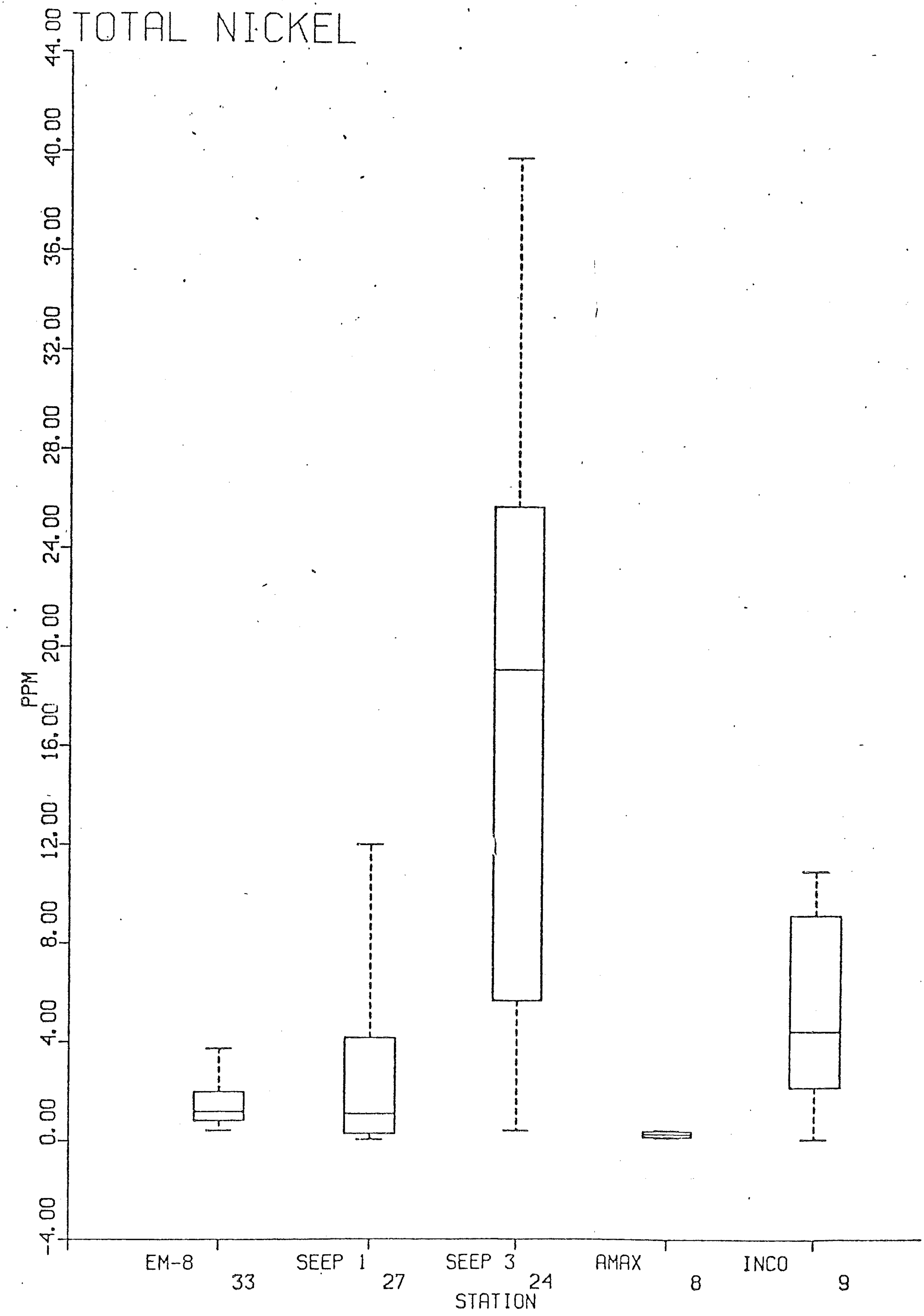


Figure 4.12 Cobalt, Box Plot Summary

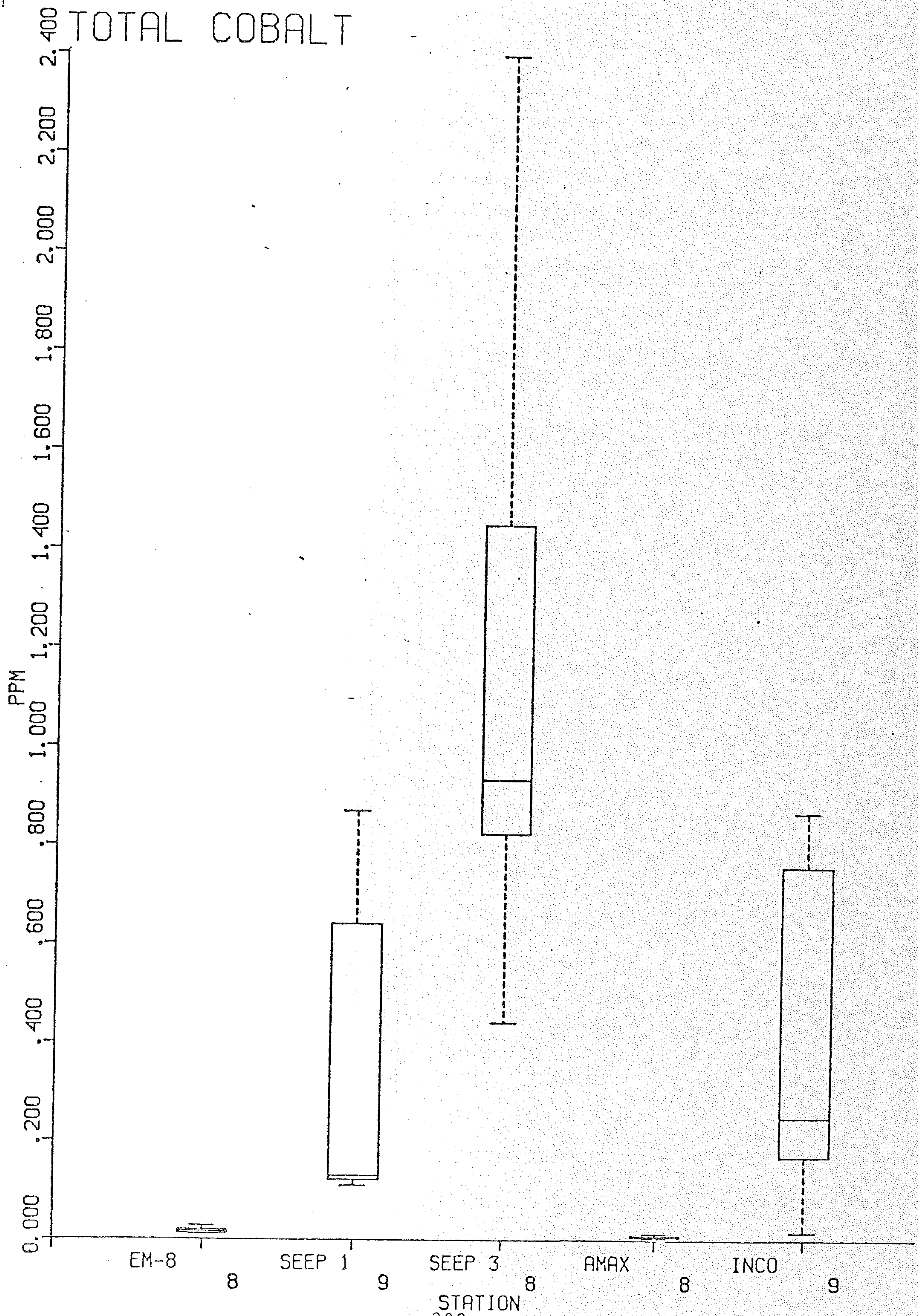
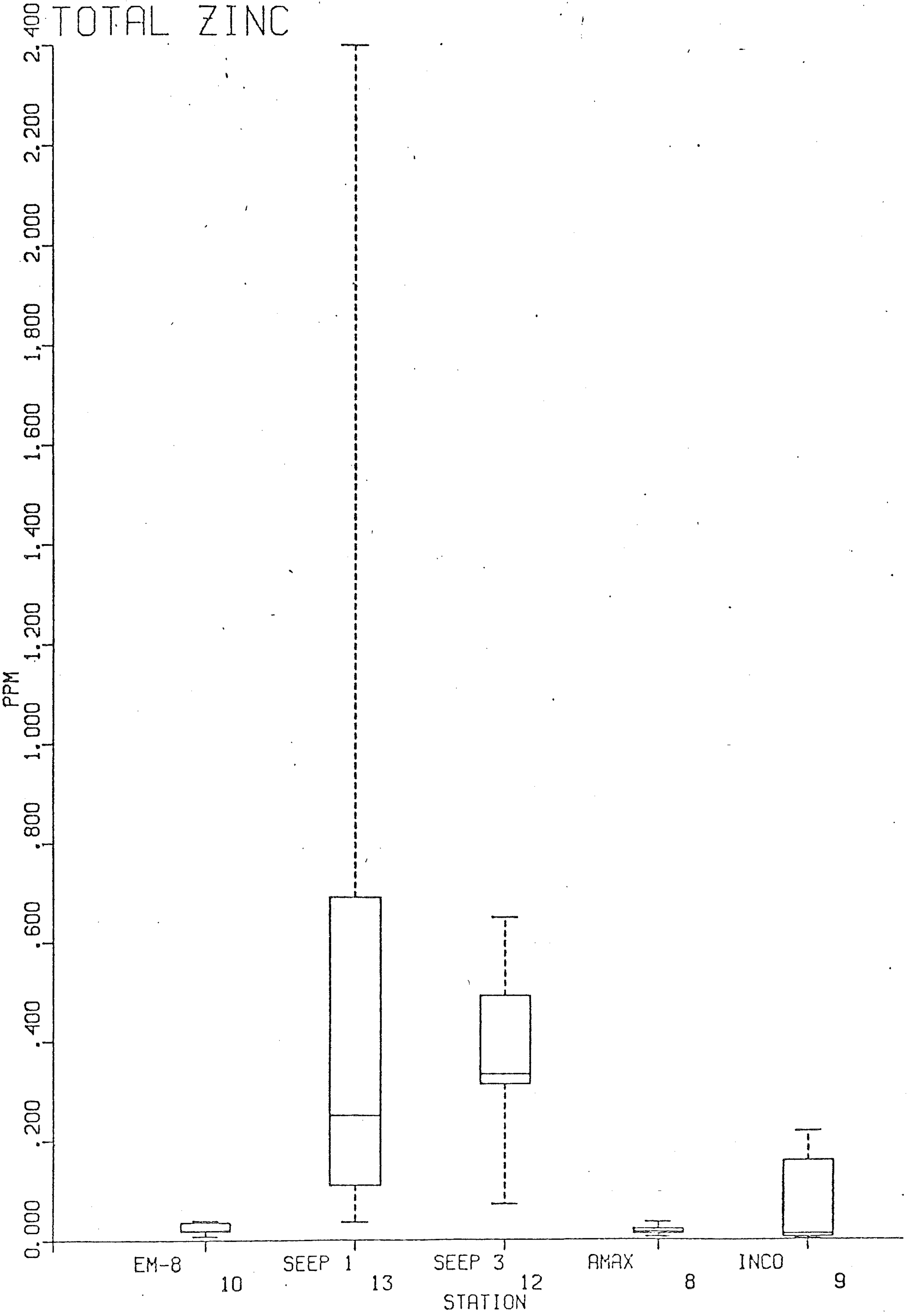


Figure 4.13 Zinc, Box Plot Summary



Lowest levels at which detrimental biological effects have been observed for each metal individually (Regional Copper-Nickel Study)

Metal	Concentration (mg/l)
copper	.01
nickel	.10
cobalt	.01
zinc	.10

3 - The ratio of copper to nickel is lower in the leachate water than in the rock. Table 4.3 compares the leachate and rock ratios for various sites. In the rock the copper concentration is about 4 times higher than nickel. In leachate solutions, copper is .1 to .33 that of nickel. Nickel has been enriched relative to copper in the solution.

Nickel is a more mobile element than copper and when released it is more likely to remain in solution (It is possible that the nickel sulfide, pentlandite, oxidizes faster than major copper sulfides, chalcopyrite and cubanite. There are no data on the dissolution behavior of the pure form of these minerals under typical environmental conditions. Some data do exist for iron sulfide dissolution under acid conditions (Eisenreich et al., 1976).

4 - Nickel is the major trace metal in the seeps. Table 4.4 shows the relative proportion of trace metals in the leachate. Correlation coefficients for nickel at the Erie sites are shown in Table 4.5. In general, as nickel increases so do the other trace metals in the leachate. This is to be expected since the conditions that would favor increased nickel

Table 4.3 Comparison of Copper/Nickel Ratios in Gabbro and Leachate

	SITE			
Copper/Nickel ratio	Em8	Seep 3	Seep 1	Amax FL-1
rock	4	3.5	3	4.5
leachate*	.16	.32	.16	.10
number of sample	33	24	27	8

Leachate* ratios are median values

Table 4.4 Comparison of Gabbro Composition with Leachate Composition

	Gabbro* (moles of metal) (total moles of metal associated with sulfide)	Leachate (moles of metal) (total moles of metal+ in leachate)
Ni	6.5	76.7
Cu	25.4	7.4
Zn	1.3	3.1
Co	.8	1.6
Fe	65.9	11.3+

*Based on analyses of Ax9001 (sample selected from FL-1)

+Iron concentration is assumed to be .8X Detection limit

Table 4.5 Nickel Correlation Coefficients for Seeps at the Dunka Pit

(all data collected from 7/76-8/77 have been used)

Seep 3	Correlation Coefficient (r)	number of point	Level of significance of the correlation
Cu	.89	24	.001
Co	.86	8	.006
Zn	.95	11	.001
Mn	.99	16	.001
Mg	.91	12	.001
Cl	.79	19	.001
pH	-.47	23	.024
alkalinity	-.61	23	.002
SO_4	.72	16	.002
Seep 1			
Cu	.64	27	.001
Co	.94	9	.001
Zn	.93	13	.001
Specific Conductance	.85	27	.001
Em8			
Cu	0.3	33	.820
Co	.44	8	.278
Zn	.82	10	.004

mobility, would increase the mobility of the other metals. The strongest correlations are found at seep 3, where substantial concentrations of all metals are found in the leachate. The negative correlation of nickel with pH (although not as strong a correlation as the other metal correlations), illustrates the effect of pH on metal mobility. As pH increases, the nickel concentration in the seepage decreases.

If it is assumed that the only source of trace metals is the sulfide minerals and that the sulfate release is a measure of the total rate of sulfide mineral dissolution, then the percent of metals that are being transported out of a stockpile can be calculated. This is illustrated in Table 4.6. The 1977 data for AMAX test pile FL-1 were chosen because the pile is controlled and its chemical composition is known. Large percentages of metal sulfides are oxidized and yet the metals are retained in the pile.

Although the exact mechanisms that prevent the transport of metals from the stockpile are not known, it is likely that large amounts are being removed by the silicate minerals in the gabbro. Some metals may form hydroxide and carbonate precipitates and be removed from solution. These removal reactions are reversible. Metals removed from solutions may be released at a later date if the solution composition changes. For example, if the pH in the pile decreased, metals that had been adsorbed could be released into solution. Decreases in pH could result from 1) increased sulfide oxidation; if the rate of acid production due to sulfide oxidation exceeded the rate of acid neutralization by the silicate minerals the pH will decrease, and 2) increasing rainfall acidity; recently collected data indicate a trend toward acid rainfall in the study area. If this

Table 4.6 Percent of Oxidized Metal that is retained in the Stockpile

(based on 1977 data for Amax test pile FL-1)

	Concentration (mg/1) predicted from chemical composition	Concentration (mg/1) observed (median)	Percent of metal retained in pile
SO_4	610[1] basis	610[1]	0
Ni	22.7	.288	98.7
Cu	95.2	.03	99.97
Zn	5.0	.013	99.7
Co	2.8	.006	99.8
Fe	217	< .05	> 99.98

[1] SO_4 is the basis of the concentration; it is assumed that SO_4 indicates total sulfide dissolution and that it is 100% removed from pile

trend continues the leaching rate may increase with time.

4.1.5 Additional constituents of stockpile runoff

Table 4.7 presents the results of a complete analysis of seep 3 leachate. The model lean ores and waste rock compositions are shown for comparison. The leachate contains not only sizable concentrations of copper, nickel, cobalt and zinc, but also several additional trace metals. The complete analysis was performed on only one sample; additional data on cadmium and lead are given in Table 4.8.

While the maximum metal values were found at the seeps at Erie, extremely high levels of chloride, nitrate, and organic carbon were observed at Amax test pile FL-1. The source of these contituents may be explosive residue and residual mine water which is associated with the stockpiled rocks. Highly saline water was encountered in the Amax test shaft (see section on mine water for more details). Hewett estimates that 1% by weight of water is associated with the rock as residual water. Figure 4.14 illustrates the behavior of test pilot FL-1 during 1977. The residual constituents show declining concentration as they were washed off the rock surface by rainfall. The elements associated with the leaching reaction (SO_4, Ni) show increasing concentrations with time. If saline water is encountered chloride levels will be elevated in the runoff.

Table 4.7 Complete Chemical Analysis, Seep 3 Leachate

ELEMENT	6/20/77 Seep 3* mg/l	+ Lean ore %	+ Waste rock %
Oxygen	-	43.34	43.96
Silica	-	22.68	22.86
Aluminum	9.34	8.98	9.45
Iron (FeO)	21.6	9.22	8.92
Magnesium	187	4.32	4.66
Calcium	331	5.55	5.67
Sodium	71	2.00	2.24
Potassium	7.0	.33	.36
Titanium	.348	1.41	.94
Phosphoro	<.11	.02	.03
Manganese	11.5	.12	.13
Chromium	.123	.03	.03
Sulfur	-	.655	.207
Copper	1.50	.306	.100
Nickel	30.2	.073	.023
Iron (FeS)	-	.697	.229
Cobalt	1.82	.009	.002
Zinc	.60	.015	.0025
Lead	<.088	.0003	.0001
Silver	<.002	.00014	.00005
Arsenic	<.038	<.00056	<.00018
Mercury	-	.0000044	.0000015
Molybdenum	<.006	.00014	.00003
Selenium	<.06	Not Detected	Not Detected
Cadmium	<.002	<.0056	<.0018
Tellerium	<.065	Not Detected	Not Detected
Boron	<.0003	.662	.586
Barium	N. D.	1.173	.723
Beryllium	<.001	.0001	.00006
Strontium	.749	.279	.285
Vanadium	.138	.277	.171
Thorium	N. D.	.00064	.00045
Zirconium	N. D.	.0081	.0098

\+ Model concentration developed by R. Stevenson (1979)

* Analysis by Barringer Laboratories, Toronto, Plasma Emission (total metal analysis)

Table 4.8 Additional Trace Metal Analyses on Erie Seeps

Station Parameter	Em8	Seep 3	Seep 1
Cadmium (Mg/1)	.0004-.001	.0089 - .0107	.0005, N.D.
Lead (Mg/1)	N.D.	N.D.	------

Samples collected 10/5/76 and 10/25/76

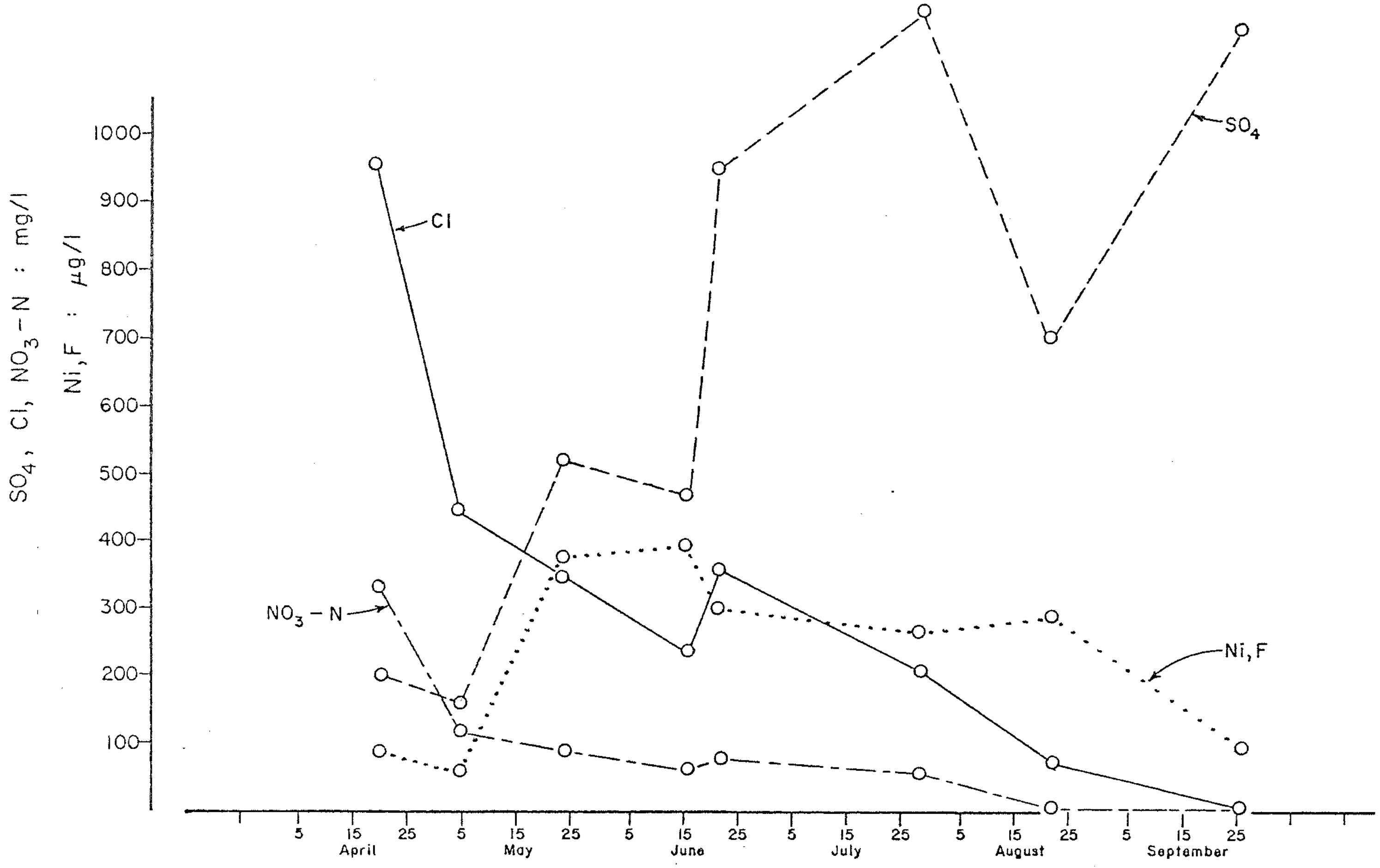
N.D. = Not detected

Figure 4.14

FL – I, 1977

CONCENTRATION VS TIME

Cl, $NO_3 - N$, SO_4, Ni



4.1.6 MODEL LEACHATES

The quality of stockpile runoff is influenced by many factors. The field and laboratory data collected as part of the regional study are only a beginning in the attempt to understand this complex phenomenon. More work, both laboratory and field, is needed before more accurate predictive models can be developed.

Future stockpiles may not resemble the ones studied at Erie. They may have a greater mass, a lower grade and smaller particle size, or they may be very similar. Table 4.9 illustrates the projected stockpile masses, surface areas and grade for the model open pit and underground mine. The Erie stockpiles are shown for comparison. The amount of stockpile mass that will be available for leaching is phenomenal.

The model open pit operation uses a stripping rate of 1.3 to 1., or for every one ton of ore mined 1.3 ton of waste rock are removed. Amax is presently investigating the possibility of using stripping ratios of 2-3 to 1. This would produce more waste rock per ton of ore than the regional study model.

Two methods can be used to predict release from future stockpiles. The first is to determine the rates at which a specific parameter is released from the stockpile. The rate must be expressed relative to stockpile mass or surface area, i.e.,

$$\text{(Kg of parameter A) released} \quad \text{per} \quad \text{(Kg gabbro) or (m}^2\text{ of surface area)} \quad \text{per (yr)} \quad = \quad \text{rate of release of A}$$

Table 4.9 STOCKPILE MASS

			Total Stockpile mass		Estimated	Stockpile Grades					
					Surface area	Lean Ore			Waste rock		
Operation	Size	Mine Life	Lean Ore	Waste rock	m^2/ton	% Cu	Ni	S	Cu	Ni	S
	(mt per yr)	(yr)	(mt)	(mt)							
Open Pit	20X10^6	25	325X10^6	325X10^6	50-200	.306	.073	.655	.10	.023	.207
Underground	12.35X10^6	23	28.2X10^6(total)		300-500						
Dunka Pit*		12	6.0X10^6 tons	15.6X10^6 tons	50-200	.28	.08	no data	.050$^+$	.014$^+$	no data

*values are totals for the 12 years of mine operation

stockpiles masses are os of January 1977

+Average

The second approach is to develop a "model" concentration for the leachate. All leachate that leaves the stockpile is assumed to have the same model concentrations. There are limitations to both approaches. Both are discussed in the following sections.

4.1.6.1 Rate of Release

Theoretically if sufficient data were available, a model incorporating the amount of precipitation input, the rate of sulfide dissolution and the identification and rate of the transport controlling reactions could be developed. The data base presently available does not permit this type of model development. Rates based on field data are based only on the outflow of the stockpile and represent a net rate for a specific time interval. Laboratory rates are based on more controlled conditions, but laboratory conditions never completely duplicate field conditions. For further discussion of rates and rate calculations refer to the section on the comparison of laboratory and field rates.

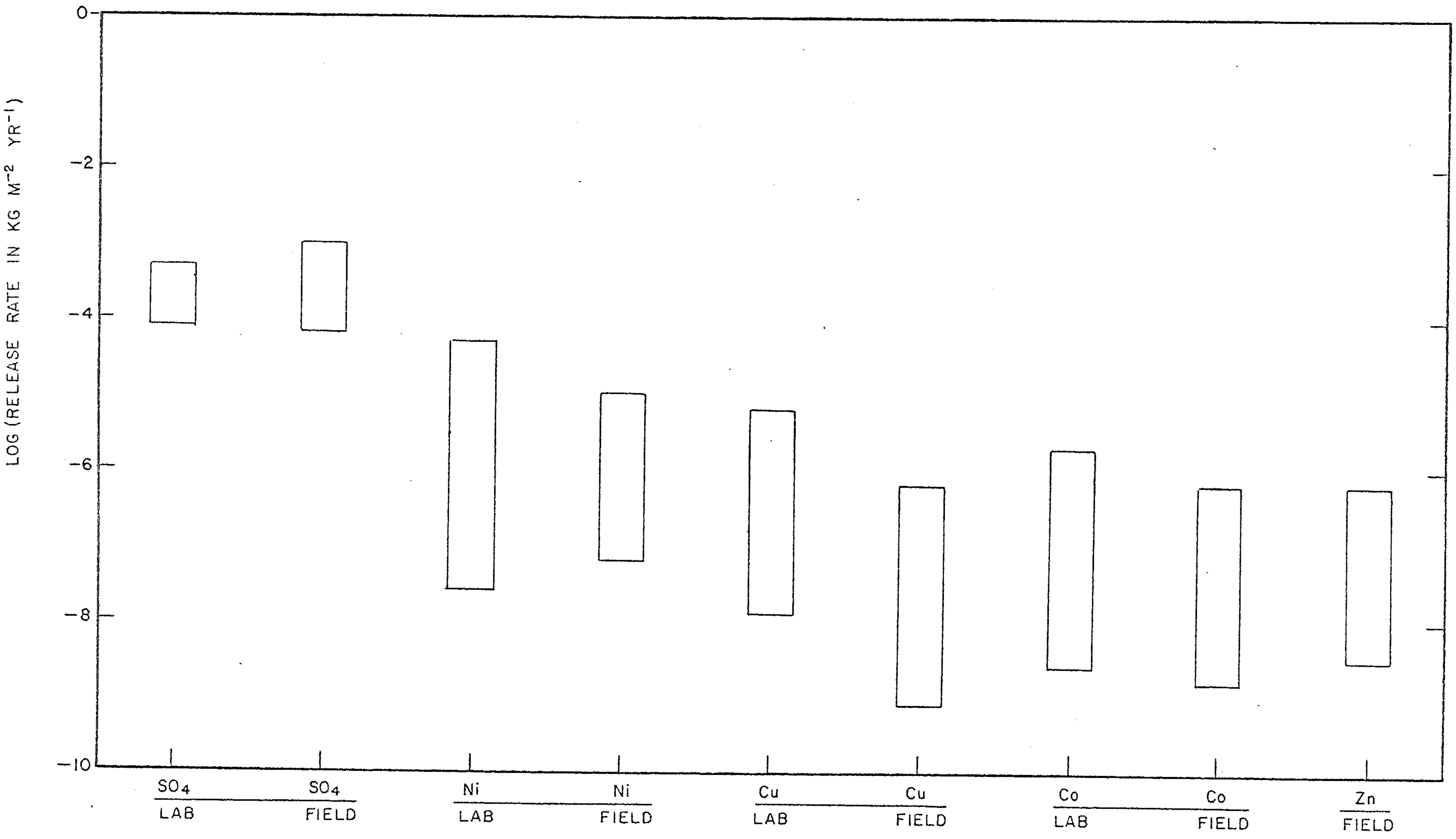
Leaching rates for various components were determined in both the laboratory and the field. The conditions under which the leaching occurred varied in both laboratory and field presenting a range of rates in both instances. The agreement between laboratory and field rates is quite good and is presented in Figure 4.15. (Rates are presented on a per M^2 basis to compensate for the large difference in specific surface area between laboratory and field samples.)

The field values for the rate of release were generally lower than laboratory results. Only for sulfate were some observed field values greater than the rates measured in the laboratory. In all cases, the rates shared a common range of values. Field values are calculated over longer time intervals and over a wider range of environmental variables than most of the laboratory experiments and therefore may better represent

Figure 4.15

LABORATORY AND FIELD RELEASE RATE

(Box indicates observed range of values)



actual conditions.

Among the factors known to affect the leaching rate are the amount of precipitation, degree of mineralization of the stockpile and amount of surface area available for leaching. Rainfall during the 1976 sampling period was low, approximately one half of a normal year. In contrast, the 1977 sampling period rainfall, was almost 15% greater than normal. An increase in leaching rate occurred with increasing rainfall, which is a factor to be considered when applying leaching rates for impact analysis. (Table 4.10)

As the degree of mineralization (the percent of metal sulfide) of a stockpile increases the rate of metal sulfide leaching increases. The chemical composition of the Erie and AMAX stockpiles is shown in Table 4.2. The degree of mineralization of future stockpiles relative to observed stockpiles will affect the predictive reliability of the rates presented. Surface area exposed per unit mass is dependent on particle size. As particle size decreases the surface area per unit weight increases. The Erie stockpiles are the product of open pit mining and have a larger particle size than products of underground mining. The surface area per ton for the underground mine is larger than that for an open pit mine by a factor of 2.5 to 10.

The fact that the laboratory and field rates share common ranges is significant. The implications are that 1-the gabbro in the field study areas, particularly the Erie stockpiles, does not exhibit anomalous leaching characteristics. 2-Gabbro stockpiled over 10 years ago show similar leaching characteristics to fresh material. There is no reason to believe that leaching is only a short term problem.

DATA SUMMARY

Table 4.10 Effect of rainfall on leaching rate

SITE	LEACHING RATE: kg (MT gabbro)$^{-1}$ yr^{-1}								$\frac{\text{RATE 1977}}{\text{RATE 1976}}$			
	SO_4		Ni x 10^4		Cu x 10^4		Ca					
	1976[a]	1977[b]	1976[a]	1977[b]	1976[a]	1977[b]	1976[a]	1977[b]	SO_4	Ni	Cu	Ca
Em-8	0.0074	0.022	0.11	0.23	0.0011	0.0087	0.0012	0.0054	2.9	2	8	4.6
Seep-1	0.094	0.12	0.34	2.9	0.0098	0.011	c,d	c,d	1.3	8	1.1	d.
Seep-3	0.025	0.069	2.8	14	0.096	0.57	0.0035	0.017	2.7	5	6	5

a From samples 7-15-76 to 11-28-76

b From samples 4-12-77 to 8-17-77

c Estimated by $SO_4/Ca^{2+}=5.3$

d Insufficient data

Precipitation during sampling period from Babbitt

1976: 4.43 inches

1977: 16.09 inches

Ratio of precipitation: $$\frac{P_{1977}}{P_{1976}} = \frac{16.09}{4.43} = 3.6$$

Stockpile mass will increase with time. Increased leaching will occur as the length of time of mining operation increases. The mining model presented dictates that 26 million tons of stockpile mass per year for a period of 25 years will be produced. The potential for generation of leachate from stockpiles exists throughout the time of mining operation. The maximum potential occurs at the end of operations when stockpile mass is at a maximum.

Leaching rates are presented as a function of both mass and base area of stockpile. The height of stockpiles is assumed to be 200 feet (61m). The variation of stockpile base area with mass is presented in Figure 4.16. Model or estimated leaching rates for sulfate, copper, nickel, cobalt and zinc are presented in Figures 4.17 to 4.21. A range of rates is presented in all cases. The range was determined by the maximum and minimum rates observed in the field. The average of these two rates is also presented and is not significantly different from the average of all rates combined.

4.1.6.2 Model Concentrations

The model concentration approach is an obvious oversimplification. Leachate concentrations vary with time, both seasonally and yearly, and may fluctuate with flow. Different stockpiles are likely to produce leachate of different water quality.

The advantage of this approach is that it uses actual measured concentrations from field samples. Two models were developed. These models are shown in Table 4.11. Values from EM-8 were chosen for model I and represent leachate having relatively low concentrations of metals.

Figure 4.16

BASE AREA VS STOCKPILE MASS

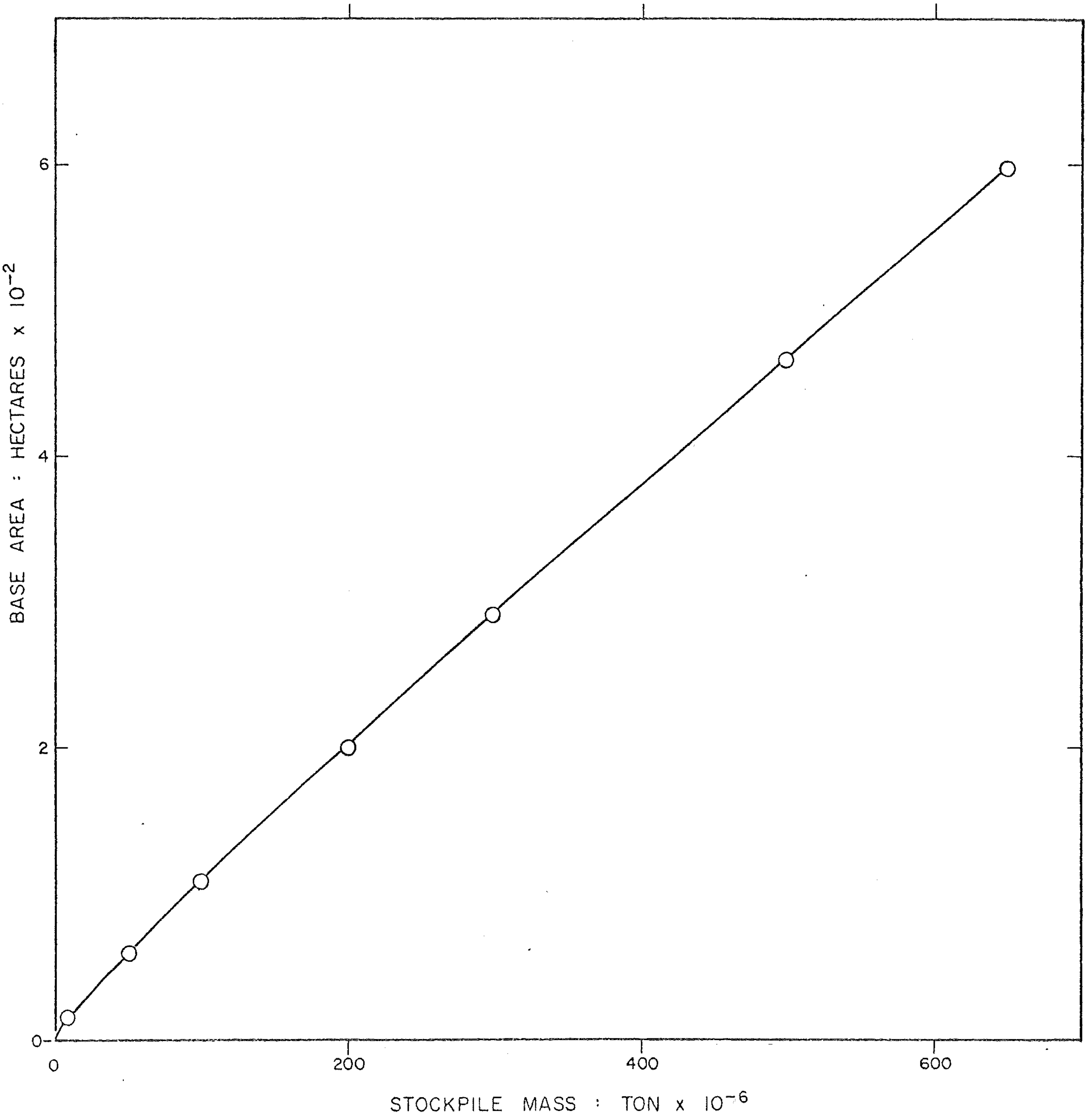


Figure 4.17

SULFATE RELEASE RATE VS STOCKPILE MASS

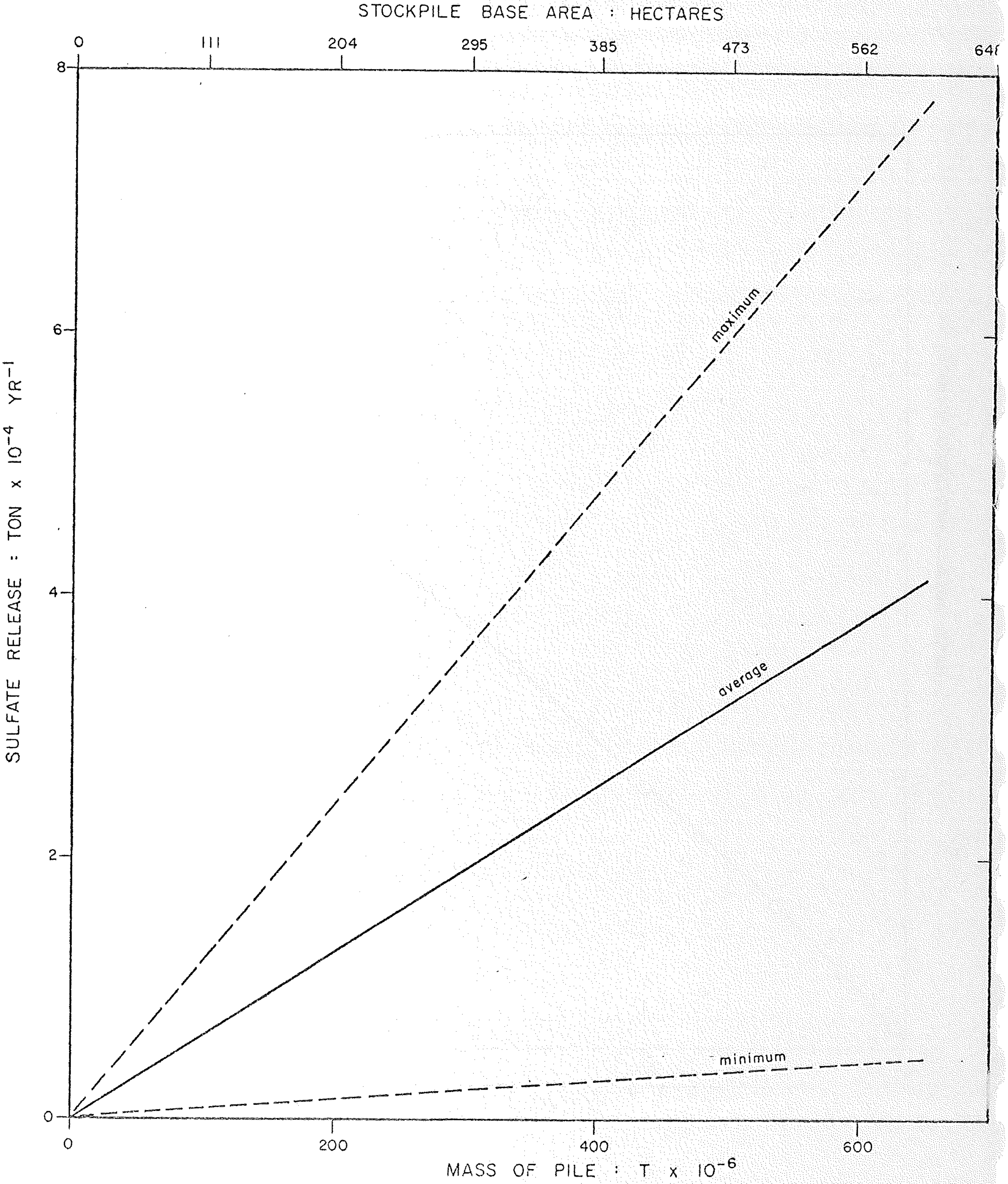


Figure 4.18

COPPER RELEASE RATE VS STOCKPILE MASS

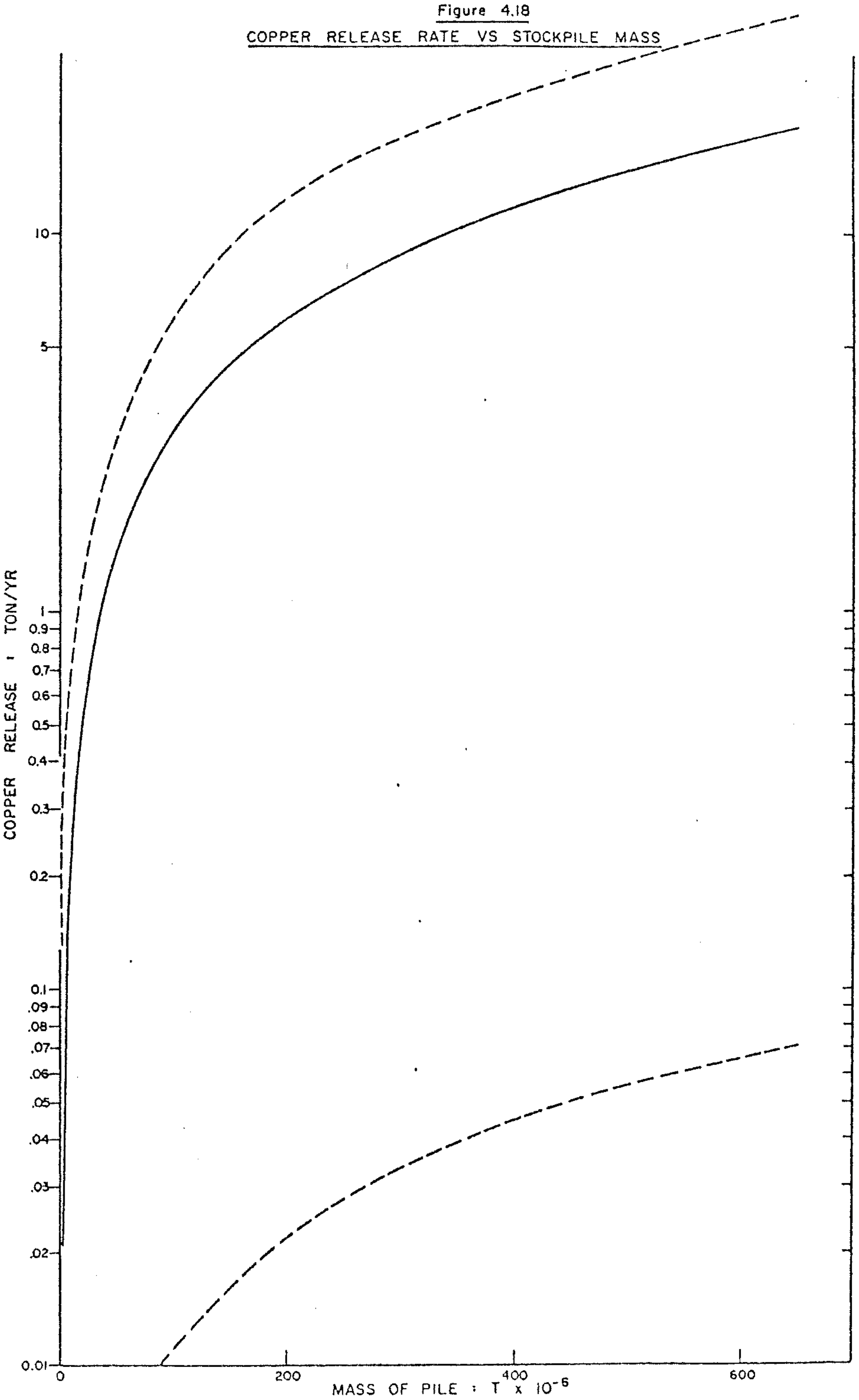


Figure 4.19

NICKEL RELEASE RATE VS STOCKPILE MASS

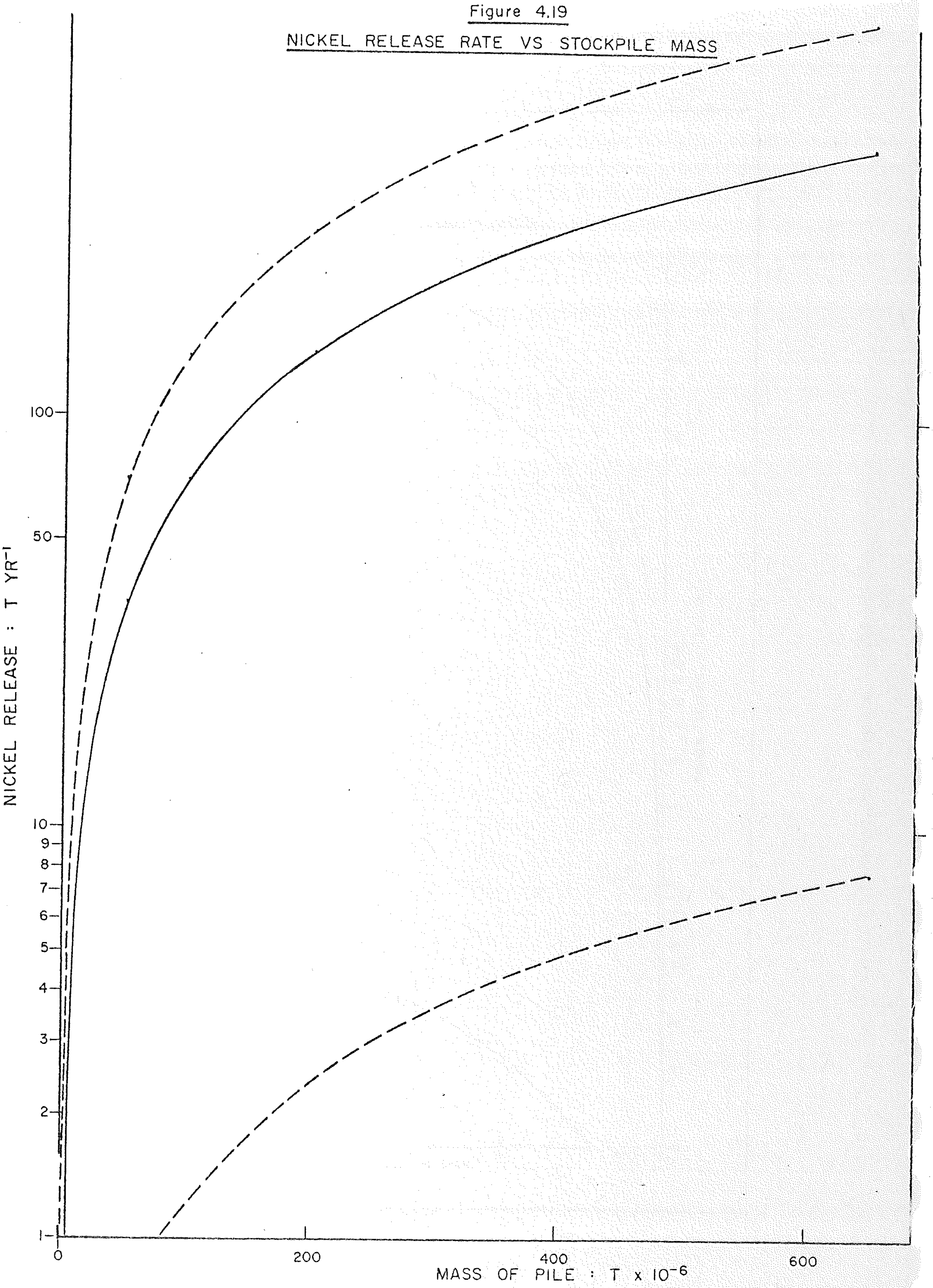


Figure 4.20

COBALT RELEASE RATE VS STOCKPILE MASS

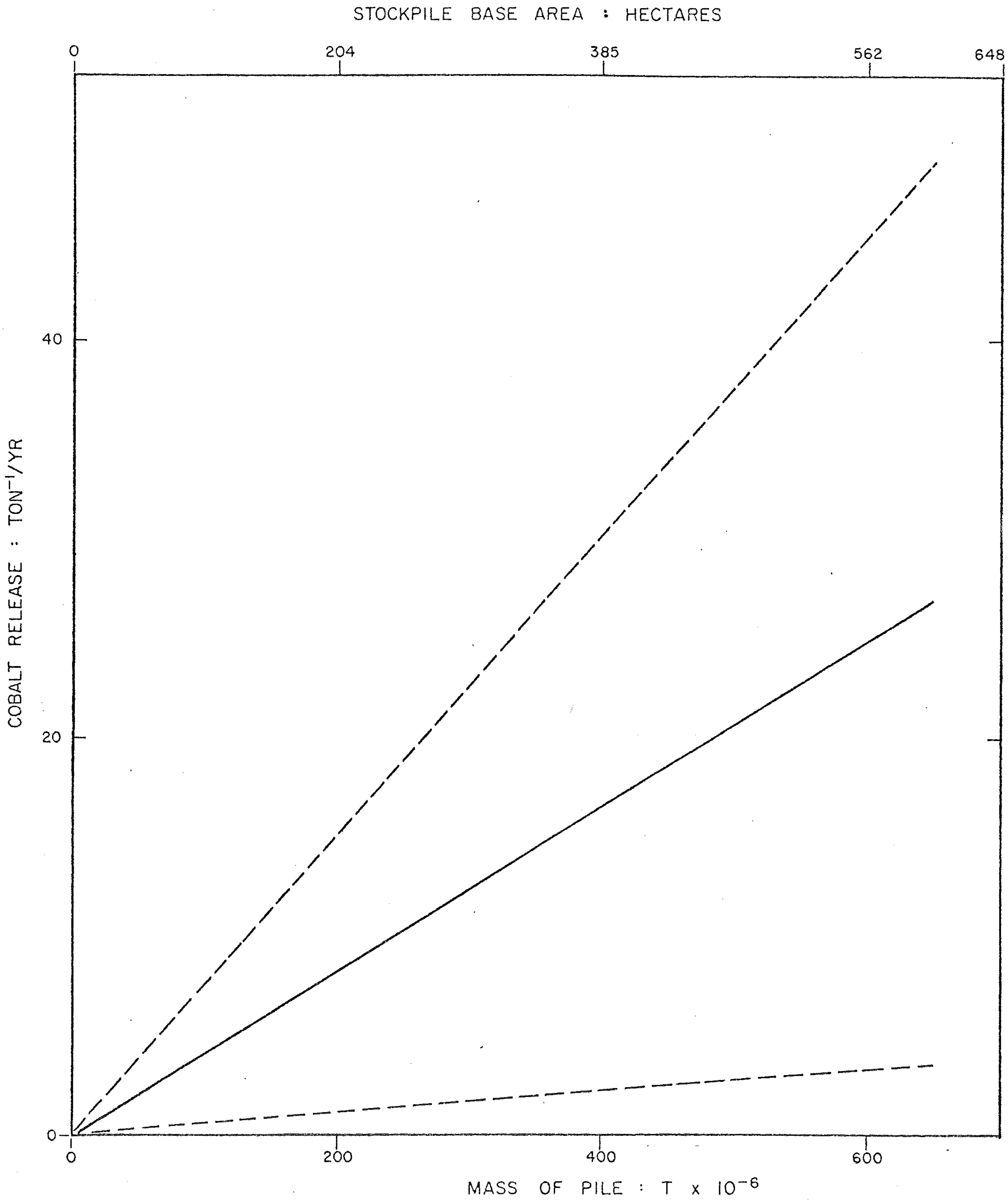


Figure 4.21

ZINC RELEASE RATE VS STOCKPILE MASS

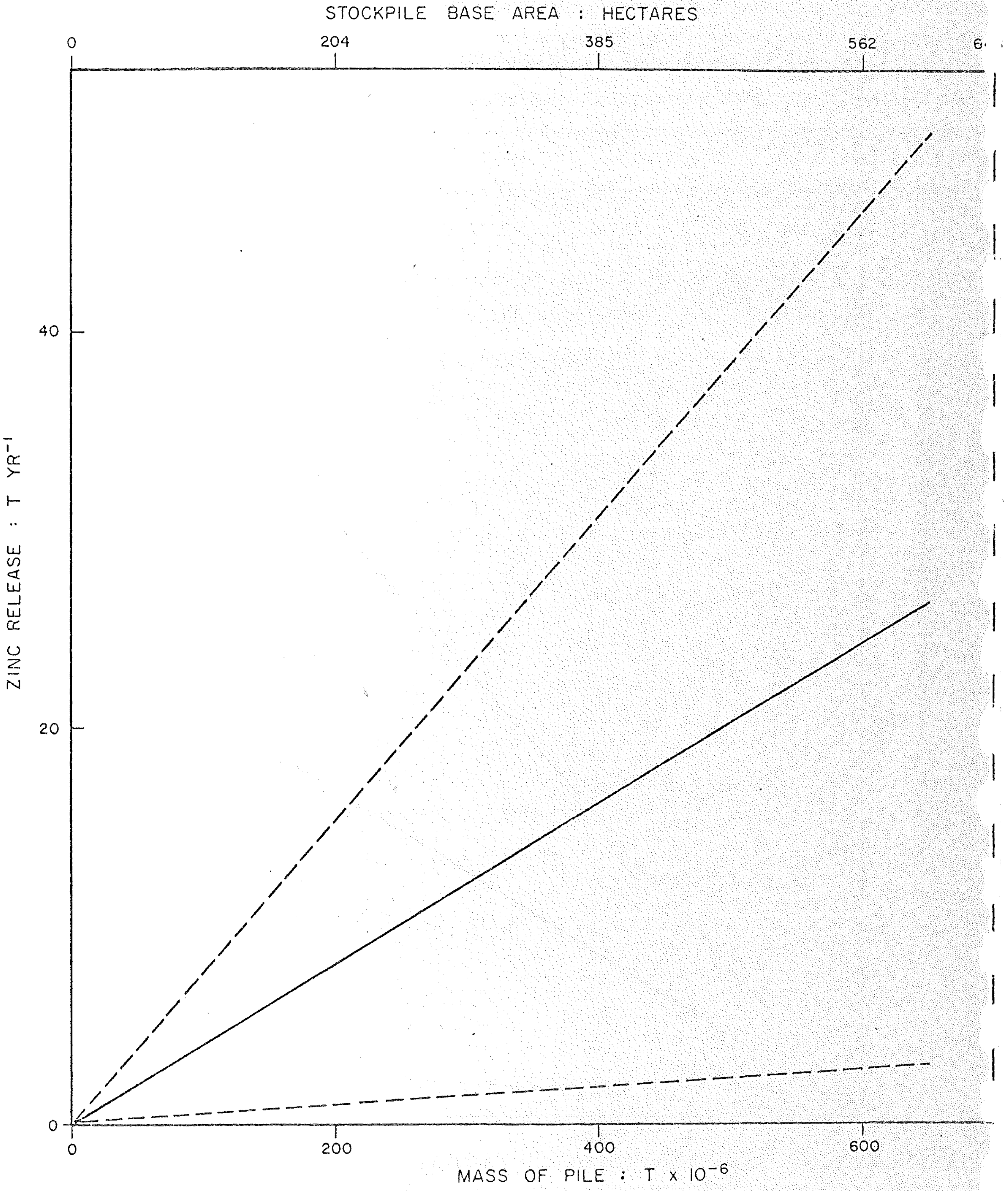


TABLE 4.11

STOCKPILE MODEL LEACHATES

PARAMETER	MODEL I	MODEL II
T(^{o}C)	6.8(13)	1.8(6)
DOC	20.9(13)	18.8(8)
Alk as $CaC0_3$	137(13)	79.5(7)
pH:(-log H^+)	7.2(13)	6.98(7)
SC(umho cm^{-1})	2020(12)	3250(8)
$S0_4$	1680(13)	2600(7)
Ni(T)	2.42(13)	39.8(8)
Cu(T)	0.053(13)	1.71(8)
Zn(T)	0.040(6)	2.40(3)
Co(T)	0.029(3)	2.40(3)
Fe(T)	0.208(13)	7.20(9)
Ca(T)	200 (13)	346 (6)
Mg(T)	123 (4)	268 (6)
Cl	41.3(12)	56.7(8)
Mn(T)	2.85(7)	11.2(8)
Cr	N.D.(0)	0.123(1)

N.D. Not Determined

Numbers in parentheses represent number of values considered
(T) = total metal analysis
SC = specific conductance

Values from Seep 3 and Seep 1 were chosen to represent leachate having relatively high metals concentrations.

Table 4.12 shows the range of values in EM-8 and Seep 1 and Seep 3 from which the model concentrations were selected. Maximum trace metal concentrations were selected in order to simulate the worst observed case.

The selection of maximum concentrations may seem to be unrealistic. The correlation coefficients shown in Table 4.5 illustrated that the concentration of trace metals tend to increase and decrease in a similiar fashion. Therefore, in leachate with high concentrations of nickel there will likely be high concentrations of copper, cobalt and zinc. From a biological impact standpoint, the aquatic system must be able to survive exposure to the maximum toxicant level that could occur. Comparison of the model leachates (Table 4.11) (maximum concentrations) with the average values, shows that the worst case values are not drastically different from the average concentrations.

Even though maximum trace metal concentrations were selected, there is no guarantee that this will provide an ultimate upper limit for stockpile runoff. Recent data show that metal concentrations at EM-8 have increased significantly.

Date	Range of Nickel Concentrations (mg/1)
July 1976 through August 1977	0.58 - 2.42
7/24/78 - 9/18/78	4.6 - 7.1

Preliminary data from Amax test plots have shown that acid conditions can be generated and metal concentrations increase dramatically when this occurs. Preliminary results indicate nickel (filtered) concentrations as high as 83 mg/1.

TABLE 4.12 Average Concentrations and Range of observed values, Em-8, Seep 3, Seep 1

CONCENTRATION IN mgl^{-1} UNLESS NOTED

PARAMETER	MODEL I (Em-8)		MODEL II (Seep1,Seep3)	
	AVE	RANGE	AVE	RANGE
DOC	20.9	11.5-36.3	18.8	11.6-27.1
ALK as $CaCO_3$	137	103-178	79.5	47.4-114
pH:(-log H+)	7.20	6.50-7.65	6.98	6.45-7.15
SO_4	1260	708-1680	3620	801-5640
Ni	1.89	0.580-2.42	30.6	24.4-39.8
Cu	0.019	0.010-0.053	1.09	0.803-1.71
Zn	0.031	0.018-0.040	2.10	1.50-2.40
Co	0.021	0.016-0.029	1.77	1.00-2.40
Fe	0.131	0.084-0.208	4.73	0.710-7.20
Ca	200	64.9-301	346	284-388
Mg	123	82.0-178	268	215-288
Mn	1.30	0.680-2.85	9.74	8.41-11.2
Cl	41.3	29.2-56.5	56.7	38.5-70.4

4.1.7 Mine Termination-Abandonment

At the end of the mining operation stockpile mass has reached its ultimate maximum value. Leachate production will be at a maximum. In Table 4.13 an estimate of the length of time leaching may continue is made. The calculation is based on the data from Amax test pile FL-1. If a constant rate of reaction is assumed, enough total sulfides are contained in the pile to continue the reaction for several hundred years. This is an approximate calculation, but it indicates the long term potential problems which can result from the leaching process. The leachate source will continue past operation unless successful mitigation techniques are developed. (Continuing studies of the Amax test piles will yield information on the variation of release rates with time. It is likely that release rates will decrease with time)

TABLE 4.13 Estimate of the time to remove all the sulfide from a stockpile

Assumptions:

1. Reaction occurs at a constant rate
2. All the sulfide in the pile is available or will become available as the minerals weather.
3. The 1977 data from Amax test pile FL-1 is representative of stockpiled material
    - a. The outflow from the pile is 48% of the inflow precipitation
    - b. The collecting area of the pile is 4250 ft^2
    - c. The samples collected over the period 4/20/77-9/26/77 are representative
    - d. The total release of sulfate is represented by the median concentration X the total outflow
    - e. The samples represent the outflow from 4/15/77-9/28/77

Table 4.13 (Con't.)

Total rainfall = 25.41 inches

median SO_4 concentration = 610 mg/1

Total outflow = 122,320 liters

total mass of S removed = 25 kg

% S in rock = .6%

total mass of rock in test pile = 1766 tons

total mass of S in pile = 9630 kg

$$\text{total leaching time} = \frac{9630 \text{ kg S in pile}}{\frac{25 \text{ kg S removed}}{\text{yr}}} = 385 \text{ yr.}$$

4.2 Mine Water

4.2.1 Introduction

Mine water is any water discharged from an underground or open pit mine. There are many factors which influence the chemistry of mine water but description of these factors is limited by the amount of presently available data. The degree of influence of a particular factor is variable and may change significantly from one area to another. It does appear that mine water will be of lower quality than natural surface water in the study area.

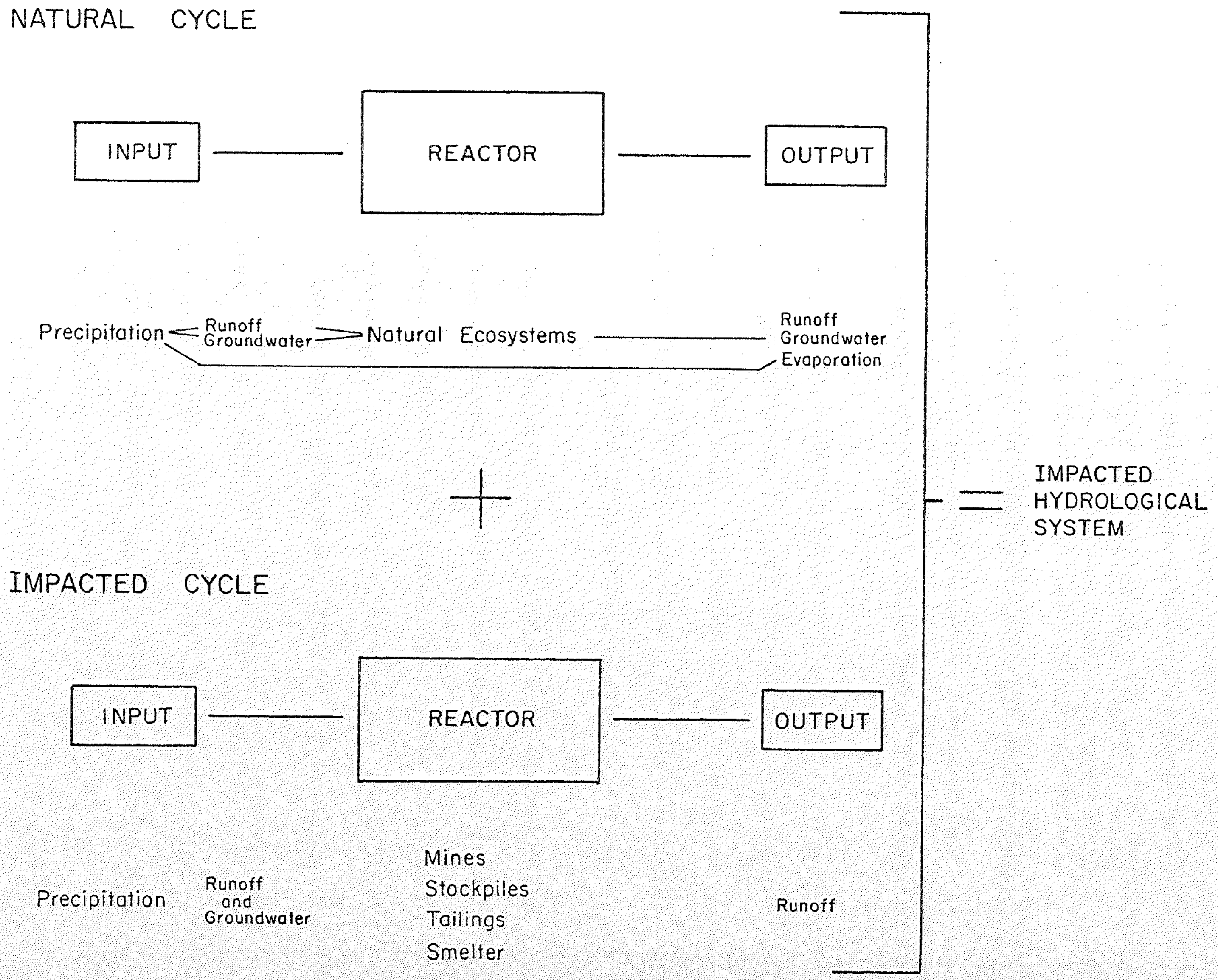
The major objective of this section is presentation of water quality models for underground and open pit mines during both operational and post operational phases. Generally, mine water is controlled during the operation of the mine but abandoned open pits can eventually fill with water and produce substantial water quality changes.

The models are based on data collected by the USGS, Amax Exploration, Erie Mining Company and the Regional Copper-Nickel Study. Estimative calculations are also employed and theoretical considerations discussed. Additional research and site specific information is required to improve the accuracy of quantity and quality predictions.

The quality of mine water is discussed in reference to the schematic presented in Figure 4.22. The inputs are discussed and chemical reactions and considerations summarized. Detailed information on the chemical reactions and factors affecting them is presented in the laboratory section. Additional information describing mining operations is available in the Mining Technical Assessment report of the Regional Copper-Nickel Study.

Figure 4.22

CONCEPTUAL FRAMEWORK FOR WATER QUALITY MODELS



4.2.2 Conceptual Model

The quality of mine water is dependent upon inputs to the mine and the chemical reaction that occur in the mine. Figure 4.23 presents a schematic model of mine water flow and the factors affecting the water quality. A schematic of the flow paths in an underground mine is presented in Figure 4.24.

4.2.2.1. Inputs

Water may enter mines under natural conditions such as seepage from bedrock or surficial materials and precipitation. Appropriation of make-up water for mining procedures such as drilling and dust suppression may also be required.

4.2.2.1.1. Bedrock Seepage

Aquifers are rock formations containing useable quantities of water. Bedrock aquifers occur in joints, fractures, leached zones and isolated pockets. (Siegal and Erickson 1978) Little flow occurs unless one of these condition exists. Some mapping of the major fractures and joint systems in the region has been completed and the preliminary indication is that the fractures are more extensive in the upper 200 or 300 feet, but some probably extend to considerable depths (Siegal and Erickson 1978). Bedrock aquifers near the ground surface are generally connected to water table aquifers in surficial materials, whereas deeper aquifers tend to be under confined conditions.

Table 4.14 lists the water-bearing characteristics of the various bedrock types. In general the water yield is low, the one exception being the

Figure 4.23

MINE WATER QUALITY : CONCEPTUAL SCHEMATIC

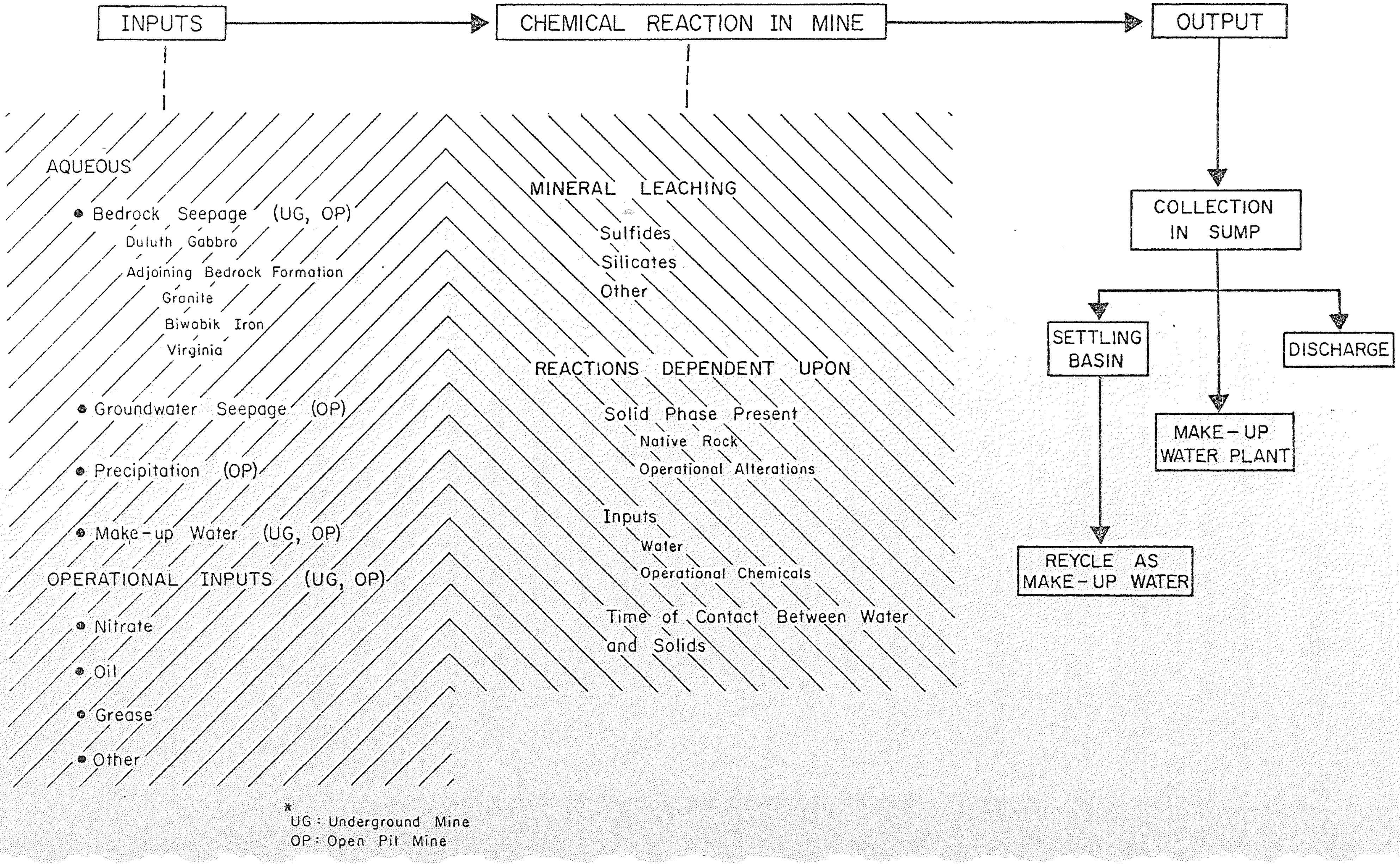


Figure 4.24

UNDERGROUND MINE WATER MODEL

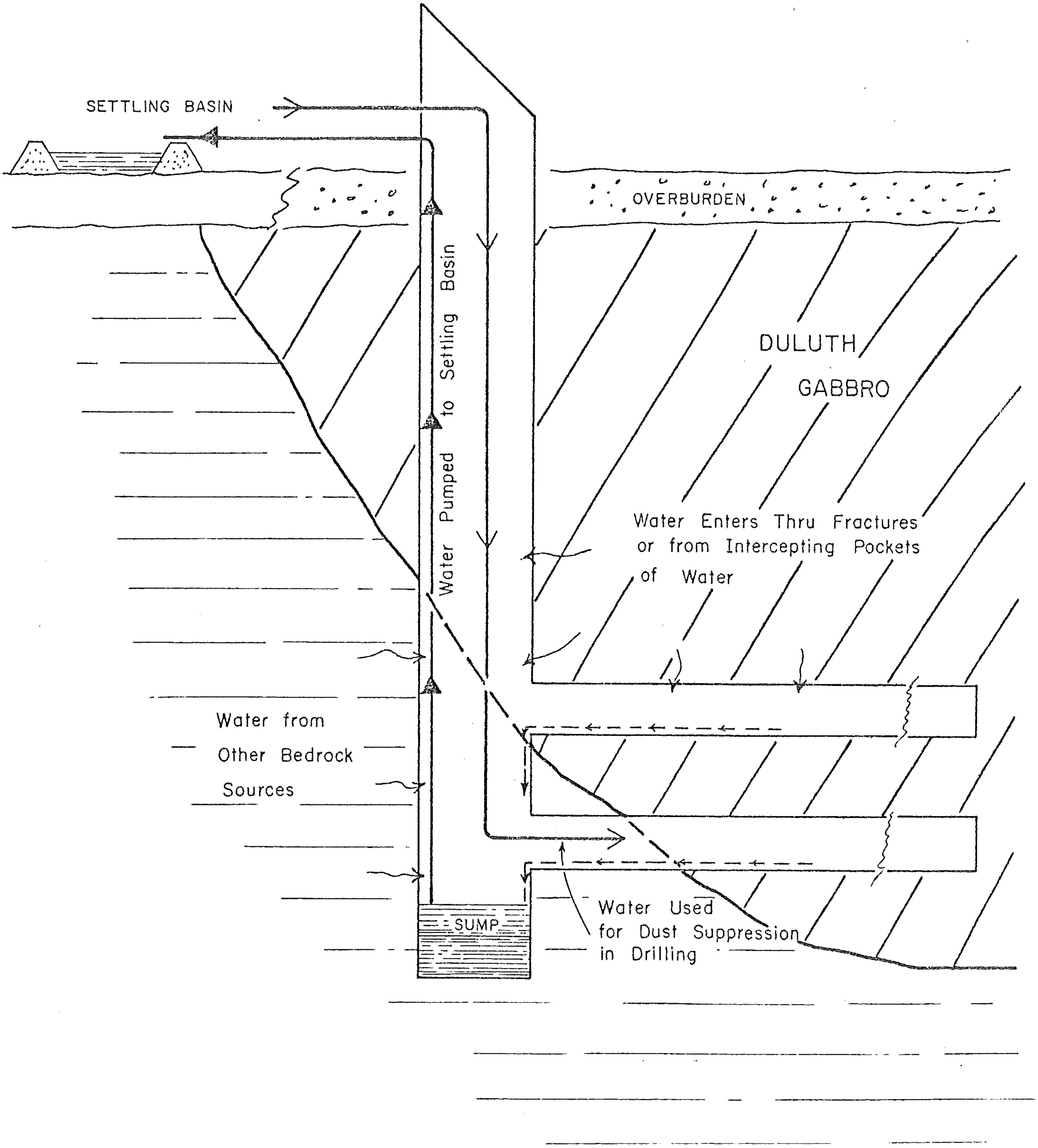


Table 4.14 Water bearing characteristics of Bedrock units in the Study Area (from Siegal and Erickson,1978)

System	Major Units	Subdivision	Estimated Max. thickness	Description	Water Supply and Water Bearing Characteristics
Pre-cambrian	Animikie Group	Duluth Complex	(?)	Largely troctolite	May yield 5-15 gal/min from fractured zones near its upper surface
		Virginia Argillite	2,000±	Thinly bedded, gray to black argilite	May yield up to 30 gal/min from fractured zones near its upper surface. Utilized for numerous domestic supplies
		Biwabik Iron-Formation	800±	Taconite-dark-colored hard dense iron-bearing silicic rock Ore-black,yellow or red, soft iron-bearing porous rock.	May yield up to 1,000 gal/min to wells in highly fractured taconite and ore. Utilized for numerous municipal and industrial supplies.
		Pokegama Quartzizite	350±	Varicolored vitreous quartize	May yield 5-15 gal/min from fractured zones near its upper surface.
		Giants Range Granite	(?)	largely granodiorite	.May yield 5-15 gal/min from fractured zones near its upper surface.

Biwabik Iron Formation in which yields can be substantial. Large quantities of water occur in this formation and the leached zone can provide a secondary porosity as high as 50 percent. This aquifer supplies water for municipal and industrial use. Prediction of seepage at a particular location is not possible due to the large variability in secondary permeability. Little is known about the permeability of the formation where it underlies the Duluth gabbro. It is possible that large quantities of bedrock water may be encountered by mines which intersect the iron formation.

Pockets of highly mineralized saline water, presumably isolated reservoirs, have been encountered in the AMAX area, where saline water was encountered in two drill holes, and three times in the exploration shaft. The origin of these saline waters is not known, but the general belief is that the pockets are relatively isolated and rare.

Data on the quality of bedrock water are limited; those available on the major constituents have been summarized by the USGS and are reproduced in Table 4.15. Table 4.16 summarizes the data on the saline water.

Although there is not enough data to perform statistical analyses, it does appear that there are differences in the major constituents among the bedrock units. Piper plots prepared by Siegal and Erickson (1978) (Figures 4.25 and 4.26) identify the major cations and anions present in the various waters. The major constituents in the gabbro samples are sodium, chloride and bicarbonate, while the water found in other bedrock formations contains predominently calcium, magnesium and bicarbonate. Bedrock water has a higher pH and mineral content than the surface water of the area (Table 4.17).

The few trace metal analyses in bedrock water that exist suggest that the

Table 4.15. Water Quality Analysis from major bedrock types in the Copper-nickel study Region. (From Seigel and Erickson, 1978)

SOURCE OF ANALYSIS	GEOLOGIC UNIT	TOTAL DEPTH OF WELL	DATE	SPECIFIC CONDUCTANCE	pH	CALCIUM	MAGNESIUM	SODIUM	POTASSIUM	BICARBONATE	SULFATE	CHLORIDE	SILICIC	TOTAL DISSOLVED SOLIDS (mg/1)
USG	gabbro	225	10/10/76	320	8.5	2.7	.1	73	.9	167	3.8	5.2	---	---
USG	gabbro	1000	10/20/76	1300	7.4	44	9.1	220	3.3	155	45	310	---	---
USG	gabbro	125	10/19/76	220	7.7	3.1	.3	48	.3	115	9.6	4.3	---	---
AMAX	gabbro	1046	2/15/77	4620	0.11	420	2.0	470	1.0	94	3.6	1500	---	---
USGS	Biwabik	398	11/ /74	380	7.4	43	22	50	23	189	41	9	18	
USGS	Biwabik	147	9/ /72	298	7.1	19	6	4.6	0.6	71	17	12	17	---
MSBOH	Biwabik	180	10-65	---	---	58	---	---	---	99	47	1.4	---	---
MSBOH	Biwabik	---	10-70	---	8.9	42	---	20	7	32	88	7.8	---	180
MDH	granite	197	8/8/75	240	8.2	93	53	7.3	0.8	207	17	1.0	---	---
USGS	granite	425	12/5/74	143	8.3	31	9.1	13.0	1.9	140	7.3	1.3	14	---
USGS	granite	147	7/8/72	672	7.5	19	6.0	4.6	0.9	71	65	7.5	13	---
USGS	granite	121	9/12/72	237	---	110	10	26	2.6	204	13.8	1.5	---	---
USGS	Virginia	90	12/3/74	745	7.8	46	66	19	4.2	523	22	1.3	19	436

Table 4.15. Water Quality Analysis from major bedrock types in the Copper-nickel study Region. (From Seigel and Erickson, 1978)

SOURCE OF ANALYSIS	GEOLOGIC UNIT	TOTAL DEPTH OF WELL	DATE	SPECIFIC CONDUCTANCE	pH	CALCIUM	MAGNESIUM	SODIUM	POTASSIUM	BICARBONATE	SULFATE	CHLORIDE	SILICIC	TOTAL DISSOLVED SOLIDS (mg/1)
USG	gabbro	225	10/10/76	320	8.5	2.7	.1	73	.9	167	3.8	5.2	---	---
USG	gabbro	1000	10/20/76	1300	7.4	44	9.1	220	3.3	155	45	310	---	---
USG	gabbro	125	10/19/76	220	7.7	3.1	.3	48	.3	115	9.6	4.3	---	---
AMAX	gabbro	1046	2/15/77	4620	0.11	420	2.0	470	1.0	94	3.6	1500	---	---
USGS	Biwabik	398	11/ /74	380	7.4	43	22	50	23	189	41	9	18	
USGS	Biwabik	147	9/ /72	298	7.1	19	6	4.6	0.6	71	17	12	17	---
MSBOH	Biwabik	180	10-65	---	---	58	---	---	---	99	47	1.4	---	---
MSBOH	Biwabik	---	10-70	---	8.9	42	---	20	7	32	88	7.8	---	180
MDH	granite	197	8/8/75	240	8.2	93	53	7.3	0.8	207	17	1.0	---	---
USGS	granite	425	12/5/74	143	8.3	31	9.1	13.0	1.9	140	7.3	1.3	14	---
USGS	granite	147	7/8/72	672	7.5	19	6.0	4.6	0.9	71	65	7.5	13	---
USGS	granite	121	9/12/72	237	---	110	10	26	2.6	204	13.8	1.5	---	---
USGS	Virginia	90	12/3/74	745	7.8	46	66	19	4.2	523	22	1.3	19	436

Table 4.16. Quality of Saline Water

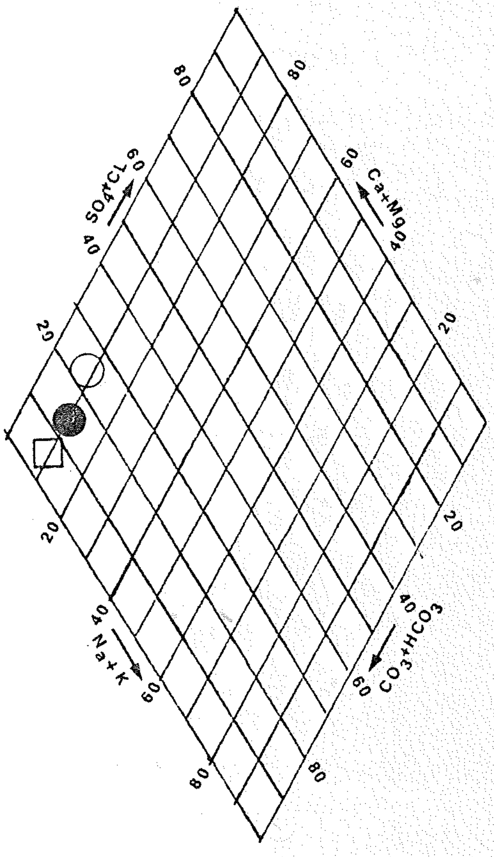
Sample Depth	Shaft Inflow (SI)						
	Shaft Floor	1046 ft		1088 ft	1194 ft		Drill Hole #303 1391 ft
	2/9/77	2/11/77	2/8/88	2/22/77	3/12/77	3/18/77	7/15/76
Acidity, MG/L as CACO3	6	2	2	2	1	1	12
Alkalinity (MO), MG/L as CACO3	144	17	18	67	17	13	6
Chloride, MG/L as CL	1200	2400	1450	2650	1100	1100	11,000
Conductivity, UMHO/CM (LAB)	5000	7000	6000	8000	3200	3500	32,000
Hardness, MG/L as CACO3	736	1780	1020	2110	506	584	12,000
pH (lab)	7.8	9.0	9.1	10.9	9.3	9.3	5.8
Sulfate, MG/L as SO4	10	2	2	6	4	2	2
Alkalinity (P), MG/L as CACO3		8	8	52		6	--
CadmiumUG/L as CD*		0.04	0.04	0.04		0.04	1.3
Cobalt, UG/L as CO*		1	2	3		2	2
Copper, UG/l as CU*		0.5	0.7	3.0		0.8	2.9
Iron, MG/l as PH*		0.05	0.05	0.05		0.05	4.9
Nickel, UG/L as NI*		0.8	0.9	5.3		1.1	3.6
Sodium, MG/L as NA		10	6	6		22	20
Zinc, UG/L as ZN*		710	480	860		474	1900
Freon Solubles, (oil), MG/		5	5	5		6	5
Barium, UG/L as BA*			3				170
Arsenic, UG/L as AS							2
Mercury, UG/l as HG							0.1
Seleniu, UG/L as SO							5
Calcium, UG/l as CA							4570

(*Filtered through 0.45 micron filter membrane)

Table 4.17 Typical Median concentrations for Study Area Streams

PARAMETER	TYPICAL MEDIAN VALUES (background)	TYPICAL MEDIAN VALUES (Impacted)
Cu (ug/1)	1-1.5 ug/1	3
Ni "	1	2
Zn "	1	2-3
Cd "	0.02	0.04
Pb "	0.5-0.7	0.5-0.7
pH	6.8-7.0	7.0-7.2
Alk mg/1 as $CaCO_3$	15-25	50-100
TOC (mg/1)	12-15	20
Ca "	6-8	16-30
Mg "	3-6	10-20
SO_4 "	5-10	40-70
Cℓ "	3-5	15-25
N "	<1 (~0.5)	1
P μg/ℓ	20-30	20-30

Figure 4.25 Piper Plot, Biwabik Iron Formation and Virginia Argillite
(from Siegal and Erickson, 1978)

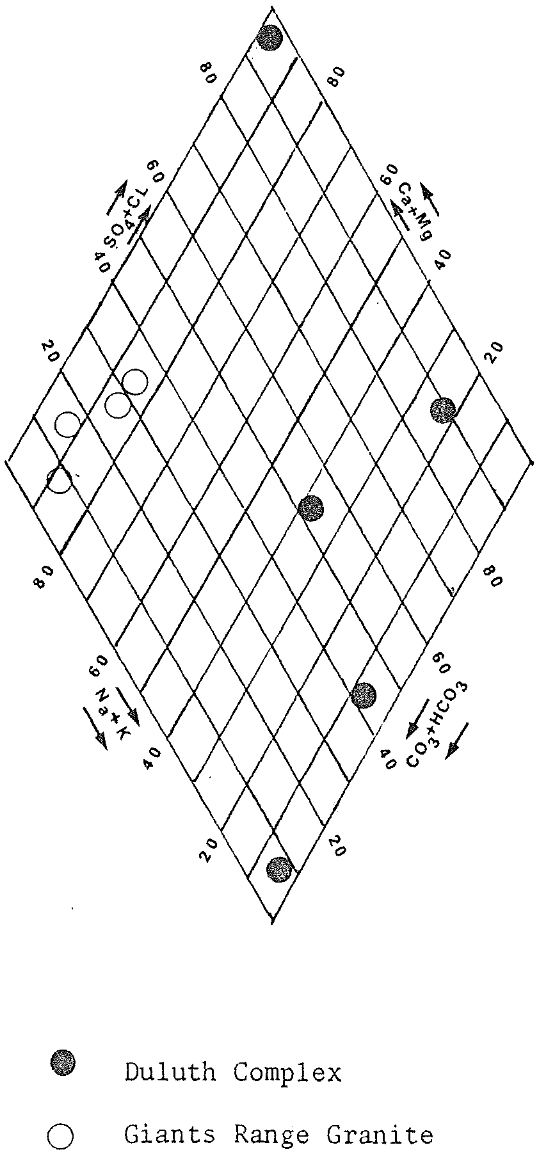


● Average concentration from municipal wells
Biwabik Iron formation

○ Biwabik Iron Formation

□ Virginia Formation

Figure 4.26 Piper Plot, Duluth Gabbro and Giants Range Granite
(from Siegal and Erickson 1978)



concentrations of dissolved copper, nickel, cadium, silver, mercury and lead are less than a few micrograms/liter (Siegal and Erickson(1978) .

Seepage from surficial materials.

The unconsolidated materials overlying bedrock are usually saturated throughout part of their thickness. They frequently yield more water than does the bedrock, though the availability of groundwater from these materials varies considerably within the study area.

The rate of seepage from surficial materials into an open pit will depend on the thickness of the surrounding soil, its permeability, the cross sectional area of flow and the hydraulic gradient. Mines which intersect buried sand and gravel deposits can receive large amounts of water. At Erie Mining Company's Dunka Pit operation, a buried valley yields up to 1000 gpm. (Siegal and Erickson, 1978).

Groundwater quality samples were collected throughout the region by the USGS; summary statistics for the major water quality parameters are shown in Table 4.18. The data indicate that, in general, the mean values for the till samples are significantly higher than those from sand and gravel aquifers (significance was determined using a t-test). Till contains more silt and fine sized material than the sand and gravel deposits, providing a larger surface area for chemical reaction and reducing permeability. The lower permeability increases the contact time between the water and the soil particles, thereby enhancing chemical reaction. Till samples also contain higher concentrations of dissolved organic carbon which can increase the rate of chemical reaction.

Table 4.18. Summary statistics for ground water quality. Concentrations in mg/l except when designated otherwise from Seigel and Erickson, 1978. Samples collected in 1976.

Constituent or Property	Samples from till aquifers					Samples from sand and gravel aquifers				
	Number samples	Maximum	Minimum	Mean	Median	Number samples	Maximum	Minimum	Mean	Median
Specific Conductance(μmho/cm)	32	1250	120	368	251	40	577	5.5	193	166
pH (unitless)	25	8.0	5.7	6.81	6.70	28	7.1	5.7	6.33	6.35
Chemical Oxygen Demand	10	870	22	198	51	38	100	0	93	18.5
Hardness (Ca,Mg)	30	637	37	173	104	40	284	26	93	71
Dissolved Calcium	31	150	6.5	38.9	22.3	40	76	6.0	20	16
Dissolved Magnesium	31	64	5.1	18.0	14.0	41	31	1.1	10.2	7.3
Dissolved Sodium	31	18	2.1	7.7	6.9	41	7.3	1.4	3.1	2.9
Dissolved Potassium	31	9.3	.1	2.7	2.1	41	3.0	0.2	1.3	1.1
Bicarbonate	30	423	45	145	120	33	392	15	95	69
Dissolved Sulfide	11	12	0	1.5	.4	17	4	0	.9	.6
Sulfate	31	450	1.8	61	11	40	35	0.7	11	6
Chloride	31	35	.4	4	1.4	40	18	0.1	4	2.2
Silica	13	37	13	20.5	18.3	21	28	10	18.6	18
Solids (residue at 180°)	13	938	97	293	187	14	284	55	148	130
Nitrate plus nitrite	11	12	0	1.5	0.4	37	10	.01	2.2	.62
Total phosphorus	13	.07	0	.006	0.001	21	.04	0	---	---
Disssolved organic carbon	22	46	2.1	18	13	31	52	0.7	11.3	6.4

The data summary in Table 4.19 indicates that trace metal concentrations in groundwater are low, but somewhat higher than the surface water values (Table 4.17). In the mineralized zone near the Duluth gabbro contact, surficial aquifers exhibit elevated aqueous concentrations of copper and nickel. (Figures 4.27 and 4.28). Some of the copper values are in the range which could produce biological effects. (A "safe" level of 10 ug/l for copper has been chosen.) (Regional Copper/Nickel Study).

4.2.2.1.2. Precipitation

Data on the quality of precipitation are limited. Available data from snow samples and rainfall collected at the AMAX site are shown in Figure 4.29. In general, concentrations are uniformly low.

4.2.2.1.3. Make-up water

Make-up water may be needed in an underground mine for dust suppression or drilling. The quantity is a function of the amount of bedrock seepage and the rate of water use. If seepage exceeds use, no additional makeup water is required. Water collected in the shaft would be pumped to a setting basin where the fine rock particles would be allowed to settle. The clarified water would then be recycled to the mine.

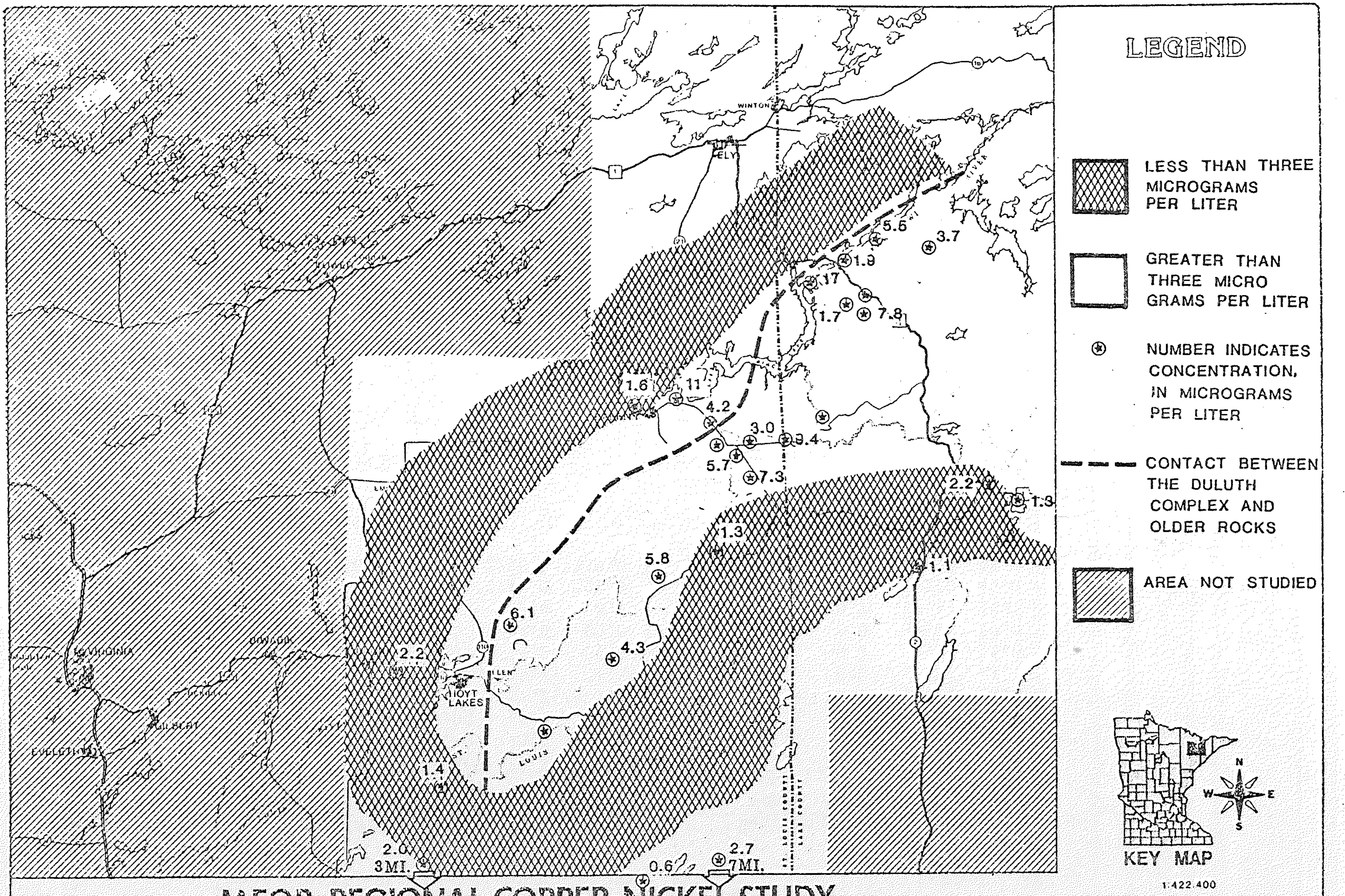
The initial quality of the make-up water is determined by its source, while the quality of the recycle water is a function of the factors discussed in the following sections.

4.2.2.1.4. Operational inputs.

Mining operations provide inputs to the mine water which include explosive residues (nitrate, oils), oils from drilling, and residues from vehicle traffic such as oil, grease and trace metals. Mining practices, such as blasting,

Table 4.19 Summary statistics for selected trace and minor metals in surficial aquifers, (concentration, in micrograms per liter) (Siegal & Erickson, 1978)

Constituent	Till Aquifers					Sand and Gravel Aquifers				
	#of samples	Maximum	Minimum	Mean	Median	#of samples	Maximum	Minimum	Mean	Median
Cadmium	29	8.4	0.00	0.8	0.3	30	1.2	0.0	0.3	0.3
Cobalt	30	28.0	.03	3.5	1.4	30	46.0	0.1	6.3	0.7
Chromium	30	5.5	0.00	0.9	0.6	31	3.2	0.0	0.6	0.5
Copper	30	190.0	0.6	11.7	3.8	30	45.0	0.2	7.2	4.2
Lead	30	6.4	0.1	1.8	1.3	31	18.0	0.0	1.9	1.1
Nickel	27	120.0	1.0	15.2	9.0	29	40.0	0.7	7.5	5.0
Aluminum	24	200.0	0.0	20.0	20.0	30	280.0	0.0	32.0	29.0
Zinc	30	170.0	3.9	27.6	8.9	30	620.0	0.7	56.1	14.1
Iron	30	3100.0	0.0	221.0	25.0	38	67000.0	0.0	5152.0	45.0
Manganese	31	7190.0	10.0	1268.0	330.0	38	26000.0	0.0	2140.0	45.0



MEQB REGIONAL COPPER-NICKEL STUDY

FIGURE 4.27 GENERAL COPPER DISTRIBUTION IN SURFICIAL AQUIFERS (from Siegel & Ericson, 1978)

(DA[illegible] FR[illegible] 10 [illegible] OF [illegible] 76 [illegible]MPL[illegible]

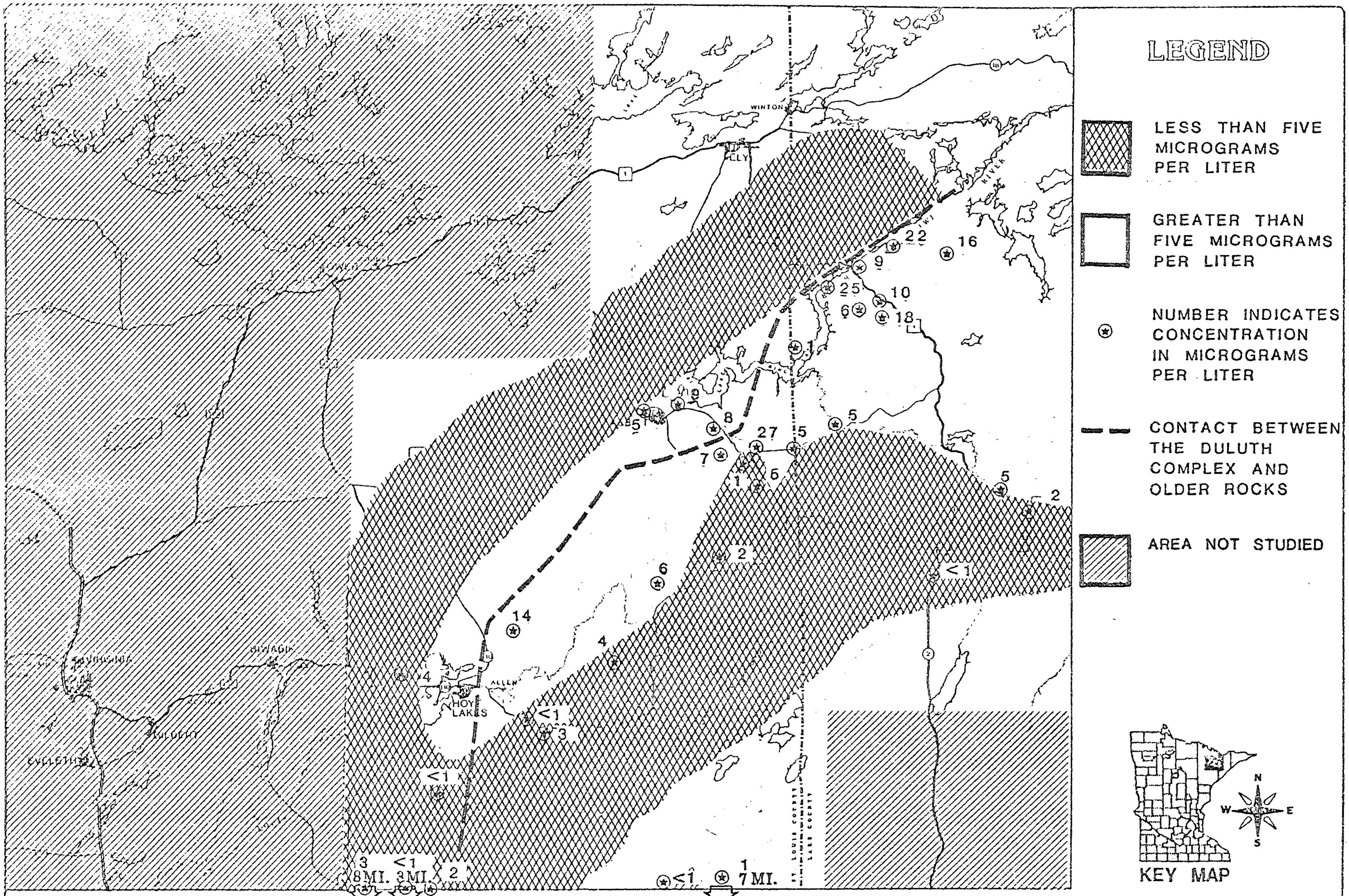


FIGURE 4.28 MEQB REGIONAL COPPER-NICKEL STUDY

GENERALIZED NICKEL DISTRIBUTION IN SURFICIAL AQUIFERS (DATA FROM 10-76 OR 4-76 SAMPLES)

(from Seigel & Ericson, 1978)

Figure 4.29

PRECIPITATION QUALITY

	SOUTHEAST SNOW STATION		NORTHWEST SNOW STATION	
	3/26/76	3/18/77	3/26/76	3/18/77
Alkalinity, mg/l as $CaCO_3$	4	1	2	1
Calcium, mg/l as Ca	13	1	5	1
Chloride, mg/l as Cℓ	1	1	1	1
Conductivity, umho/cm(lab)	25	20	20	20
Copper, μg/ℓ as CU	1.4	1.4	0.90	.7
Fluoride, mg/l as F	0.02	--	0.02	--
Iron, mg/l as Fe	0.28	.25	0.19	.10
Magnesium, mg/l as Mg	0.10	.2	0.10	.2
Nickel, ug/l as Ni	1	2	1	2
Nitrogen-Nitrate, mg/l as N	0.40	.2	0.50	.1
pH (Lab)	7.5	6.0	7.6	7.3
Phosphorous-Total, mg/l as P	0.44	.2	0.10	.1
Potassium, mg/l as K	0.16	.7	0.08	.40
Silica, mg/l as SiO_2	0.20	2.2	0.40	1.2
Sodium, mg/l as Na	0.03	.30	0.03	.40
Sulfate, mg/l as SO_4	2	1	1	1
Suspended Solids, mg/l	6	170	4	96

RAINFALL SAMPLE

	9/13/76	6/6/77
Alkalinity, mg/l as $CaCO_3$	14	
Calcium, mg/l as Ca	1	
Chloride, mg/l as Cℓ	10	
Conductivity, umho/cm (Lab)	60	
Copper, μg/ℓ as Cu*	3.0	6.4
Fluoride, mg/l as F	NS	
Iron, mg/l as Fe*	0.05	0.05
Magnesium, mg/l as Mg	1.2	
Nickel, μg/ℓ as Ni*	4	2
Nitrogen-Nitrate, mg/l as N	1.0	
pH (Lab)	6.0	
Phosphorous-Total, mg/l as P	0.35	
Potassium, mg/l as K	7.8	
Silica, mg/l as SIO_2	NS	
Sodium, mg/l as Na	0.4	
Sulfate, mg/l as SO_4	10	
Suspended solids, mg/l	82	

* filtered through 0.45 micron filter membrane.

Source: 1976 & 1977
Physical Chemical Data Summary
Water Resources Monitoring
Minnamax Project

increase the available locations for chemical reactions by increasing the specific surface of the particles in the mine walls.

Although detailed data are not available, it is likely that the concentration of operational inputs would be higher in the underground mine than the open pit. The enclosed area should retain a higher percentage of the residues, and in general, a smaller volume of water would be available for dilution. An indication of this phenomenon is illustrated, in Table 4.20 in which the nitrate content of the samples from Amax's main basin is significantly higher than that of the samples collected from nearby open pit mines. (This difference could also result from different blasting techniques).

4.2.2.2. Chemical reactions in mines

The potential for leaching exists whenever water contacts a mineral phase, the net result being release of metals to solution. Metals such as calcium and magnesium , associated with silicate minerals, as well as those associated with sulfide minerals (copper, nickel, cobalt, and zinc) are released due to leaching.

The extent of leaching is dependent upon the solid and aqueous phase compositions and the time of contact between phases.

> Leaching of given component increases with decreasing particle size and increasing percent composition of the component in the solid phase. Aqueous conditions of increasing acidity, dissolved oxygen, complexing ligand concentration, ionic strength and temperature enhance the leaching process as does increased time of contact.

Leaching is likely to be more significant in the open pit operation than in the underground mine since a greater surface area will be exposed in the open pit. This area includes not only the wall and the

Table 4.20

Nitrate concentrations (NO_3 - N in mg/l)

site	number of samples	dates	concentration range	median value
Amax's Main Basin	12	1/77 - 12/77	10-112	30
Open Pit Taconite*	3	1975 - 1976	11.2-23.0	15.3 (average)

*composite of pit samples collected at Reserve Mining Company's Peter Mitchell pit, Erie Mining Company's Dunka Pit and Eveleth Taconite Company's Thunderbird Pit.

floor of the pit, but also the area contributed by all the fine particles and rock dust within the pit. This material will be subject to all the processes which tend to increase leaching; wet-dry cycles, freeze-thaw cycles, and a continual supply of water (via precipitation) to transport reaction products.

In contrast, the underground mine has much less exposed surface area and its environment is more uniform. Parts of the mine may be totally dry, so there would be no water to transport products from the rock surface. (If the sulfide concentration in the rock is high, the acid that is formed on the rock surface can adsorb water from the air. Water can be adsorbed to the point where the rock surface is wet and reaction products are removed as water drips off the surface.) (Smith and Shumate 1976).

4.2.2.3. Summary of inputs and chemical reactions

The net effect of inputs and chemical reactions determines the final quality of the mine water. In the schematic shown in Figure 4.23, mine water is collected in the sump and is either recycled or discharged. It is impossible to predict the actual concentration in a given mine water even on a site specific proposal. Despite more detailed information, certain factors such as the quantity and quality of bedrock water encountered will be impossible to predict accurately. With the data available some qualified generalizations can be made. The USGS has divided the region into seven physiographic regions (Figure 4.30) with the major potential for open pit mines in regions A and C. They predict that groundwater discharge into open pit mines would be small in region A (shallow bedrock-moraine area), but that in region C (the Embarrass-Dunka sand plain) significant discharges (up to 3,000 gpm depending in the cross sectional area available for flow) could occur. It is likely that this water will have copper and nickel contents of 5-20 ug/l (Figures 4.27 and 4.28).

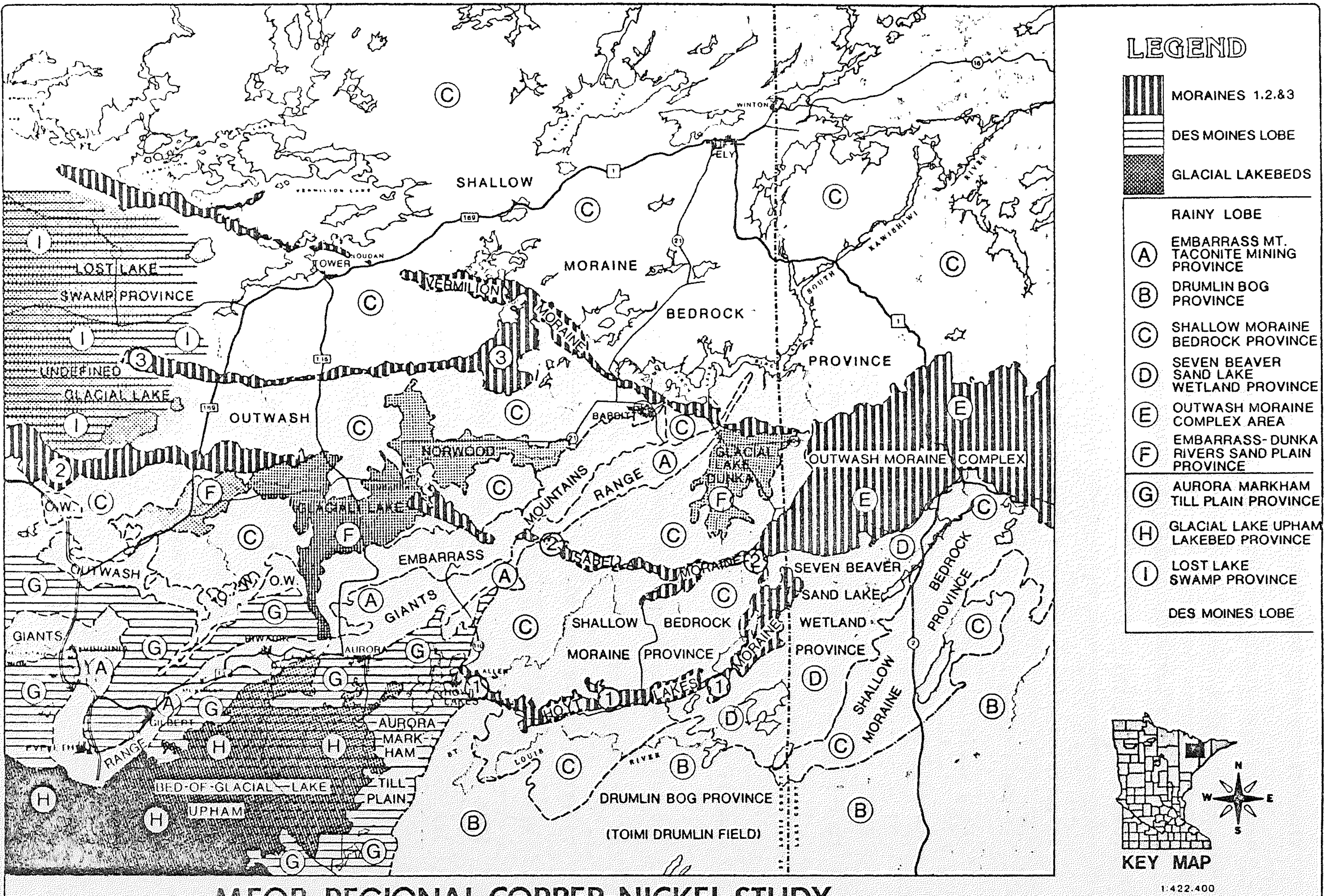


FIGURE 4.30 **MEQB REGIONAL COPPER-NICKEL STUDY**

PHYSIOGRAPHIC PROVINCES & GLACIAL FEATURES (from Siegal & Eriscon, 1978)

Bedrock water is more likely to be encountered in areas which adjoin the Biwabik formation than either the granite or the Virginia formation (Figure 4.31). Most of the fracture zones are less than 200-300 feet deep and there are limited data on permeabilities at greater depths. Bedrock water will likely have elevated levels of dissolved solids alkalinity and pH but contain low levels of trace metals.

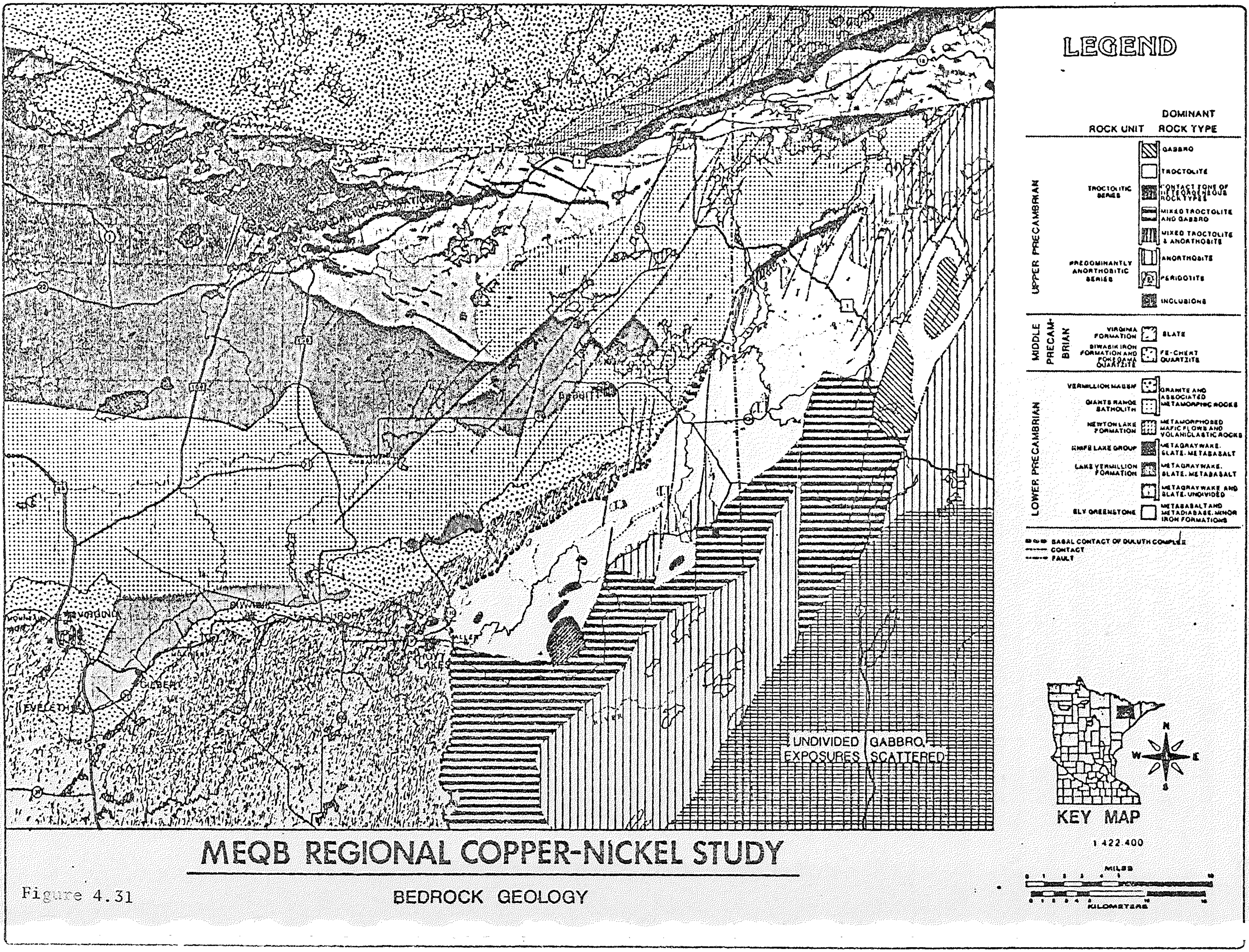
The mining process itself will produce changes in water quality, including increased levels of dissolved solids, nitrates, oil and grease.

The oxidation of the exposed sulfide minerals on mine surfaces will add trace metals to the mine water. The extent of this metal addition will depend on many factors. Some of the more important ones are the exposed surface area, concentration of sulfide minerals in the rock and the availability of water for the transport of the reaction products.

4.2.3. Model mine water

4.2.3.1. Underground mine

In an attempt to summarize the effect of the various factors affecting mine water quality and to consider potential environmental impacts, "model" mine waters are presented. The data available to produce model concentrations are limited. For an underground operation the only data available are from the Amax area. While this operation is an actual copper-nickel exploration project several unexpected occurrences have greatly influenced the water quality data. The first, which has already been mentioned, is the encounter of highly mineralized saline water. The second may have been a result of the saline water. To prevent loose rock from falling down the shaft, the shaft walls were covered with a galvanized mesh; the saline water dripping down the shaft walls has accelerated corrosion of this mesh and as a result, high levels of zinc were found in the mine water. However, data from the Amax leaching test piles does show measurable zinc release.



MEQB REGIONAL COPPER-NICKEL STUDY

BEDROCK GEOLOGY

Figure 4.31

It is impossible to predict at this time how representative the Amax situation is of the entire region. A model based on this situation may tend to overestimate the average conditions, but there is no guarantee that it is a worst case. The data from 1977 for the main settling basin were used as the basis of the model. Exploration activities continued throughout the entire year and although some runoff from test plots was added to the basin, most of the water was from the mine.

The main basin is comparable to the sump in Figure 4.23; its quality is the result of the various factors which influence mine water quality (Table 4.21) The model concentrations are shown in Table 4.22. With the limited data it is difficult to determine the changes in the input water although the data are consistent with the general concepts. Increases in trace metals, sulfate, nitrate and ammonia are observed in the main basin. (Unfortunately, the only data on nitrate in bedrock water are from an artesian drill hole at Amax which was sampled semiannually in 1976 and 1977. All samples had nitrate < 0.1 mg/l).

4.2.3.2. Open pit

The sources of data are more limited for the open pit model than for the underground mine, the best available data coming from Erie Mining Company's Dunka pit (Table 4.23). Even though this is a taconite operation, part of its east wall is exposed gabbro. (The situation at the Dunka pit is discussed in more detail in the introduction.) As discussed previously, this mine receives a large groundwater discharge which tends to dilute the chemical concentrations in the mine water. The mine also has less exposed gabbro than an actual copper-nickel operation so it is likely that this model represents the lower end of the range of open pit mine water quality. As the amount of exposed sulfide increases, and the amount of diluting groundwater and bedrock seepage decreases, aqueous chemical concentrations will

Table 4.21
Factors Influencing Mine Water Quality Model

Input ~~wat~~water + Processes = Output Water

Input water

Bedrock Water

1. Nonsaline (1976)
   Depth 147 ft.

pH	10.0
alkalinity (mg/l as $CaCO_3$)	82
specific conductance (umho/cm)	800
sulfate (mg/l)	12
chloride (mg/l)	161
copper (mg/l)	.0012
nickel (mg/l)	.010
cobalt (mg/l)	.001
zinc (mg/l)	.005

2. Saline (1977) average
   Depth 1046(2), 1088(1), 1194(2)

	median	range	n
pH	9.3	9.0-10.9	5
alkalinity	17	13-67	5
specific conductance	6000	3200-8000	5
sulfate	2	2-6	5
chloride	1450	1100-2650	5
copper	.0075	.0005-.003	4
nickel	.008	.006-.022	4
cobalt	.002	.001-.003	4
zinc	.005	.005-.006	4

* Numbers in parantheses refer to number of samples collected at that depth n = number of samples

+ Processes

→ Weathering Mining →

= Output Water

Main Basin-1977 median values

	median	range	n
pH	7.9	6.5-10.7	12
alkalinity	44	29-190	12
specific conductance	4700	3500-10,000	12
sulfate	59	20-420	12
chloride	1575	1190-9100	12
copper	.012	.0064-.043	12
nickel	.068	.015-.136	12
cobalt	.003	.002-.028	4
zinc	.034	.016-.740	12
nitrate-N	32	10-112	12
ammonia-N	9.8	4.9-47	4
oil	1	.5-2	5
cadmium ug/l	.28	.06-.44	4
lead ug/l	4	1.3-4	12
arsenic ug/l	7	5-10	4
silver ug/l	.25	.04-1.1	4
chromium ug/l	8.0	.6-32	4
mercury ug/l	.15	.1-.6	4
selenium ug/l	1	1-7	4

Table 4.22 Underground mine water quality model

pH	7.9
Alkalinity (mg/l as $CaCO_3$)	44
Specific conductance (mg/l as Ca)	4700
Sulfate	59
Chloride	1575
copper	.012
nickel	.068
cobalt	.003
zinc	.034
nitrate-N	.31
ammonia-N	9.8
oil	1
cadmium ug/l	.28
lead ug/l	4
arsenic ug/l	7
silver ug/l	.25
chromium ug/l	8.0
mercury ug/l	.15
selenium ug/l	1

Table 4.23 Mine Water Quality - Open Pit Taconite Operations

Parameter	Dunka Pit				Other[1]
	South Pit(011 Discharge)		North Pit(012 Discharge)		(Reserve, Eveleth, and Erie)
	conc. (mg/l) *	range	conc. (mg/l)	range	conc(mg/l)
pH	7.9	7.2-8.3	7.9	6.9-8.4	7.92
sulfate	89	22-480	274	140-400	150
copper,filtered	.005	.002- .05[+] (.014)	.005	.002- .05[+] (.019)	.00055
nickel,filtered	.009	.002- .05[+] (.013)	.009	.002- .05[+] (.009)	
Alkalinity					89
chloride					31
nitrate-N					15.3
zinc, total					.0035
cadmium, total					.00004
arsenic, total					.035
lead, total					.00025
silver, total					.00004

(* average of medians for 1975,76,77)

([+] Maximum is a detection limit, maximum measurement is shown in parentheses)

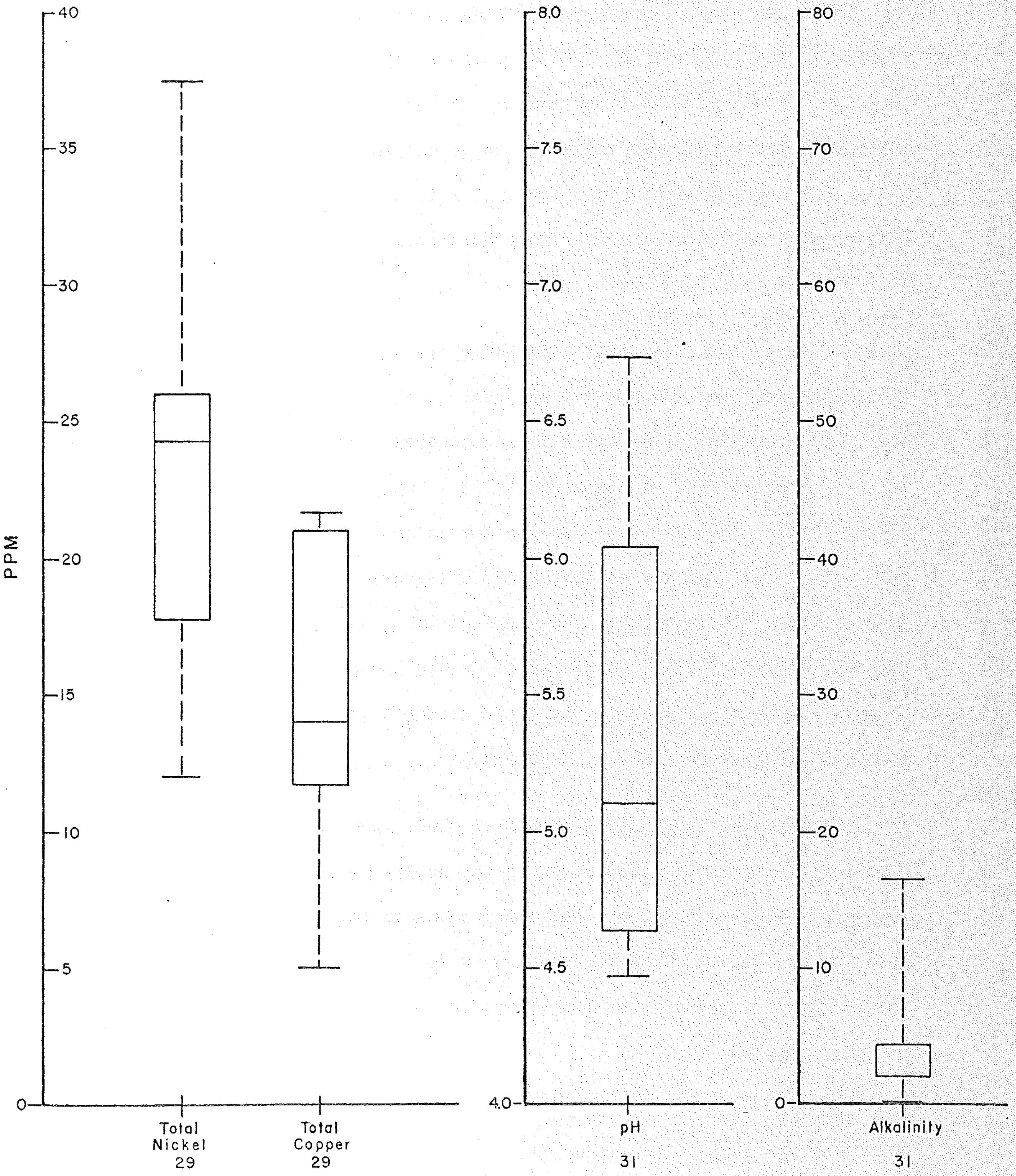
([1] based on single value from Reserve pit) increase. An extreme example of this is the U.S. Steel bulk sample site which is a small (100' long x 50' wide x 10' deep) abandoned pit that has filled with rain and surface runoff. Due to its small size, the surface area to volume ratio is much larger than in an operating mine. Some of the field data collected in 1977 are summarized in Figure 4.32, illustrating the low pH and alkalinity and elevated trace metal concentrations. This water was bioassayed and shown to be extremely toxic. (Lind, 1978) Conditions approximating those found at this site could exist at water collecting sumps in open pits. More detailed information on this site will be available in a future report.

Actual open pit mine water will probably lie somewhere between that at Erie Mining Company's Dunka Pit and that at the U.S. Steel site. If highly mineralized saline water is encountered, the water could have much higher concentrations of dissolved solids than predicted by either of the cases. All of the available data on the saline water indicate that trace metal concentrations are on the order of several micrograms per liter (Table 4.16). The effect of this type of water on the dissolution of the sulfide minerals in the pit walls is not known. (Laboratory results (Chapter 3) indicate that as the ionic strength of the solution increased, a slight increase in leaching occurred.)

An important concern is the final water quality in an abandoned pit. Since precipitation exceeds evaporation in the study area an abandoned pit can eventually fill with water. The water level in the pit will rise to the level of the water in the surrounding surficial materials and can then seep into the regional groundwater system and eventually to the streams and lakes of the region.

Figure 4.32

Water Quality Data at the U. S. Steel Site



The critical factors determining the rate at which a pit fills are the rates of surficial and bedrock water seepage which, as mentioned previously, are difficult to estimate. For the 20 x 10^6 mtpy model open pit, the estimate of filling time, assuming a seepage rate into the pit of 300 gpm, is 300 years. (Hewett, 1980)

The final water quality of the abandoned pit will be a function of the water sources, pit size, the composition of the pit walls and the floor, and the total surface area available for leaching. The total surface area includes the degree of fracture in the pit walls, since water would be able to contact minerals in these regions.

One method of estimating an ultimate concentration is to assume that all of the metal remaining in the pit walls to a fixed depth dissolves. All metals that dissolve are assumed to remain in solution, yielding a maximum concentration. An example is shown in Table 4.24.

In order to maintain all the copper in solution the pH must be less than 5.5. If significant amounts of water seep into the pit, and/or residual sulfide content in the pit walls is low, the pH will probably be closer to neutral (6-8, see Table 4.25). Even if a neutral pH is maintained in the pit, nickel concentrations may exceed biological concern levels.

The results in Table 4.24 are useful since they indicate that there may be enough metal left in the pit wall to produce potential water quality problems. Additional research is needed before accurate water quality predictions can be made.

Table 4.24 Open pit Quality

Aqeuous Elemental Concentration as a Function of Water Depth in Pit

	Concentrations in mg/1					
Water Depth (ft)	10	50	100	200	500	900
Cu (3)*	100	21	11	6.1	3.2	2.2
Ni (0.69)	23	4.8	2.5	1.4	0.73	0.52
Co (0.06)	2.0	0.42	0.22	0.12	0.063	0.045
Zn (0.078)	2.6	0.54	0.29	0.16	0.082	0.058

Values in parentheses represent Cr, mg cm^{-3} from waste rock model by Stevenson.

Data used for calculations

Final Concentration is function of

1) Concentration in rock, Cr, mg/cm^3

2) Depth of reactive zone, dr_z, cm

3) Surface area to volume ratio

Pit dimensions

$l = 4780' = 1.46 \times 10^5$ cm

$w = 1660' = 5.06 \times 10^4$ cm

$hmax = 900' = 2.75 \times 10^4$ cm

Density of gabbro = 3g cm^{-3}

$d_{rz} = 10$ cm

* copper can attain these concentrations only if the pH is low. For example, to maintain a copper concentration of 2.2 mg/1, the pH must be less than 5.5.

Table 4.25 Redeql 2 Primary Distribution, Open Pit;pe=8, alkalinity 10 mg/l as $CaCO_3$; 14 mg/l $SO_4^=$

	Values as percent of input									
pH	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5
Cu:2.2mg/l										
Cu^{2+}	97.8	97.7	97.6	96.9	83.3	11.4	1.7			
OH^-				0.6	3.1	2.9	3.8	6.1	10.5	18.5
$CO_3^=$					0.9					
$SO_4^=$	2.2	2.2	2.2	2.2	1.9					
Cu_2S										
$Cu(OH)_2CO_3$				10.3	10.8	84.9	94.1	93.5	89.4	81.4
$Cu(OH)_2$										
Ni: 0.52 mg/l										
Ni^{2+}	97.8	97.8	97.7	97.6	97.4	97.0	96.1	93.5	86.3	69.7
OH^-									1.1	3.0
$CO_3^=$						0.7	1.7	4.1	10.7	25.8
$SO_4^=$	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.0	1.9	1.5
NiS										
$Ni(OH)_2$										
Co:0.045mg/l										
Co^{2+}	96.5	96.5	96.5	96.4	96.2	95.7	94.7	91.7	57.5	18.2
OH^-							0.6	2.0	4.1	4.8
$CO_3^=$						0.6	1.3	3.2	5.6	5.3
$SO_4^=$	3.5	3.5	3.5	3.5	3.5	3.5	3.4	3.2	2.0	0.6
CoS										
$CoCO_3$									30.7	71.1
Zn:0.058mg/l										
Zn^{2+}	97.8	97.8	97.7	97.7	97.4	97.0	95.7	91.0	73.0	30.8
OH^-							1.2	4.5	19.8	61.3
$CO_3^=$							1.0	2.5	5.7	7.2
$SO_4^=$	2.2	2.2	2.2	2.2	2.2	2.2	2.1	2.0	1.6	0.7
ZnS										
$Zn(OH)_2$										

4.2.4. Summary

The Amax shaft is the only source of underground water quality data and probably represents a worse than average case but not necessarily the worst case.

The water quality from the Dunka pit is probably better than that from an average open pit operation, while the U.S. Steel case represents a worse than average case.

There are many uncertainties in the development of the model mine waters. Control and careful monitoring of mine waters is recommended.

4.3 Tailings

Tailings basin have historically been a source of water quality problems, particularly in sulfide mining operations (Hawley, 1972). Large quanitities of unwanted sulfides (iron sulfides) are often present in the tailings providing conditions conducive to the formation of acid seepage containing high concentrations of trace metals.

This section:

1) presents factors affecting the quality of tailings basin discharge water,
2) presents a model of tailings basin water quality,
3) discusses the potential quality of tailings basin seepage and discharge,
4) discusses post operational water quality of discharge.

It is assumed that the tailings basin is the receiving area for various waste water and make-up water streams. A closed system operation (as recommended by Kealy et al., 1972) is presented. In closed system operations water is recycled from the tailings basin to the mill complex, the tailings basin acting as a reservoir and settling basin. In accord with the closed system concept, the tailings basin and mill are discussed jointly as the tailings basin-mill system.

Water leaves the tailings basin by three principle routes:

discharge or overflow of water in the basin,
seepage through the dams, and
deep seepage to the groundwater system.

(Discharge may also occur due to accidental pipe leakage. If a break occurs in the line from mill to the basin, the water quality is that of mill water.) The factors affecting the water quality of discharge are the inputs to the tailings basin-mill system and chemical reactions which occur in the system and along discharge flow paths. A flow diagram for the system is presented in Figure 4.3.3.

4.3.1. Input

4.3.1.1. Precipitation

The amount of precipitation collected in the basin is a function of basin size, therefore dependent upon design. It is possible the amount of precipitation that enters the basin may initially be small and reach a maximum when the basin reaches its ultimate size. The operational dimensions used in this section represent projected sizes at the end of mining operations.

In general, the rainfall in the study area tends to be acidic ($pH < 7$) with low concentrations of all constituents.

4.3.1.2. Collected runoff

The specific runoff components and the amounts of runoff that are collected will depend on the water management plan for the mining operation. Table 4.26 lists the potential components. For most of the Minnesota taconite operations these components are not collected directly, although some indirect collection occurs (Eveleth Taconite, Erie Mining Company) "Indirect Collection" refers to a situation in which mine water is discharged into a natural water course upstream from the point at which the company appropriates its make-up water. This does not provide complete runoff collection as some of the discharge remains in the natural water course. One method of control during operation is collection of mining impacted runoff for use as make-up water (Hewett, 1979).

Runoff components include stockpiles, the plant site, mine dewatering and undisturbed watershed areas. Since the amount of runoff generated by

Figure 4.33

TAILINGS BASIN FLOW DIAGRAM

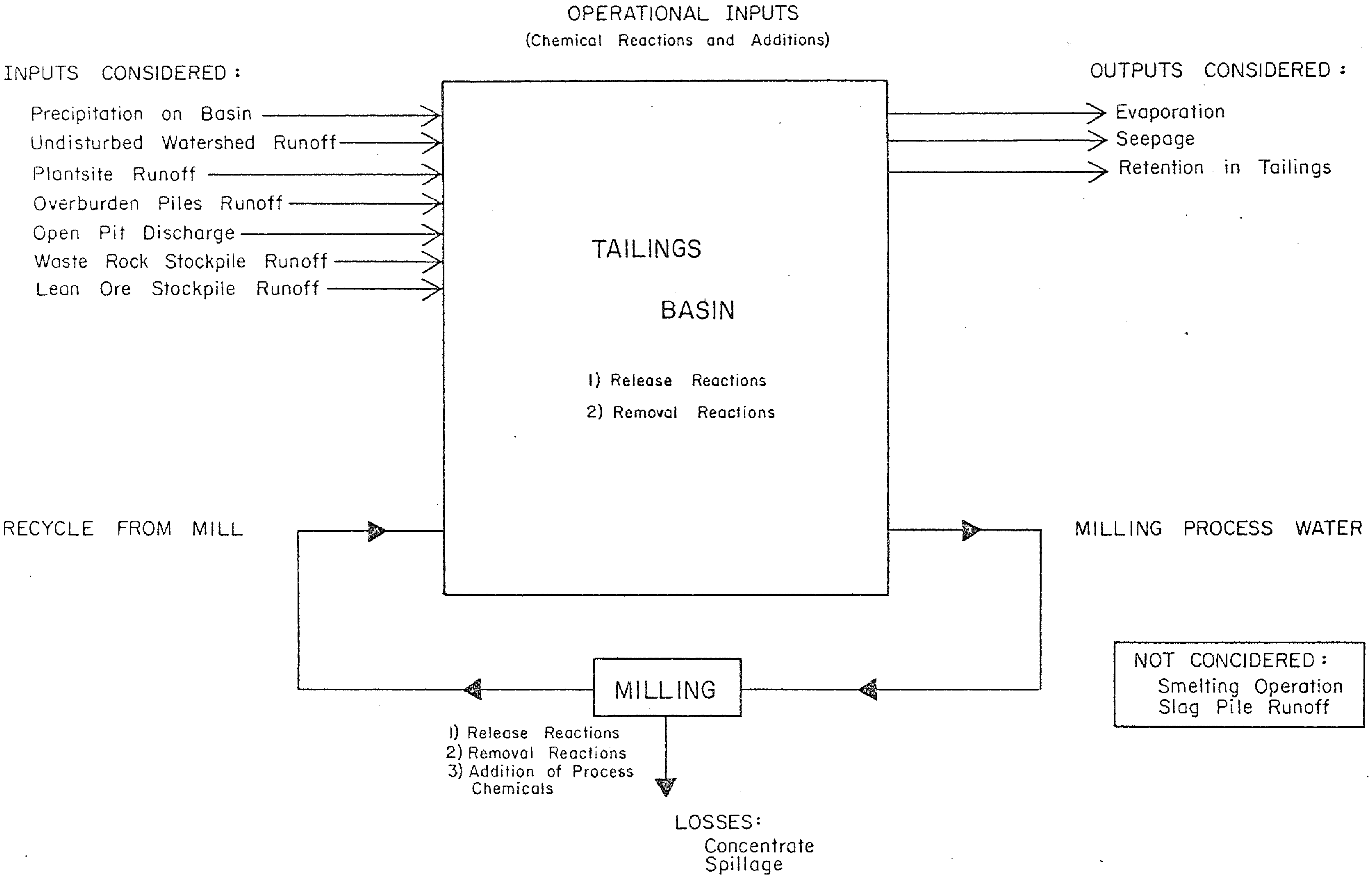


Table 4.26

Runoff Components

- Runoff from stockpile areas
- Runoff from plant site
- Mine dewatering
- Runoff from undisturbed watershed

each source is a function of the source area, the volume of runoff will initially be small and reach a maximum sometime prior to the end of mining operations. Since the quality of the pit water and stockpile runoff is poor (see section on stockpiles and mine water), the worst case situation will occur when runoff is at a maximum. Table 4.27 lists the volume of runoff for an average year of precipitation for the 20 x 10^6 mtpy open pit mine model, assuming maximum source areas.

The quality of stockpile runoff and mine water is discussed in the preceeding sections; based on the best available information, uncontrolled discharge of either of these components would produce environmental problems. (Lind, 1978). Model I and II leachate (refer to section on stockpiles) are used to represent the concentrations in the waste rock and lean ore stockpile runoff, respectively, with the U.S. Steel bulk sample site (Model A) and the Erie Mining Company's Dunka Pit (Model B) used to provide a wide range concentration for the open pit runoff (refer to section on mine water).

> If large amounts of saline water are encountered in the mine, and pumped to the basin, chloride concentrations in the basin will increase.
>
> Since it is impossible to predict if, when, or how much saline water may be encountered, chloride concentration in the basin must be monitored and treatment applied if an acceptable concentration level is exceeded.

Data on overburden pile runoff are limited and plant runoff data for the type of operation that might occur in Minnesota do not exist. Since it is likely that water associated with these sources will contain concentrations above those found in the natural waters of the study area, they will be included as part of the collected runoff.

If all the runoff is collected and mixed, and no chemical removal reactions (e.g., precipitation) occur, the resulting water quality can be

Table 4.27 Runoff Components volumes (Average year of precipitation 20×10^6 mtpy open pit mine model)

Source	Volume+ x 10^{-6} (ℓ/yr.)
Plant site	880
open pit	760
overburden	180
waste rock	880
lean ore	880
undisturbed watershed	3800
net precipitation input on basin (precipitation-evaporation)	4800

+ maximum source areas are assumed

calculated by

$$\text{final concentration of parameter A} = \frac{\text{concentration of parameter A in runoff component i} \times \text{volume of runoff of component i}}{\text{total runoff volume}}$$

The results of the calculation is given in Table 4.28.

The assumption that no removal reactions occur produces a "worst" case model.

4.3.1.3. Mill Recycle Water

The mill recycle water is the largest water input to the tailings basin. While the other input components continue to increase over the life of the mine, the recycle is a function of the production rate and will remain relatively constant. Even when the other inputs are at their maximum values, the mill recycle accounts for 80% of the water input to the tailings basin (Figure 4.34). It is clear that the mill recycle will have a major influence on the resulting water quality of the tailings basin.

4.3.1.4. Operational Inputs

Because the mill operates with a recycling water system, the quality of the mill output is influenced by the quality of the mill input and vice versa. Since detailed information on water quality in recycling mill circuits of the type proposed for Minnesota operations is not available, it is only possible to focus on the general consideration of the effects of the mill process on water quality. With the limited data available, the integration of the recycle system with the mill can only be described in a qualitative fashion.

Table 4.28

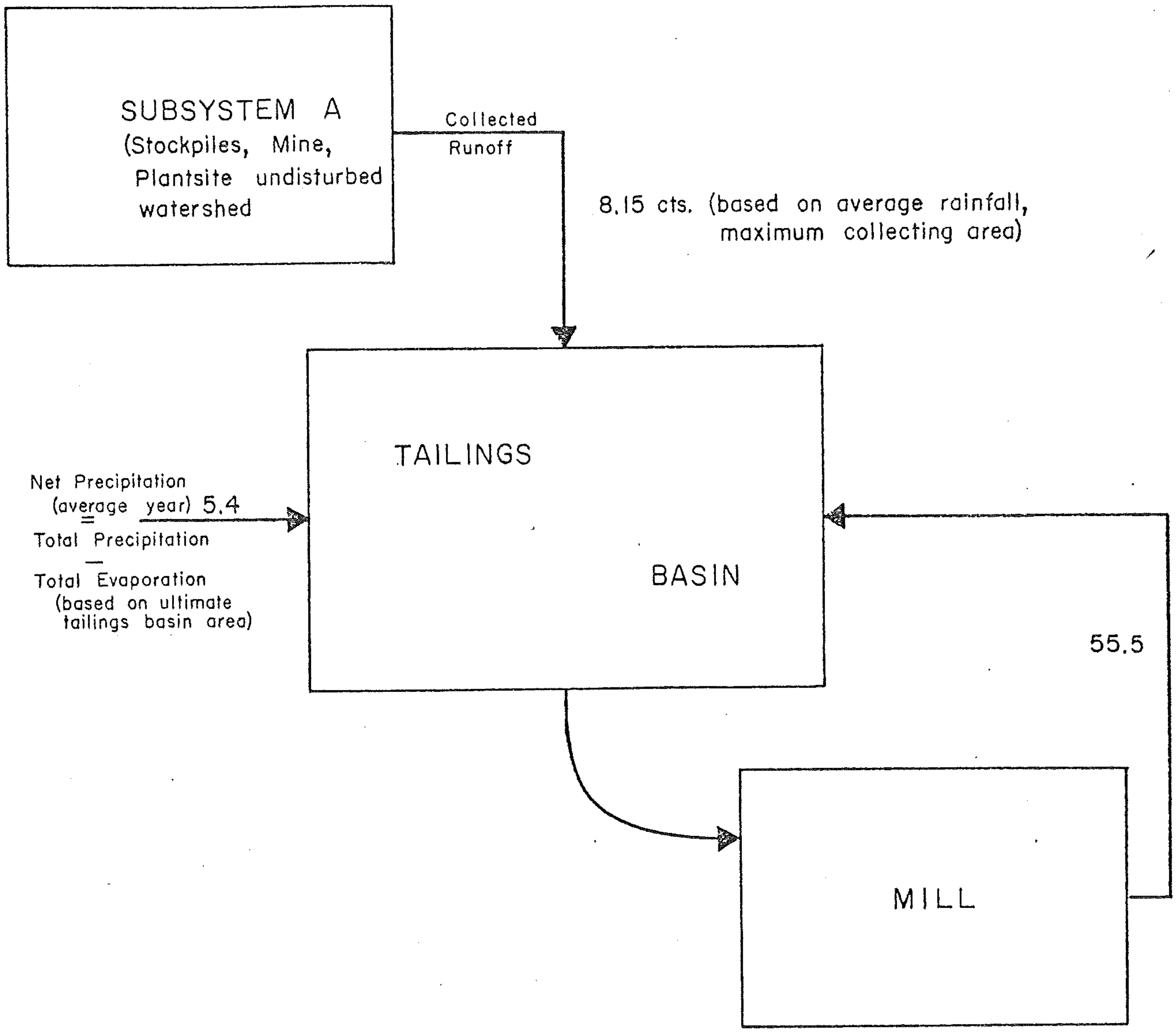
Predicted volumes ($1x10^{-8}$) and Concentrations (in mgl^{-1}) for collected runoff

Pit	Vol	Average year					Vol	Wet year				
Model	$1*10^{-8}$	(Cu)	(Ni)	(Co)	(Zn)	)SO_4)	$1*10^{-8}$	(Cu)	(Ni)	(Co)	(Zn)	(SO_4)
A	120	1.5	4.7	0.22	0.19	380	260	1.4	5.4	0.25	0.23	460
B	120	0.13	3.1	0.18	0.18	260	260	0.15	3.7	0.22	0.22	420

Figure 4.34

FLOW RATES – AVERAGE YEAR FOR MODEL OPEN PIT

20 x 10^6 mtpy



Production Rate = 20 x 10^6 mtpy

4.3.1.5. Release Reactions

Data from bench scale tests and pilot plant operation performed by the Mineral Resources Research (MRRC) (Iwasaki et al., 1978) indicate that in the mill cycle the concentration of dissolved solids increase and a pH around 8.0 is produced. In addition, the crushing and grinding processes can result in the liberation of asbestiform fibers (Stevenson, 1979).

4.3.1.6. Removal Reactions

In the processing circuit, thirty percent (by weight) of the solution is solids. Given a pH of 8 and a solution containing an estimated adsorbing surface area of 10-25m^2/liter of solution, substantial amounts of trace metals may be removed by precipitation or adsorption. (The ability of the silicate matrix of the gabbro to adsorb metals was discussed in the section on laboratory results.)

4.3.1.7. Chemical Additions

Organic chemicals in the form of frothers (e.g., MIBC) and collectors (e.g., xanthates) are added in the mill for the flotation process. A description of the nature of these compounds, the various types of these additives, the role they play in the flotation process and description of the flotation process is presented in the technical assessment report of the Regional Copper Nickel Study. Residual concentrations of these chemicals will remain in the mill water. Samples from pilot plant operations (Interim report MRRC 1969-19) contained residual concentrations on the order of 1-5 mg/l.

4.3.1.8. Summary

The mill water will probably have a pH around 8 and elevated levels of dissolved solids, residual organic chemicals, asbestiform fibers and relatively low levels of trace metals. A qualitative model, based on pilot plant studies by MRRC (Iwasaki et al.,) is shown in Table 4.29. This model is based on limited data, but does give a general idea of the water quality characteristic of the mill water.

4.3.2. Tailings Basin

The water quality of the tailings basin will be strongly influenced by the mill circuit since the mill recycle is the largest flow component to the basin. The physical and chemical environment in the mill provides conditions unfavorable for metal release to solution and actually favors metal removal reactions, indicating that trace metal concentrations may actually decrease as water flows through the mill. The reactions that occur in the tailings basin are influenced by the input water quality and by the physical and chemical conditions that are encountered by the water in the tailings basin. Although evidence indicates that pH of the input water will be slightly basic, discussion of acid conditions is pertinent due to the magnitude of their influence on water quality.

Historically, tailings containing iron sulfides have been a major source of mine related water pollution. Dissolution of iron sulfides can generate acid conditions which are conducive to producing leachate containing elevated concentrations of trace metals (Table 2.1 introduction).

Figure 4.35 compares the sulfur in the various gabbro samples with the range over which acid mine drainage problems have been observed in Canada (Hawley, 1972). Only the semi-massive tail from Amax falls in the range in which acid conditions have been observed. However, Hawley states that acid conditions may be a problem even with tailings that are less than 2.5% sulfur.

Table 4.29. PILOT PLANT WATER QUALITY
(Iwasaki et al, 1978)

pH	8.7
Calcium	70.3
Magnesium	37.4
Sodium	56
Potassium	17
Copper	.009
Nickel	ND
Cobalt	ND
Zinc	ND
Iron	.149
Manganese	.079

ND Not detected

All values in mg/ℓ

Figure 4.35

comparison of the percent sulfur in the Bench Scale tailings with acid mine drainage conditions.

% Sulfur (log scale)		Tailings$^+$
.1	- Inco	(Ip9003)
.2	- Amax	(AX9005)
.3	- U.S.Steel	(US9001)
.4	- Erie	(DP9002)
.5	- Amax	(AX9002)
1.0	- Amax	(AX9003)
2.0		
	- Amax	(AX9004)
3.0		
	observed acid conditions	
10	Canada (Hawley, 1972)	
20		
50		
70		
100		

+tailing data
MRRC report

data is for rougher tails, one stage grind

> "Therefore, in order to prevent an acid mine drainage situation from developing in any particular tailing area, the (iron) sulfide content of the mass must be kept substantially below 2.5 percent and probably as much below 1 percent as possible."

Figure 4.36 compares the pH and sulfur content of the gabbro used in the laboratory leaching experiment and from the field study areas with the range for observed acid mine drainage. Although the data are limited and the Amax data is preliminary, the general trend of decreasing pH with increasing sulfur is suggested. Leachate from Amax test pile FL-5 has been acidic, but the exact cause is not yet known. This pile was covered with overburden, fertilized, and revegetated; the effects of these processes on the pH are presently being investigated. The pH in Amax test pile FL-6 which received no treatment has recently begun to decline. (More information is available in "1979 Progress Report", Eger et al,.).

Although additional work is needed to quantify the relationship between sulfur content and the production of acid mine drainage in the Duluth gabbro, it is clear that under certain conditions acid conditions can develop. These conditions could be produced if the ore body were high graded, high grading being the practice of mining the richest ore first. In certain circumstances, this ore could be a massive to semi-massive sulfide and high concentrations of residual sulfide would be left in the tailings, thus enhancing acid production.

4.3.2.1. Release reactions

At present there are no field data on the leaching behavior of gabbro tailings. A small plot has recently been established at Amax for the purpose of conducting preliminary studies on runoff quality and the effect of revegetation. The only data on the release from tailings are from laboratory studies which are discussed in the section on laboratory results.

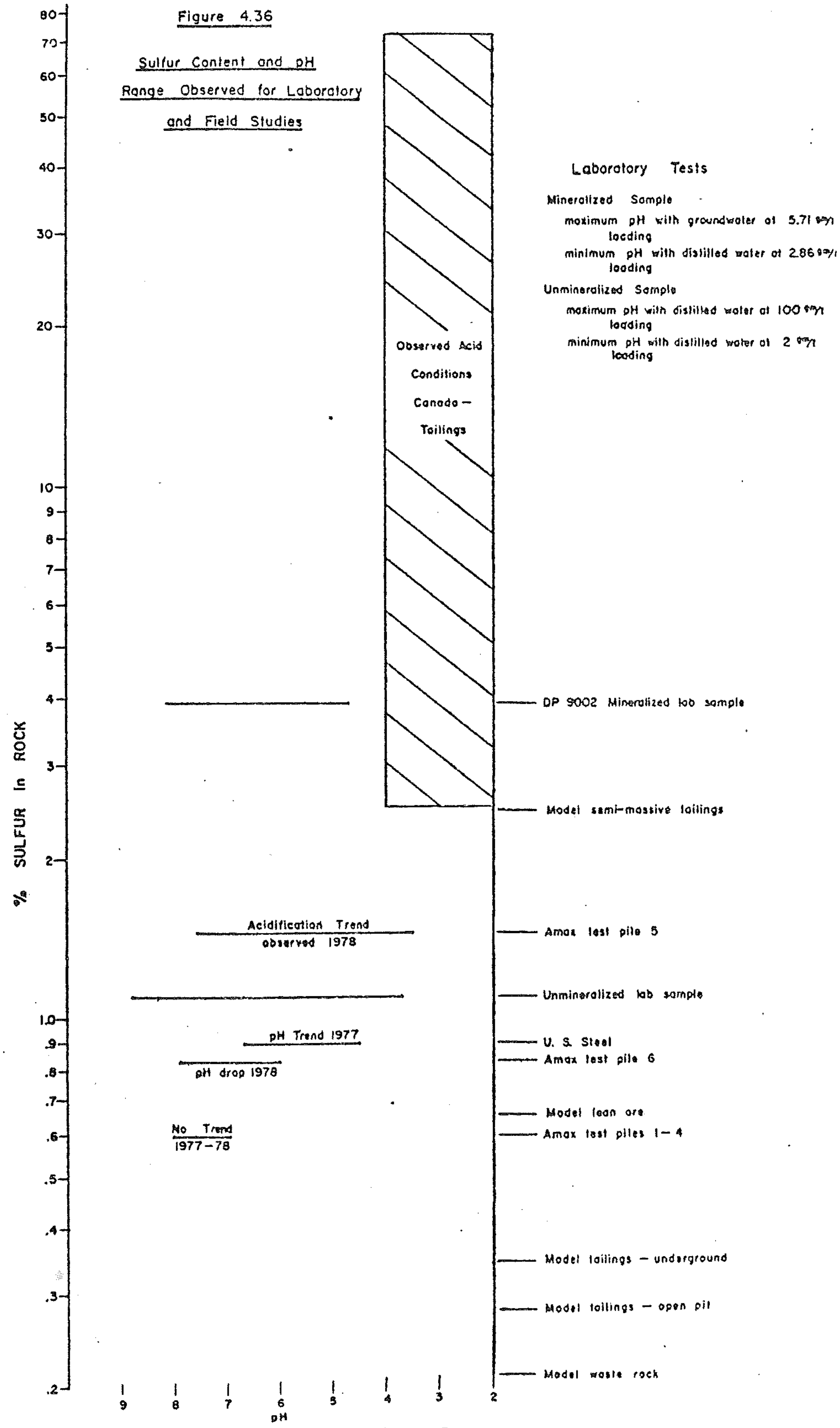


Figure 4.36

Sulfur Content and pH Range Observed for Laboratory and Field Studies

In general the tailings tended to buffer the pH to around 8 and metal release was small. When pH was maintained at low levels (4 or 3.5) substantial release of trace metals occurred, indicating that pH is one of the key factors in controlling release.

As discussed earlier, the quality of the basin water is strongly influenced by the mill recycle. Since pH of the recycle will probably be around 8, the release from the tailings in the basin is likely to be small.

4.3.2.2. Removal reactions

In general, as the pH of a solution increases, the amount of metal remaining in solution decreases. In calculating the concentration of the collected runoff (Table 4.29), no removal reactions were considered. The pH of the basin is likely to be greater than the pH of the runoff (the pH values used in the stockpile runoff models were 7.2 for Model 1 and 6.98 for model II). It is likely that some of the metals may be removed from solution as they are added to the basin. An equilibrium model (REDEQL 2, McDuff, 1973) was used to examine how the concentrations of metal solution in the collected runoff would change with pH; the results are shown in Table 4.30. Above pH 7, the model predicts that most of the copper and cobalt will be removed from solution by the formation of precipitates. Nickel and zinc will tend to remain in solution.

In summary, release of material from tailings to the basin water is likely to be small. The basin water quality will likely be dominated by the chemistry of the mill ciruit.

4.3.3. Model basin water quality

As a result of the limited data on the effects of processing of gabbro on mill water quality and the limited laboratory data, it is difficult to con-

Table 4.30 Redeql 2 Primary Distribution in Tailings Basin

Values as percent of metal input
pH variable
Talk 10 mg/l^{-1} as $CaCO_3$
pe = 8.0

pH	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5
Cu:2.4 mg/l										
in solution										
Cu^{2+}	65.5	65.4	65.3	65.1	63.9	14.8	2.3			
OH^-					1.6	2.6	3.5	5.7	10.2	18.9
$CO_3^{=}$										
$SO_4^{=}$	34.5	34.6	34.6	34.5	33.9	7.9	1.2			
Precipitates										
$CuS(s)$										
$Cu_2S(s)$										
$Cu(OH)_2CO_3(s)$						74.3	92.7	93.6	89.6	81.0
$Cu(OH)_2(s)$										
Ni:8.2 mg/l										
in solution										
Ni^{2+}	65.5	65.4	65.3	65.3	65.2	65.1	64.8	64.1	62.1	50.7
OH^-									0.6	1.5
$CO_3^{=}$							0.7	1.7	4.2	9.3
$SO_4^{=}$	34.5	34.6	34.6	34.6	34.6	34.6	34.4	34.1	33.1	27.0
precipitates										
NiS										
$Ni(OH)_2$										11.4
Co 0.38mg/l										
in solution										
Co^{2+}	54.5	54.4	54.3	54.3	54.2	54.1	53.9	37.7	12.4	4.3
OH^-								0.6	0.6	0.8
$CO_3^{=}$								0.8	0.7	0.6
$SO_4^{=}$	45.5	45.6	45.7	45.7	45.6	45.6	45.4	31.8	10.5	3.7
precipitates										
CoS										
$CoCO_3$								29.1	75.8	90.6
Zn:0.38mg/l										
in solution										
- Zn^{2+}	65.5	65.4	65.3	65.3	65.2	65.0	64.6	63.2	56.8	33.3
OH^-							0.6	2.2	10.6	45.2
$CO_3^{=}$								1.0	2.4	3.9
$SO_4^{=}$	34.5	34.6	34.7	34.6	34.6	34.6	34.4	33.6	30.2	17.7
precipitates										
ZnS										
$Zn(OH)_2$										

struct a model of the quality of tailings basin water. In an attempt to provide an approximate model, data from a taconite tailings basin and INCO's Shebandowan operation are presented (Table 4.31).

The Shebandowan operation is a massive nickel and copper sulfide deposit (1.06% nickel, .8% copper). The host rock is peridodite which, like the gabbro, is an ultramafic rock unit (high in iron and magnesium) composed primarily of pyroxene and olivene. The host rock has a substantial buffering capacity which has prevented acid formation.

The Shebandowan operation is an underground mine where mine water is pumped to a basin but where there are no stockpile areas associated with the operation. The taconite basin does not receive runoff collected from disturbed areas. Although the data are limited, there is a general similarity in the water quality of the two basins, except that Shebandowan has higher sulfate and trace metal concentrations as would be expected for a metal sulfide operation. The values of metal concentrations measured in the Shebandowan basin are of the same order of magnitude as the maximum concentration observed in the batch tests (Table 4.32).

In conclusion, tailings basin water is expected to have high levels of dissolved solids , a pH in the range of 7 to 8, and trace metals concentrations in the range .01-.1mg/l. Although metal concentrations are expected to be low, they will be above background values and may approach biological concern levels.

4.3.4. Discharge

The quality of untreated direct discharge would be the same as that in the tailings basin, whereas seepage discharge quality would be altered due to chemical reaction along the seepage flow path. Seepage losses can occur in

Table 4.31 Tailings Basin Water Quality; Shebandowan and Taconite

	TACONITE	(1974-1977) (mg/l) SHEBANDOWAN (massive Ni sulfide basic host rock)
pH	6.8 - 8.2^{5}	6.7 - 8.3
TDS	116 -439^{5}	341 - 751
SO_4	19 - 82^{5}	122-- 447
Ammonia	- - - -	.1 - 3.7
Nitrates	1.81 -2.66^{3}	.2 - 3.75
Nitrite	.04^{1}	.01 - .08 (.28)$^{+}$
total P		.01 - .29
Cu	.001^{1}	.001-.014 (.23)$^{+}$
Zn	.005^{1}	.001-.054 (.17)$^{+}$
Fe	.1-.6^{3}	.06 - .54 (42)$^{+}$
Ni	.005^{1}	.046-.077*

Samples collected at Eveleth taconite tailing basin during the period 1967-1975 superscript denote the number of samples

(Impacted runoff not collected)

+ apparent outlier

* = limited data 5 pts (3 in 75, 2 in 78)

Table 4.32

Companson of Metal Concentration in Shebandowan Tailings Basin with maximum observed concentrations in Laboratory experiments.

Parameter	Shebandowan	Laboratory Tailings leached with ground water and bog water
Copper	.001 - .014	.017, .032
Nickel	.046 - .077	.005, .016
Iron	.06 - .54	.091, .350
pH	6.7 - 8.3	8.15 - 8.34

two areas, seepage through the dams, which should be collectable, and seepage to the groundwater. Figure 4.37 illustrates the seepage route and includes estimates of the relative magnitude of the rates. (Hewett 1979)

4.3.5. Dam Seepage

This is the water that has been identified in the past (Hawley) as a major water quality problem. Oxygenated water from the basin moves through the tailings and seeps out along the dam perimeter. Significant oxidation can occur which historically has resulted in low pH and high metal concentrations.

4.3.5.1. Release reactions

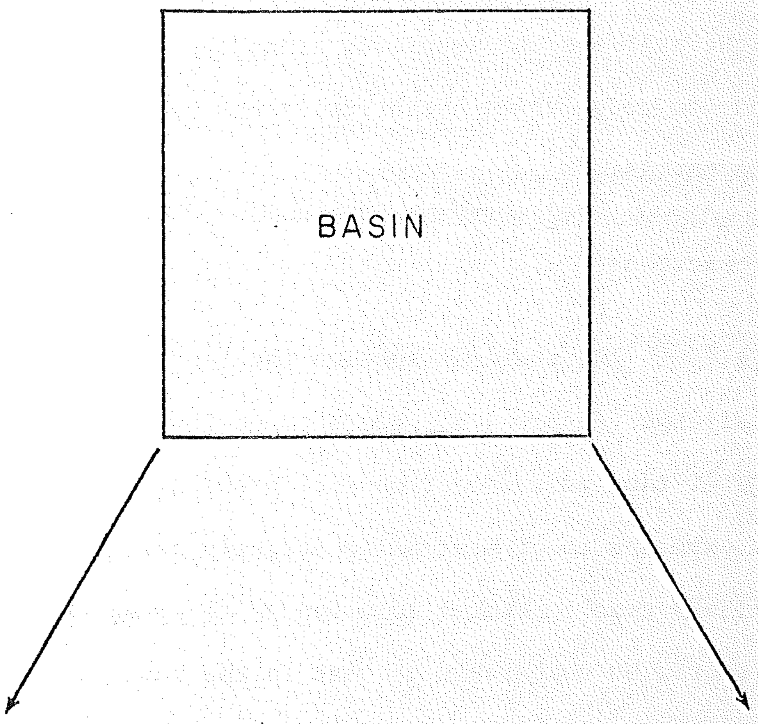
As discussed in the previous section the residual sulfide content of gabbro tailings (Figure 4.35) tends to be low and the laboratory and field data suggest that acid formation will probably not be a problem. The basin is expected to be neutral to slightly basic, laboratory test indicate that tailings tend to buffer solution pH to around 8. The pH of the seepage should be comparable to that in the basin. Laboratory experiments indicate that at this pH metal release is very low.

4.3.5.2. Removal reactions

At pH of 8 a large proportion of any metal in solution would likely be adsorbed onto the tailings as the water moves through the dam or precipitate as metal carbonates or hydroxides. Laboratory data from the batch reactor experiments (Chapter 3) indicate that metals are removed from solution by adsorption onto solid phases. The potential adsorptive surfaces include silicate surfaces and oxides of iron, manganese and titanium. As water seeps through the tailings and the dam it must traverse a large surface area of solids. Significant amounts of trace metals will probably be adsorbed.

Figure 4.37

SEEPAGE LOSSES FROM TAILINGS BASINS



DAM SEEPAGE

Seepage is highly dependent on dam design, can be designed to be ~ 0 if a clay liner is placed on the inside face of the dam or a drain can be placed at the toe to allow seepage

DEEP (Ground Water) SEEPAGE

~ 0 for impermeable base

2 ft/yr for permeable base

Dam seepage will likely have a pH in the range of 7 to 8, high levels of dissolved solids and may have elevated concentrations of iron and manganese; mobile elements in reducing environments. The dissolved oxygen content of the seepage will decrease as the water moves through the dam.

The decrease in oxygen depends on several factors including the rate of water movement, the position of the phreatic surface and the nature of the dike surface (coarse vs fine, vegetated vs unvegetated) and the oxygen demand of the tailings. It is likely that some oxygen will remain in solution (comparable to shallow groundwater) but probably not enough to suppress iron and manganese dissolution and transport.

Trace metal concentrations will probably be above background values and may reach several hundred ug/l.

4.3.6. Deep seepage (Loss to groundwater)

Due to the very fine nature of the tailings, vertical seepage will be slow. Bulk permeability of pilot plant tailings from MRRC was 2.88×10^{-4} cm/sec. Golder Associates (1978) estimates that the very fine fraction of the tailings, called "slimes" will have a permeability much less than the bulk, on the order of 2×10^{-6} cm/sec. Golder states that by controlling tailing deposition the slime layer can effectively be distributed throughout the basin, thereby producing a net permeability of 2×10^{-6} cm/sec for the entire basin. The bulk permeability is a function of the processing method used. The MRRC tails were obtained from a bulk flotation process, which utilized conventional ball and rod crushing. Amax is presently investigating a selective flotation process with autogenous grinding, which would produce a coarser tailing (J. Sturgess, personal communication).

Table 4.33 REDEQL 2 Primary Distribution in Tailings Basin

Values as percent of input metal
pH 8.5, TALK 10 mgL^{-1} as $CaCO_3$

pe	-4.0	-5.0	-6.0	-7.0	-8.0	-9.0	-10.0
Cu:2.4 mg/l							
Cu^{2+}							
OH^-							
$CO_3^=$							
$SO_4^=$							
CuS		100	100	100			
Cu_2S	100				100	100	100
$Cu(OH)_2CO_3$							
$Cu(OH)_2$							
Ni:8.2 mg/l							
Ni^{2+}	50.7						
OH^-	1.5						
$CO_3^=$	11.1						
$SO_4^=$	26.9						
NiS		100	100	100	100	100	100
$Ni(OH)_2$	9.7						
Co:0.38mg/l							
Co^{2+}	3.6						
OH^-	0.7						
$CO_3^=$	0.6						
$SO_4^=$	3.1						
CoS		100	100	100	100	100	100
$CoCO_3$	92.0						
Zn:0.38mg/l							
Zn^{2+}	33.0						
OH^-	44.8						
$CO_3^=$	4.6						
$SO_4^=$	17.5						
Zn S		100	100	100	100	100	100

shifts to favor sulfate and less sulfide is present to precipitate the metals (More discussion of sulfide dissolution is given in Chapter 3. The equilibrium predictions provide insight on the possible controlling mechanisms of metal solubility. As the system becomes more reducing (pE decreases) more sulfide will be solution and the solid metal sulfide will increase. Information on the reducing conditions in the deep portion of tailings basins is not available (a value of pE-4 was used by Morel et al., 1973 to represent bottom lake waters during summer stratification).

4.3.6.2. Removal reactions

Removal of trace metal will occur by adsorption onto the silicate minerals. Metals contained in the basin water may precipitate as metal sulfides (as discussed above) or if the pH is too high, there will be an increased tendency for metal hydroxide precipitates to form.

4.3.6.3. Summary

Deep seepage will have elevated concentrations of dissolved solids and as a result of the anoxic conditions, iron and manganese concentrations will also increase. The chloride concentration in the seepage will be approximately equal to its concentration in the basin. Chloride is a very mobile ion and has been used as a tracer in groundwater studies. It forms very few compounds of limited solubility, and is not readily removable by adsorption. Nickel and zinc are likely to be the major trace metals in the seepage, since they are more mobile than copper or cobalt. Concentrations of all trace metals are likely to be above background concentrations and probably will on the order of .01 - .1 mg/1, but exact concentrations are difficult to predict based on available data. It should be pointed out that initially seepage from the basin can be much higher than predicted in Figure 4.37. As the basin fills slime layers accumulate, and there is a tendency for the basin to be self-sealing (Golder Associates). (There is always the possibility of having zones of higher permeability and increased seepage in portions of the basin). In the initial phases of the operation, the seepage rate will be determined by the permeability of the underlying soil. The quality of the seepage will be comparable to the mill water.

4.3.7. Post operation

The post operational water budget for the tailings basin is discussed in the water budget report of the Regional Copper Nickel Study. The final pathway of the water can be controlled by appropriate engineering and construction. Three possible routes were identified; surface runoff, seepage through dams, or vertical seepage to the groundwater system (see section on mine water balance for details).

From a water quality standpoint, it is advisable to minimize infiltration and maximize surface runoff. This is particularly important since data suggest a trend of increasing precipitation acidity. The data from the laboratory studies indicate substantial metal release can occur from tailings under and conditions. In addition, metals that were adsorbed onto the tailings under basic pH conditions could be released is subjected to low pH rainfall.

Chapter 5 Comparison of Laboratory and Field Leaching Rates

5.1 Introduction:

Leaching rates under laboratory and field conditions were determined for sulfate, metals occurring as metal sulfides (Cu, Ni, Co, Zn) and metals bound in silicate minerals (Ca, Mg). Batch reactor and column experiments were conducted in the laboratory, field rates were determined for stockpiles at the Erie Mining Company Dunka site and AMAX test piles.

5.2 Summary

Laboratory and field observation indicate that the rate of trace metal leaching increases with increases in:

- ..available metal sulfide surface area
- ..hydrogen ion concentration (equivalently, decreases in pH)
- ..availability of oxygen at the metal sulfide surface
- ..the presence of complexing organics
- ..amount of precipitation (water available for the transport of reaction products in the case of stockpiles).

The rates determined are presented in Table 5.1 and do not vary radically among the reaction environments investigated.

5.3 Relevant Literature

Hoffmann et al. (1979) determined that release of nickel to solution in the batch reactor experiments was a function of surface area, dissolved oxygen concentration, pH and concentration of citrate:

$$\frac{d\,(Ni^{2+})}{dt} = k\,A_s^{0.4}\,(O_2)^{0.8}\,(H^+)^{0.2}\,(Cit)^{0.3} \qquad (5.1)$$

Table 5.1 Release rates from laboratory and field (kg/m^2-yr)

	COLUMN EXPERIMENT						BATCH REACTORS						AMAX PL-1	Em - 8[2]		Seep-1[2]		Seep-3[2]	
	Ground Min.	Ground Unmin.	Surface Min.	Surface Unmin.	Rain Min.	Rain Unmin.	Min. pH 5	Min. pH 6	Min. pH 7	Unmin. pH 6.9	Min. 44mgl^{-1}D.O.	Unmin. pH 7 1.29$\cdot 10^{-4}$M Cit		1976 7/15 to 11/28	1977 4/12 to 8/17	1976 7/15 to 11/28	1977 4/12 to 8/17	1976 7/15 to 11/28	1977 4/12 to 8/17
$SO_4^=$ $\cdot 10^4$	5.4	2.5	2.5	1.9	3.8	2.0	2.5	1.0	0.84	0.86	3.2	0.27	1.3	0.59	1.8	7.5	9.6	2.0	5.5
Ni $\cdot 10^7$	320	8.8	200	4.0	160	0.25	130	100	65	170	230	540	0.55	0.88	1.8	2.7	23	22	110
Cu $\cdot 10^7$	0.85	0.65	2.0	2.7	0.35	0.13	31	6.1	2.2			65	0.091	0.0088	0.070	0.078	0.088	0.77	4.6
Zn $\cdot 10^7$													0.035	0.031	0.042	0.38	6.1	0.39	1.9
Co $\cdot 10^7$	18	0.40	8.5	0.19	7.9	0.023							0.015	0.022	0.042	0.46	1.9	1.2	6.0
Ca $\cdot 10^7$							65[4]	76[4]	37[4]	88[4]	94[4]	76[4]	320	96	440	1400[3]	1760[3]	280	1400
Mg $\cdot 10^7$							49[4]	49[4]	31[4]	45[4]	54[4]	42[4]	29						
Fe $\cdot 10^7$	2.1	3.5	7.7	4.6	0.31	0.60							1.1						
Mn $\cdot 10^7$	38	5.4	23	3.1	16	0.23							0.073						

[1] using 400 m^2/MT
[2] using 125 m^2/MT
[3] Approximated assuming a constant ratio (Ca)/(SO$_4$) = 5.3
[4] AT t=500 hours

The authors concluded the overall linear dissolution rate was probably a function of three mechanistic pathways: diffusion, solution phase and surface phase reactions. Dissolution rate control by solution phase oxidation of HS^- or a surface reaction between bound HS^- groups and oxygen was proposed in the two models developed.

Shumate et al. (1976) concluded that pyrite (FeS_2) oxidation rate was significantly greater for surfaces exposed to the atmosphere in comparison with those submerged in water. This conclusion was based on the relatively small amount of dissolved oxygen in water (~9 mg/l) and the fact that oxygen diffusivity in water is $1*10^{-4}$ that in air. The authors suggested that oxygen transport to non-submerged reaction sites was rate limiting and was accomplished via the vapor phase.

5.4 Comparison of Reaction Environments

Batch reactor experiments were conducted using finely ground ($d < 0.074$ mm) gabbro suspended in a well-mixed aqueous solution (2.86 and 5.71 g gabbro/l) with air introduced to the solution by means of gas diffusion tubes. Gabbro of two different compositions (see Table 5.2) was used and physical solid phase and solution composition variations were introduced to examine their effect on leaching.

In column experiments two different types of gabbro (see Table 5.2 for composition), $0.25 < d < 0.62$ cm, were subjected to a constant slow flow ($Q = 50\text{-}100$ ml/d) of three different compositions (see Table 5.3 for solution composition).

The stockpiles studied are located in northeastern Minnesota and are exposed to the environment. Compositional data for the Erie stockpiles and AMAX test pile are presented in Table 5.2. Leaching rates at Erie

TABLE 5.2 CHEMICAL COMPOSITION AND SIZE OF ROCK

	BATCH REACTORS		COLUMN STUDY[2]		ERIE SITE[4]		
ELEMENT	UNMIN.[1]	MINERALIZED[2]	UNMIN.	MINERALIZED	WASTE ROCK	LEAN ORE	AMAX[2]
S	1.1[3]	3.92[3]	1.1[3]	3.92[3]	0.207	0.634	0.655
Cu	0.16	0.98	0.22	0.98	.053*	0.29*	0.306
Ni	0.14	0.18	0.069	0.18	.014*	0.08*	0.073
Co	0.082	0.020	0.0096	0.020	0.002	0.007	0.009
Zn	< 0.00088	0.023	0.015	0.023	0.0026	0.0078	0.0078
Fe					0.229	0.701	0.701
Particle Size	$d < 7.4 * 10^{-5}$ m		$2.5 * 10^{-3} < d < 6.2 \times 10^{-3}$ m		$d < 1.2$ m		$d < 0.61$ m
Estimated Surface Area (m^2 T^{-1})	$1.7 * 10^5$		480		50 - 200		300 - 500

1 Neutron activation analysis
2 Plasma emission spectrometry
3 MRRC analysis
4 Model values from Stevenson (1979)

* analysis by Erie Mining Company

Table 5.3 Composition of synthetic groundwater and surface water from column leaching experiment

Component	Concentrations in mgl^{-1} Groundwater	Surface Water
Na^+	25.5	11.2
K^+	2.0	2.0
Ca^{2+}	15	8.2
Mg^{2+}	25	5.0
HCO_3^-	46	25
$SO_4^=$	36	11.3
Cl^-	1.8	8.0
$SiO_3^{\equiv}$(as Si)	5	4.0
NO_3^-	129	26
PO_4^{3-}	0.5	0.5 as PO_4^{3-}
Tannic Acid (As C)	0	10.0
Citric Acid (As C)	0	5.0

The third solution was mega pure water, intended to simulate rainwater were calculated for both 1976 and 1977 and for 1977 at the AMAX test pile. Additional description of the stockpiles is presented in Chapter 4.

Expression of stockpile leaching rates in terms of surface area is difficult. The lack of adequate characterization of the particle size distribution of stockpiled materials and the flow patterns in the stockpiles introduced a high degree of uncertainty into the rate calculations since the actual surface area contacted by flow is unknown. Size distributions were estimated based on data obtained from crushing products; subsequent analysis of blasted products yielded a specific surface area five times as large. Rainfall may not contact all surfaces within the pile. Howard (1968) concluded that in some regions of dump leaching piles there is little or no contact of rock surface and leach solutions. In addition the leaching rates in stockpiles appear to be controlled by the aqueous transport (via precipitation) of reaction products from the reaction site, thus the rates are dependent upon the amount of precipitation (Table 4.10).

The leaching environments for the batch reactors, columns and stockpiles varied in respect to transport of oxygen and metals and in host rock composition. The thickness of the aqueous layer separating the gabbro surface from atmospheric oxygen was greatest in the batch reactors (gabbro particles were suspended in solution) and least in the stockpiles where the thickness of the layer was reduced to zero during periods of no precipitation. Reducing the thickness of the aqueous layer enhances the transport of oxygen for chemical reactions such as sulfide oxidation (Shumate et al., 1976).

The iron sulfide oxidation model presented by Nelson (1978) would suggest that the oxidation may be enhanced due to contact of the solid metal sulfide surface with the atmosphere. Nelson (1978) observed that the rate of iron sulfide oxidation increased with increasing concentration of dissolved oxygen in solution. Since the concentration of oxygen in the atmosphere is $2 * 10^4$ that in water, an enhancement in the oxidation rate might also occur. Direct extrapolation of Nelson's (1978) model to a gas-solid system is not, however, feasible due to potential changes in the nature of reaction sites and solution effects on the electron structure of oxygen (Nelson, 1979).

Transport of reaction products from reaction sites was also a factor in the determination of leaching rates and was affected by the water available for transport and the solid surface area loading. In laboratory experiments water was continuously available whereas in the field, precipitation was a major factor in providing water for transport of products from reaction sites and was intermittent as opposed to continuous.

The solid surface area loading in batch reactors varied from 0.5 to 1 m^2/l for rates presented in this discussion. In column leaching experiments and in the unsaturated zone of stockpiles a loading of 1 to 10 m^2/l appears reasonable based on an assumed thickness of 0.1-1.0 mm for the aqueous layer in contact with solid surface. Surface area loading affects adsorption reactions, adsorption increasing with increasing loading.

The rock used in the laboratory experiments (Table 5.2) was of higher grade than that stockpiled in the field. The higher metal sulfide content may have enhanced the potential for leaching in the laboratory tests.

5.5 Sulfide Oxidation Rates

The observed sulfate leaching rates exhibited a dependence on the type of leaching situation, sulfate transport (as controlled by available water) and rock composition.

Rates were most rapid at the Erie stockpiles and slowest in the batch reactors, reflecting the importance of the transport of oxygen (controlled by the thickness of the aqueous layer separating the mineral surface from the atmosphere). The wet-dry cycling in the stockpiles apparently enhanced sulfide oxidation as the rates exceeded those observed in column experiments despite the paucity of available transport water at the stockpiles and the lower sulfide content of the stockpile rock. Comparison of stockpile rates in 1976 and 1977 suggests that the rate was transport limited and may further increase with increasing precipitation. Table 5.4 compares the leaching rates at Erie stockpiles in 1976 and 1977, with precipitation during the sampling periods of 4.43 and 16.1 inches, respectively. Sulfate release from all three stockpiles was greater in 1977 than in 1976 indicating rate control by aqueous transport of sulfate from the reaction site. Data from the AMAX test pile FL-5 indicate that sulfate concentration in leachate was independent of pH in the pH range of 3.5 to 7.5, as shown in Figure 5.1.

As the percent sulfur in the gabbro increased the sulfate leaching rate increased with the exception of Seep 1 at the Erie site where the sulfate leaching rate was anomolously high. With every type of leach solution in the column experiment the sulfate leaching rate increased with percent sulfur in the solid phase as is presented in Figure 5.2.

Sulfate concentrations observed at AMAX test piles also increased with increasing sulfide in the solid phase (Figure 5.3).

The dependence of the sulfate leaching rate on percent sulfide in the solid can be expressed in the form

$$k_{SO_4} = a(\%S)^n \qquad (5.2)$$

DATA SUMMARY

Table 5.4 Effect of rainfall on leaching rate

SITE	LEACHING RATE: kg (MT gabbro)$^{-1}$ yr^{-1}								$\frac{\text{RATE 1977}}{\text{RATE 1976}}$			
	SO_4		Ni x 10^4		Cu x 10^4		Ca					
	1976[a]	1977[b]	1976[a]	1977[b]	1976[a]	1977[b]	1976[a]	1977[b]	SO_4	Ni	Cu	Ca
Em-8	0.0074	0.022	0.11	0.23	0.0011	0.0087	0.0012	0.0054	2.9	2	8	4.6
Seep-1	0.094	0.12	0.34	2.9	0.0098	0.011	c,d	c,d	1.3	8	1.1	d.
Seep-3	0.025	0.069	2.8	14	0.096	0.57	0.0035	0.017	2.7	5	6	5

a From samples 7-15-76 to 11-28-76

b From samples 4-12-77 to 8-17-77

c Estimated by $SO_4/Ca^{2+}=5.3$

d Insufficient data

Precipitation during sampling period from Babbitt

1976: 4.43 inches

1977: 16.09 inches

Ratio of precipitation: $$\frac{P_{1977}}{P_{1976}} = \frac{16.09}{4.43} = 3.6$$

Figure 5.1

$[SO_4^=]$ VS pH at FL-5, 1978

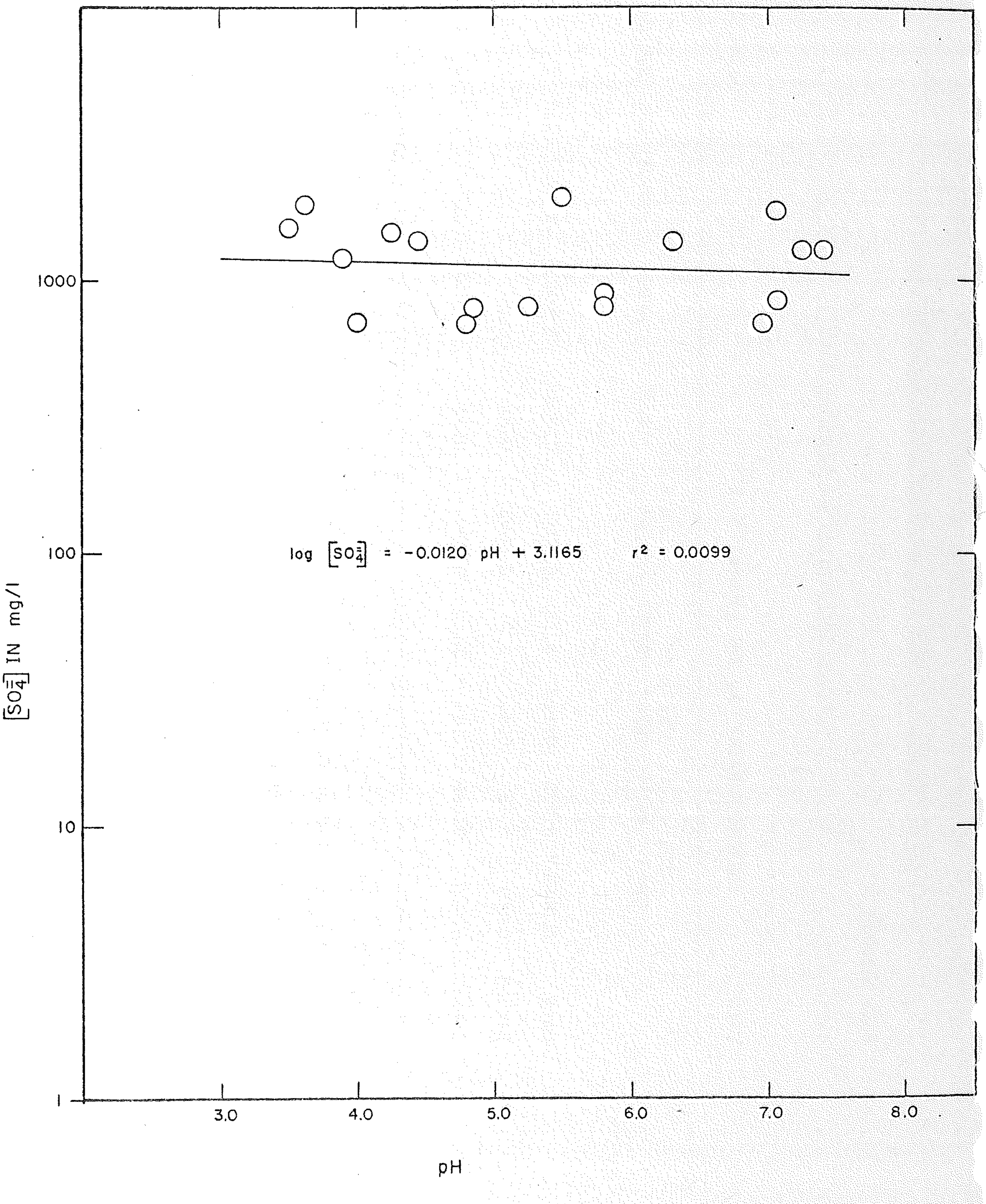


Figure 5.2

SULFATE LEACHING RATE VS PERCENT S IN ROCK, COLUMN LEACH

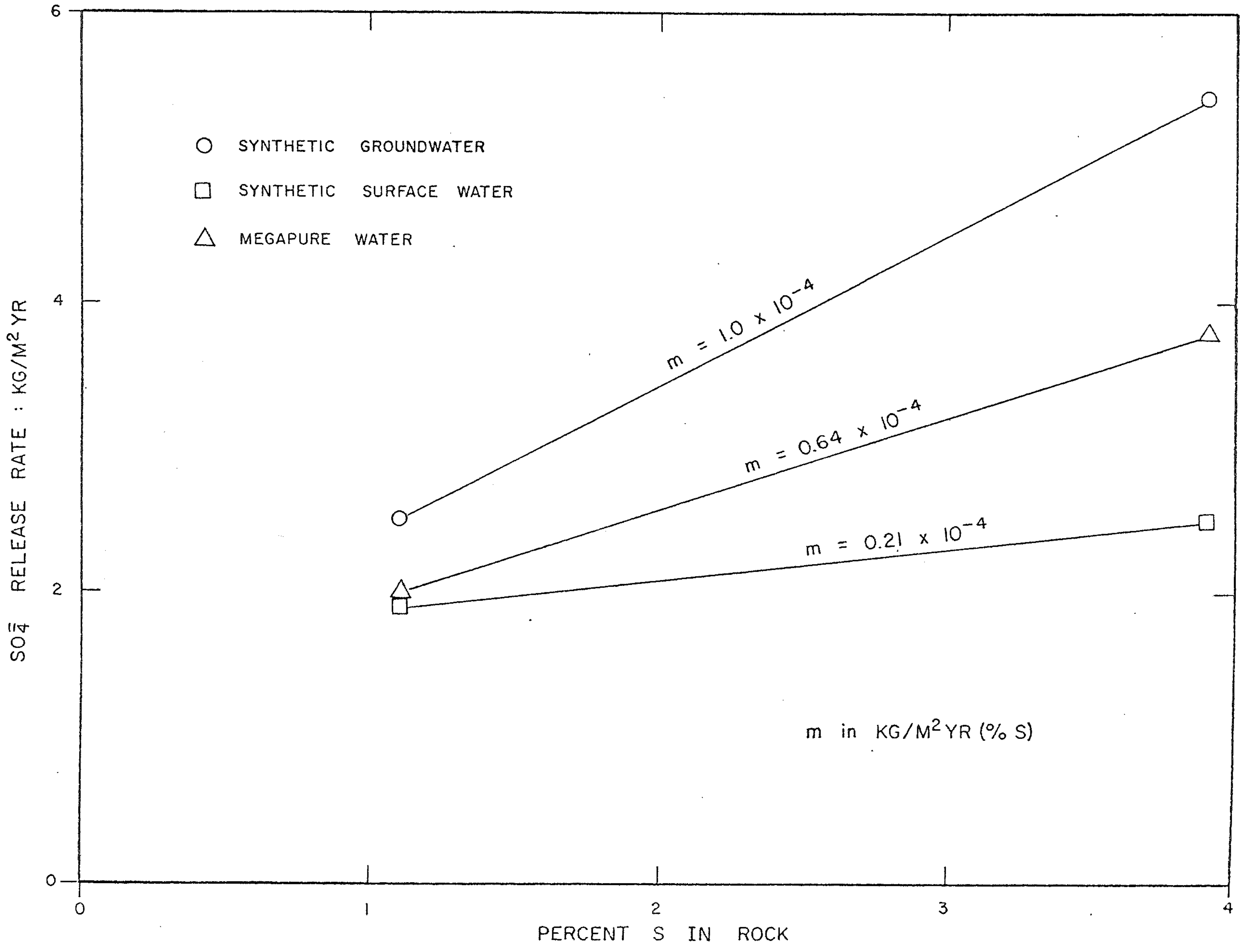
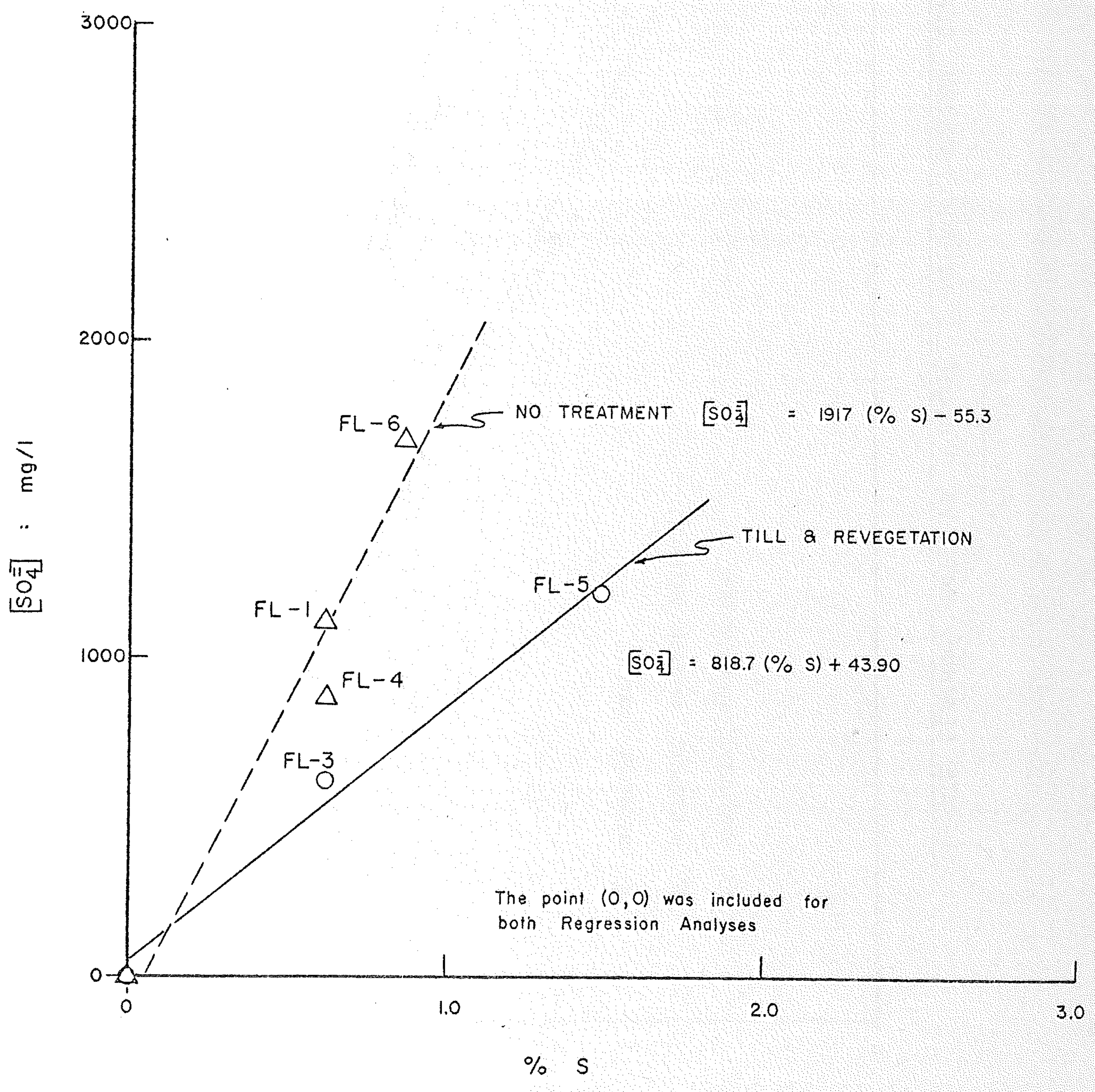


Figure 5.3

$[SO_4^=]$ VS % S, FROM AMAX TEST PILES



The point (0,0) was included for both Regression Analyses

Using the limited data points from the column leaching experiment the value of n varied from 0.22 to 0.61 (Table 5.5). Assuming average concentration was directly proportional to leaching rate at the AMAX test piles, n values of 0.76 and 1.7 were obtained (for piles with till plus vegetation cover and untreated piles respectively).

Table 5.5 Variation of K_{SO4} with %S in solid

Assume $K_{SO4} = a(\%S)^n$

Column Experiment

Leach Solution	n
Synthetic Groundwater	0.61
Synthetic Surface Water	0.22
Megapure Water	0.51

AMAX Test Piles

Type of Cover	n
None	1.7
Till and Vegetation	0.76

5.6 Trace Metal Leaching Rates

The effect of reaction environment was analyzed by comparing rates from the batch reactor at pH 7, the column leach of mineralized gabbro with rainwater and Seep 3 during 1977.

Nickel leaching rates increased slightly in the order batch reactor < stockpile < column study. Although the sulfate leaching rate (reflecting the rate of metal sulfide oxidation) was most rapid in stockpiles, the readily available transport water in the column experiment provided means for more rapid trace metal leaching.

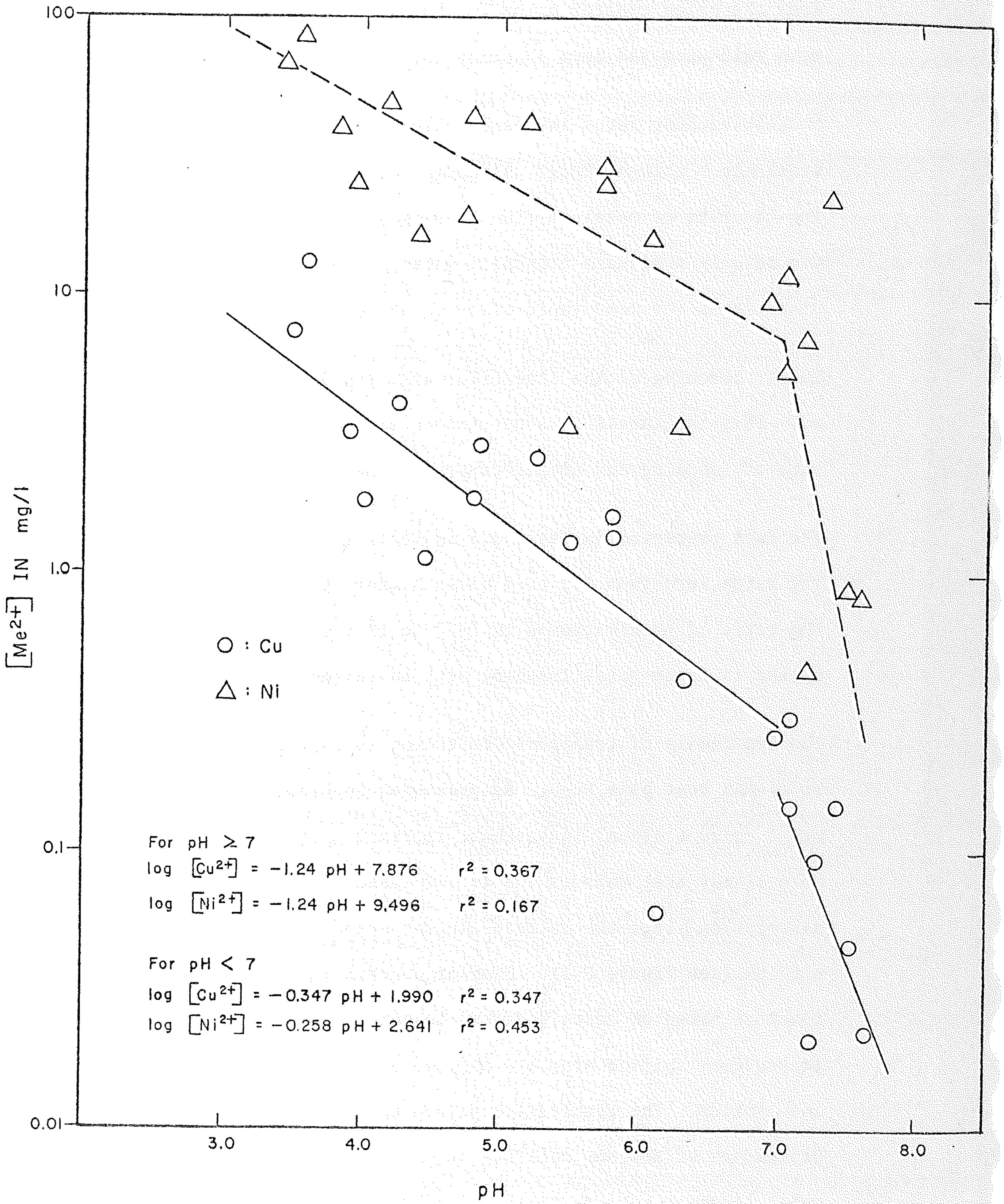
Copper leaching of the stockpiles also appeared to be transport limited. This hypothesis is supported by the relationship between the rate of leaching and amount of precipitation at the Erie site.

The data presented in Table 5.3 indicate that copper and nickel leaching rates were from 1.1 to 8 times higher in 1977 than 1976.
The ratio of precipitation in 1977 to 1976 was 3.6 suggesting an increase in trace metal leaching with increased precipitation.

The hypothesis of transport limitation is further supported by data from AMAX test pile FL-5. As presented in Figures 5.4 and 5.5, trace metal concentrations in leachate increase with decreasing pH. It is more likely that this is due to increased transport than increased dissolution since the sulfate concentrations are relatively constant with pH (see Figure 5.1). Similar observations were made for batch reactors based on tests designed to determine the amount of metals released from sulfide minerals and subsequently precipitated or adsorbed into solids. The results are presented in Figure 5.6 and reflect the dependence of aqueous mobility on pH. The dependence of the trace metal leaching rate on pH was similar in the batch reactors and the

Figure 5.4

$[Cu^{2+}]$, $[Ni^{2+}]$ VS pH at FL-5, 1978



For pH $\geq$ 7

log $[Cu^{2+}]$ = −1.24 pH + 7.876 $r^2 = 0.367$

log $[Ni^{2+}]$ = −1.24 pH + 9.496 $r^2 = 0.167$

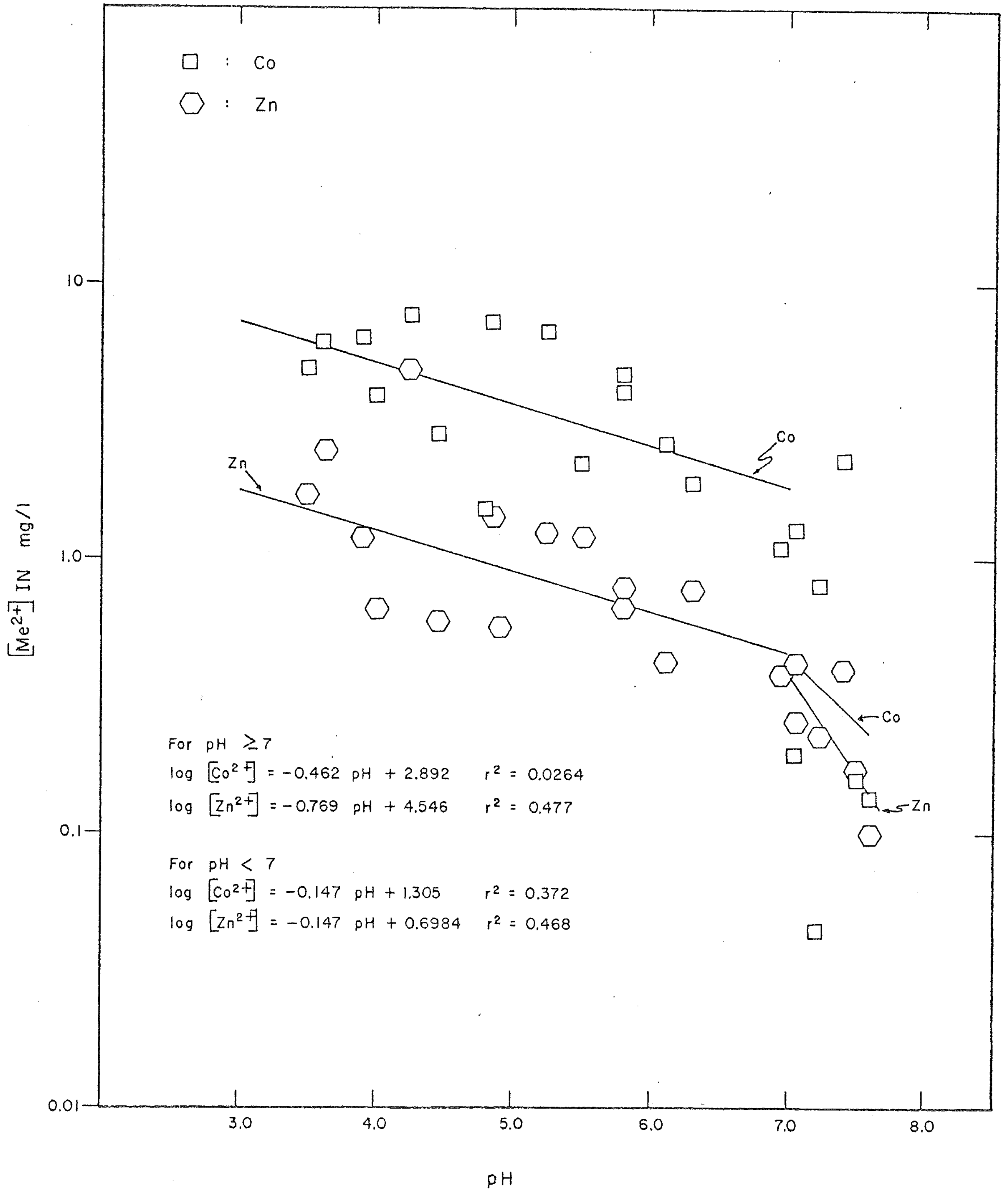
For pH < 7

log $[Cu^{2+}]$ = −0.347 pH + 1.990 $r^2 = 0.347$

log $[Ni^{2+}]$ = −0.258 pH + 2.641 $r^2 = 0.453$

Figure 5.5

$[Co^{2+}]$, $[Zn^{2+}]$ VS pH at FL-5, 1978



For pH ≥ 7

$\log [Co^{2+}] = -0.462\ pH + 2.892 \qquad r^2 = 0.0264$

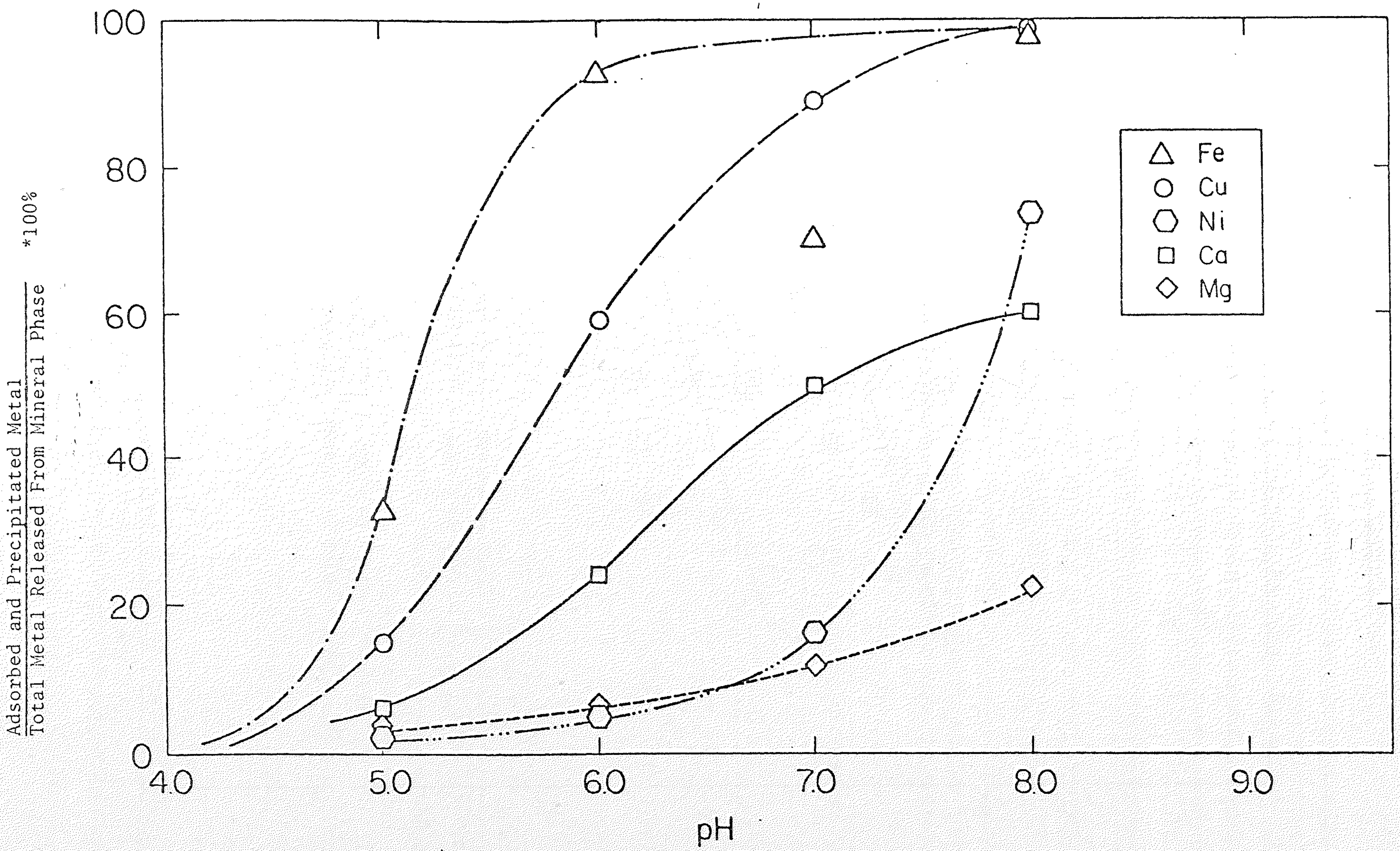
$\log [Zn^{2+}] = -0.769\ pH + 4.546 \qquad r^2 = 0.477$

For pH < 7

$\log [Co^{2+}] = -0.147\ pH + 1.305 \qquad r^2 = 0.372$

$\log [Zn^{2+}] = -0.147\ pH + 0.6984 \qquad r^2 = 0.468$

Figure 5.6 Metal Removal as a Function of pH in Batch Reactors



field. Data from Hoffmann et al. (1979) indicated the rate of nickel leaching varied with $(H^+)^{0.2}$ as compared with exponential values of 0.15 to 0.35 for copper, nickel, cobalt and zinc in the field (see Figures 5.4 and 5.5). The field computation incorporated the assumption that the leaching rate was directly proportional to the observed concentration.

Rock composition was also a factor in trace metal leaching rates in both the Erie piles and column experiments. At Erie the Seep 3 flow was generated from a lean ore pile and the EM-8 and Seep 1 flows were from waste rock piles. The trace metal leaching rates for a given year from the lean ore pile were consistently greater than those from waste rock (with the exception of zinc in 1978). The mineralized gabbro in column experiments also yielded greater trace metal leaching rates than the unmineralized samples.

Generation of Acid Conditions

6.1 Introduction

Acid is generated by the oxidative dissolution of iron sulfides and consumed by dissolution of silicate minerals and reaction of aqueous components such as bicarbonate (HCO_3^-) with hydrogen ions. The net effect of the acid producing and acid consuming reactions determines the change of pH in a system.

6.2 Relevant Literature

Acid mine drainage is commonly associated with the oxidative dissolution of pyrite (FeS_2) via the mechanism in reaction 6.1; the acid production is a result of iron oxidation and precipitation and oxidation of $S_2^=$ (Shumate et al., 1969).

$$FeS_2 + \frac{7}{2} H_2O + \frac{15}{4} O_2 = Fe(OH)_3 + 2SO_4^= + 4H^+ \qquad (6.1)$$

$$Fe^{2+} + \frac{1}{4} O_2 + \frac{5}{2} H_2O = Fe(OH)_3 + 2H^+ \qquad (6.2)$$

$$S_2^= + H_2O + \frac{7}{2} O_2 = 2SO_4^= + 2H^+ \qquad (6.3)$$

The major sulfide minerals present in the Duluth gabbro (Stevenson et al., 1979) are pyrrhotite ($Fe_{1-x}S, 0< x<0.2$), chalcopyrite ($CuFeS_2$), cubanite ($CuFe_2S_3$) and pentlandite ($(Fe, Ni)_9S_8$). Minor sulfide minerals include violarite (Ni_2FeS_4), mackinawite ($(Fe, Ni)_{1.1}S$), pyrite (FeS_2), Sphalerite ($(Zn,Fe)S$), and bornite (Cu_5FeS_4).

The acid producing reactions in the dissolution of iron sulfides in which sulfur occurs as $S^=$ are the oxidation of ferrous to ferric iron and subsequent precipitation of ferric hydroxide.

$$Fe^{2+} + H^+ + \frac{1}{4}O_2 = Fe^{3+} + \frac{1}{2}H_2O \tag{6.4}$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3(s) + 3H^+ \tag*{(6.5)[1]}$$

Reaction 6.2 is the sum of reactions 6.4 and 6.5 and indicates the generation of 2 moles of H^+ for each mole of Fe^{2+} oxidized. Oxidation of sulfide to sulfate involves no generation or consumption of protons as is demonstrated by reaction 6.6. Oxidation of sulfide to oxidation states less than the +4 state (e.g.,to $SO_3^=$) is an acid consuming reaction as is presented in reactions 6.7 to 6.10 (Nelson, 1978).

$$S^= + 2O_2 = SO_4^= \tag{6.6}$$

$$S^= + 2H^+ + \frac{1}{2}O_2 = S^o + H_2O \tag{6.7}$$

$$S^= + H^+ + O_2 = \frac{1}{2}S_2O_3^{2-} + \frac{1}{2}H_2O \tag{6.8}$$

$$S^= + \frac{3}{2}H^+ + \frac{9}{8}O_2 = \frac{1}{4}S_4O_6^{2-} + \frac{3}{4}H_2O \tag{6.9}$$

$$S^= + \frac{4}{3}H^+ + \frac{4}{3}O_2 = \frac{1}{3}S_3O_6^{2-} + \frac{2}{3}H_2O \tag{6.10}$$

$$S^= + \frac{3}{2}O_2 = SO_3^{2-} \tag{6.11}$$

If sulfide is oxidized to sulfate the oxidative dissolution of ferrous sulfide can be expressed as

$$FeS(s) + \frac{9}{4}O_2 + H_2O = \frac{1}{2}Fe_2O_3(s) + SO_4^= + 2H^+ \tag{6.12}$$

The acid production due to this reaction will increase with increasing iron sulfide content of the material leached.

[1] The $Fe(OH)_3$ will react to form $Fe_2O_3(s)$ with no contribution to the acid balance.

Dissolution of silicate minerals present in the gabbro matrix is an acid consuming reaction. Plagioclase and olivine are the most abundant silicate minerals (see Table 6.1); their dissolution reactions are presented below (Helgeson, 1969; Hem, 1970).

$$NaAlSi_3O_8 + H^+ + 4.5H_2O = 0.5\ Al_2Si_2O_5(OH)_4 + Na^+ + 2H_4SiO_4 \qquad (6.13)$$

$$CaAl_2Si_2O_8 + 2H^+ + H_2O = Al_2Si_2O_5(OH)_4 + Ca^{2+} \qquad (6.14)$$

$$5Mg_2SiO_4 + 8H^+ + 2H_2O = Mg_6(OH)_8Si_4O_{10} + 4Mg^{2+} + H_4SiO_4 \qquad (6.15)$$

In each case the metal release is equal to the acid consumption, both measured in equivalents. This occurrence was experimentally observed by Busenberg and Clemency (1976) during the first minute of silicate dissolution (oligoclase, anorthite, microcline):

$$(H^+)\ \text{consumed} = \Sigma Me*z \qquad (6.16)$$

Where Me are molar concentrations of cations released and z, their charge. The number of cations released during the first minute was approximately equal to the number of cations present in one unit cell over the entire surface of the solid ($8.3 \mu m/m^2$ for anorthite). Luce et al. (1971) observed that in dissolution of magnesium silicates (serpentine-lizardite, forsterite, enstatite) the rapidly exchanged ions corresponded to a layer thinner than one unit cell and concluded that transport in the solid itself was rate contolling. Busenberg and Clemency (1976) described the weathering of feldspars as a four stage process:

1. an initial ion exchange stage lasting approximately 1 minute during which the surface cations were replaced by hydrogen ions from the bulk solution:
2. an up-to-4-day non-parabolic stage characterized by the very rapid release of cations and silicic acid into the bulk solution;

Table 6.1 Mean mineralogical composition of test samples (volume percent). From Stevenson et al (1979)

GABBRO CLASSIFICATION	"WASTE ROCK" DP9001	"LEAN ORE" AX9001	"DISSEMINATED ORE" US9001	AX9002	AX9003	AX9005	IP9002	IP9003	Average	"SEMI-MASSIVE ORE" DP9002	AX9004
Plagioclase	64.041	59.112	64.881	61.457	47.363	47.403	65.443	66.166	58.786	47.242	47.855
Sericite	1.569	2.176	0.188	2.518	1.911	0.245	2.683	0.373	1.320	0.069	0.091
Olivine	13.996	10.510	16.173	13.586	18.267	25.841	16.308	17.123	17.823	10.766	1.513
Clinopyroxene	7.604	11.185	7.237	6.809	5.024	7.622	3.723	3.717	5.689	26.102	2.656
Orthopyroxene	2.763	3.716	1.834	2.882	1.407	2.132	0.231	0.618	1.517	2.315	18.472
Monocrystalline amphibole	0.054	3.567	--[b]	0.095	12.225	0.066	1.387	1.055	2.471	--	0.025
Fibrous amphibole	0.005	0.288	--	0.835	0.850	--	0.934	0.077	0.366	--	0.024
Chlorite	1.696	1.136	1.349	1.950	3.887	1.337	2.078	2.612	2.202	0.403	0.145
Serpentine	0.016	0.257	0.097	0.441	0.033	7.659	0.731	0.026	1.498	0.014	--
Iddingsite	0.017	0.075	0.172	0.006	0.019	0.194	0.079	0.064	0.090	0.053	--
Talc	--	--	--	--	--	0.006	0.061	0.463	0.087	--	--
Biotite	3.284	1.738	3.785	3.037	3.010	2.431	1.696	1.788	2.624	5.031	4.475
Smectite	--	0.021	0.051	0.030	0.053	--	0.025	0.026	0.031	--	--
Celadonite	0.014	--	--	--	--	--	--	--	--	--	--
Opaques[a]	4.565	5.098	4.025	4.776	5.190	4.720	3.474	5.365	4.592	7.923	19.239
Chalcopyrite-cubanite	0.133	0.769	0.875	0.962	1.458	1.355	1.403	1.778	1.305	1.341	3.231
Pentlandite	0.032	0.037	0.102	0.012	0.113	0.043	0.117	0.025	0.069	0.341	0.161
Pyrrhotite	0.403	0.844	0.882	1.093	1.105	0.497	0.953	1.571	1.017	3.073	12.816
Ilmenite-magnetite	3.995	3.447	2.164	2.694	2.510	2.885	0.998	1.989	2.197	3.143	2.564
Graphite	--	--	--	0.015	0.004	--	--	--	0.003	0.025	0.467
Spinel	--	--	--	0.009	--	--	--	--	0.001	--	--
Myrmekite	--	--	0.106	0.042	--	--	0.288	0.065	0.084	--	--
Apatite	0.182	0.085	0.075	0.149	0.172	0.346	0.050	0.013	0.134	0.074	0.118
Epidote	0.167	0.953	0.017	0.203	0.470	--	0.698	0.322	0.255	--	--
Allanite	--	--	--	0.090	--	--	0.007	0.051	0.025	--	--
Calcite	0.026	0.056	0.007	0.065	0.017	--	0.089	0.077	0.042	0.006	--
Quartz	--	--	--	--	--	--	--	--	--	--	0.037
Cordierite	--	0.027	--	1.515	0.106	--	0.013	--	0.272	--	5.350

[a] The value shown for opaques is the sum of the 5 following values

[b] -- means not detected or not present (0%).

3. a diffusion-controlled parabolic stage lasting approximately 19 days;

4. a steady-state stage characterized by the very slow release of cations and silicic acid.

Calcium, magnesium, sodium and potassium may also be present in solution as the result of the dissolution of chloride salts[1]:

$$Me^{z+}Cl_z(s) = Me^{z+} + zCl^- \qquad (6.17)$$

Equation 6.16 must therefore be adjusted to

$$(H^+) \text{ consumed} = \Sigma Me{*}z \;-\; (Cl^-) \qquad (6.18)$$

since reaction 6.17 adds Me^{z+} to solution but involves no consumption of H^+.

6.3 Acid Generation Model

The dissolution of one mole of ferrous sulfide (FeS) with oxidation of sulfide to sulfate results in the production of one mole of sulfate and two moles of H^+.

$$FeS + \frac{9}{4} O_2 + H_2O = \tfrac{1}{2}Fe_2O_3(s) + SO_4^= + 2H^+ \qquad (6.19)$$

The release of one mole of Me^{z+} from a silicate mineral phase indicates the consumption of z moles of H^+. The net rate of acid production due to these processes can be written

$$\frac{d\,(acidity)}{dt} = \frac{2\,d(SO_4^=)}{dt} - \Sigma \frac{d(Me^{2+})*z}{dt} + \frac{d(Cl^-)}{dt} \qquad (6.20)$$

(6.20)

---

[1] the chloride content of the gabbro is minimal but salt water was encountered in Amax test shafts.

If the net change in acidity is positive, $R_a = 2\ (SO_4^=)/\Sigma(Me^{z+})*z > 1$ and if net acid production is negative, $R_a < 1$. Agnew and Corbett (1969) found that the sum of acidity and hardness $((Ca^{2+}) + (Mg^{2+}))$, in consistent units, was equal to the sulfate concentration for acid mine drainage in Indiana. Morth et al. (1972) observed a similar occurrence at 7 sites at the McDaniels Research Site in southeastern Ohio. Paces (1972) discussed a proton balance based on chemical analyses of groundwater circulating in felsic rocks.

6.4 Laboratory Results and Discussion

Data from batch reactor experiments provide qualitative support for the approach presented in equation 6.20 and Figure 6.1. The increase in $(SO_4^=)$ is accompanied by a parallel increase in (H^+) although a quantitative verification of the equation does not exist.

The theoretical change in (H^+) at $t = 860$ hours is

$$2 * 162 - 2 * 107 = 110\mu M \tag{6.21}$$

While the actual (H^+) is 19 $\mu\underline{M}$. This discrepancy may be accounted for by (Na^+) and (K^+), which were not measured, and by sulfate generated by dissolution of metal sulfides which do not produce acid (e.g., CuS,NiS,ZnS,CoS).

In order to correct for sulfate generated by dissolution of metal sulfides other than iron sulfide it is necessary to muliply the sulfate concentration by Θ, where

$$\Theta = \frac{(SO_4^=)\text{ due to iron sulfide dissolution}}{(SO_4^=)\text{ total}} \tag{6.22}$$

If the rate of metal sulfide oxidation were dependent only on the amount of metal sulfide present, iron sulfide oxidation would contribute 86% of the sulfate concentration (since 86% of the sulfide in the solid was associated with iron). Batch reactor data indicate that 10% of the sulfate concentration

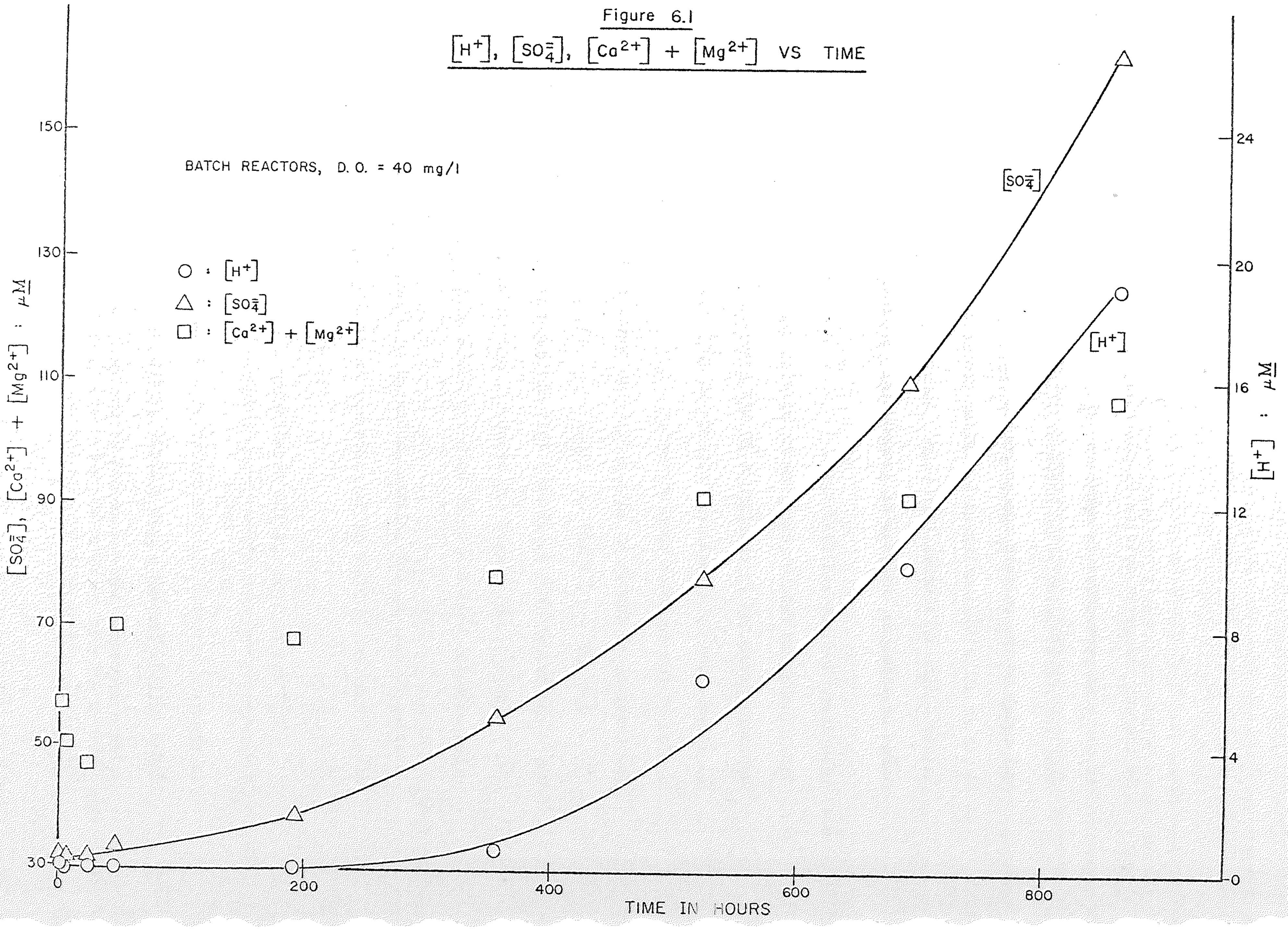


Figure 6.1

$[H^+]$, $[SO_4^=]$, $[Ca^{2+}] + [Mg^{2+}]$ VS TIME at pH 5 was due to oxidation of copper and nickel sulfides. Using a value of $\Theta = 0.86$,

$$(H^+) = 2\,\Theta\,(SO_4^=) - \Sigma\,(Me^{z+})*z = 65\ \mu\underline{M}. \tag{6.23}$$

6.5 Field Results and Discussion

Water quality data from 10 sites in the copper-nickel study area were analyzed for a relationship between concentrations of sulfate and metals released from silicate minerals. The ratio

$$R_A = 2\,(SO_4^=)\,/\,\Sigma\,(Me^{z+})z - (Cl^-) \tag{6.24}$$

was calculated for all water quality samples with results from the Amax test piles presented in Figure 6.2.[1]

The average values of R_A for each site are presented in Table 6.2 (Na^+, K^+ and Cl^- were not analyzed in all cases). An increase in R_A should be accompanied by a decrease in pH. The mean of all values from the Amax piles, $R_A = 0.89$, indicates that acid consumption is generally greater than acid production, which is consistent with the median pH values (7.5 to 7.8) observed at 5 of the 6 piles (Table 6.2). The greatest R_A value among the Amax piles was observed at FL-5 where the lowest median pH was observed. The variation of R_A with pH at FL-5 is presented in Figure 6.3 and indicates, although not conclusively, the increase of R_A with decreasing pH.

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[1] The calculation of the change in acidity is impractical since the concentrations of $SO_4^=$ and Me^{z+} are on the order of 10^{-2} $\underline{M}$ and change in (H^+) is generally less than 10^{-4} $\underline{M}$. The general trend of the predicted change in acidity is reflected by the trend observed for R_A.

Figure 6.2

FREQUENCY ANALYSIS FOR R_A

(AMAX Files FL 1 — FL 6)

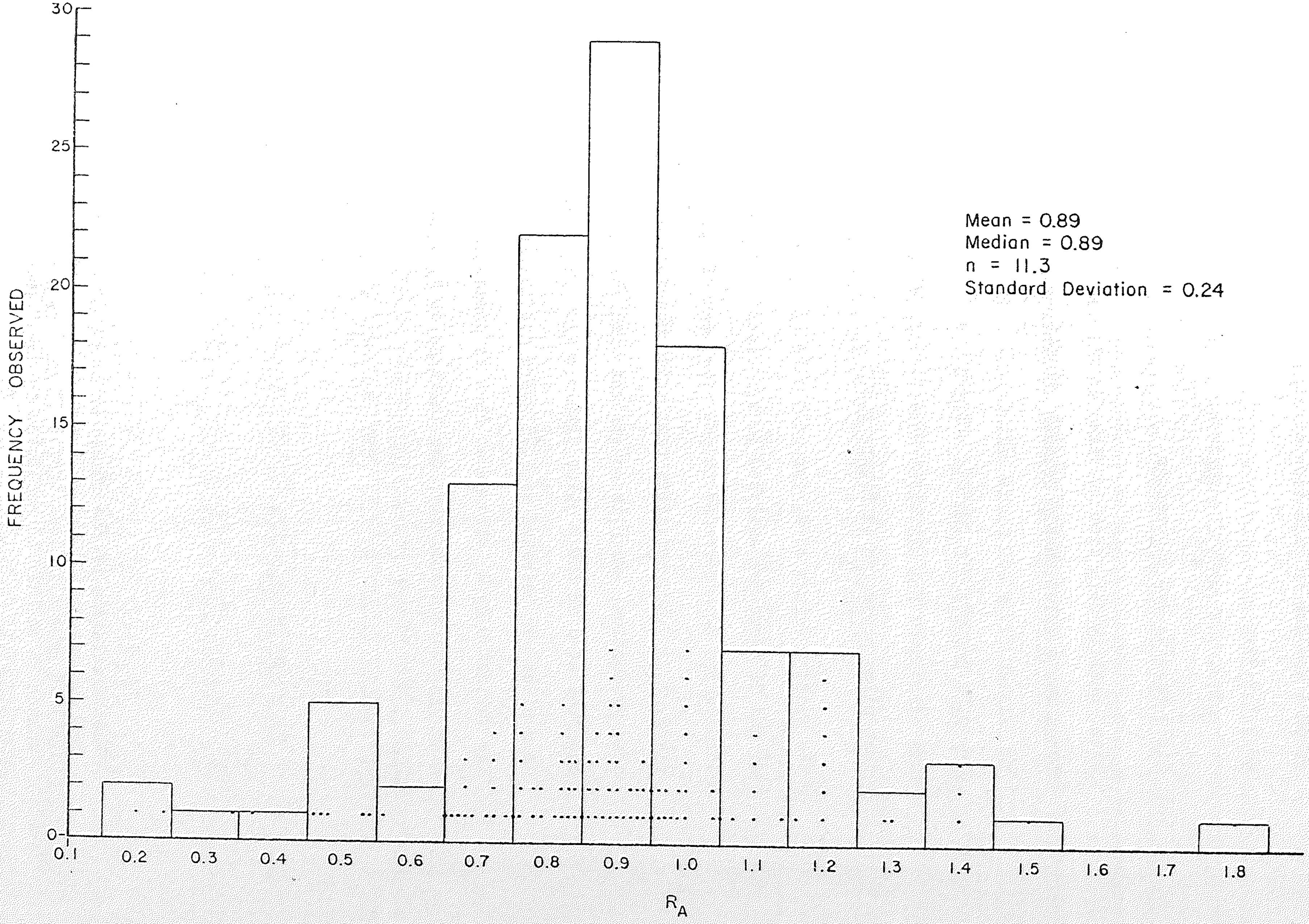


Table 6.2 R_A, Median pH and Rock Composition at Field Sites

SITE	R_A	pH MEDIAN	n	PARAMETERS USED	DESCRIPTION	% S as[1] FeS	COMPOSITION (Wt %)[2] S	FeS	CuS	NiS
FL-1	0.92	7.8	16	Ca,Mg,Na,K,Cl,SO_4	Test Stockpile	65	0.6	1.1	0.51	0.12
FL-2	0.95	7.6	12	"	"	65	0.6	1.1	0.51	0.12
FL-3	0.90	7.5	10	"	"	65	0.6	1.1	0.51	0.12
FL-4	0.84	7.5	45	"	"	65	0.6	1.1	0.51	0.12
FL-5	0.96	5.4	18	"	"	86	1.45	3.4	0.45	0.14
FL-6	0.88	7.6	12	"	"	71	0.83	1.6	0.57	0.14
EM-8	0.89	7.2	13	Ca,Mg,SO_4	Waste rock Stockpile	NA[3]	NA	NA	0.057[4]	0.014[5]
Seep-1	0.96	7.0	11	Ca,Mg,SO_4	"	NA	NA	NA	0.043[4]	0.014[5]
Seep-3	0.94	7.0	7	Ca,Mg,SO_4	Lean Ore Stockpile	NA	NA	NA	0.29[4]	0.08[5]
US Steel Pit	1.21	5.4	13	Ca,Mg,SO_4	Bulk sample site	60	0.9	1.5	0.80	0.26

[1] on a molar basis

[2] calculations based on weight composition using S,Cu,Ni and assuming Co,Zn negligible

[3] NA: not available

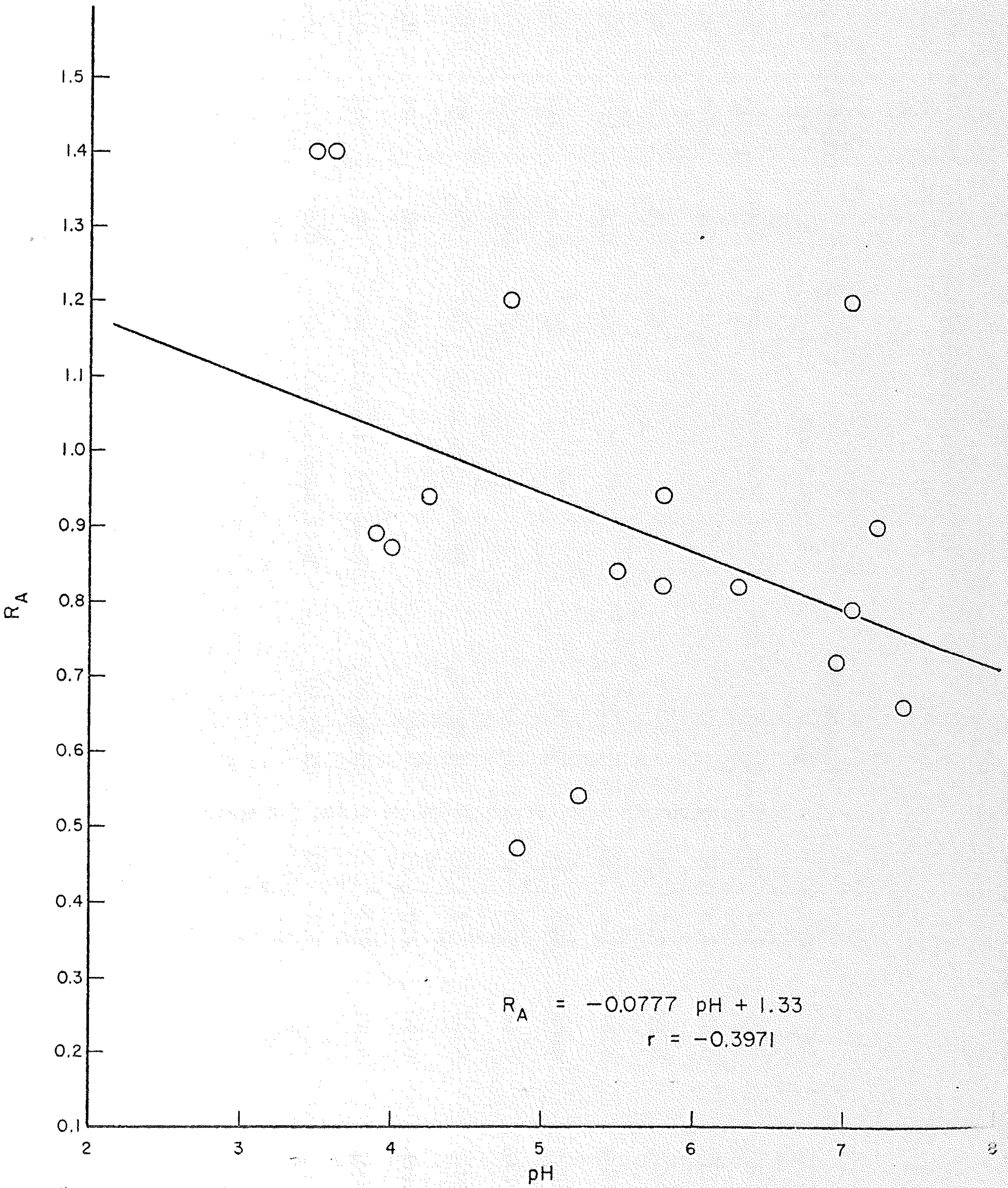
[4] weight percent Cu

[5] weight percent Ni

Figure 6.3

R_A^* VS pH

(1978 Data for AMAX File FL 5)



$^*R_A = 2[SO_4^=]/(\Sigma[Me^+] - [Cl^-])$

An estimation of Θ was made based on samples taken at FL-5 for which pH was less than 5. It was assumed that all Cu, Ni, Co and Zn were transported from the site of metal sulfide oxidation. The calculation of Θ was made using equation 6.25; the resultant values ranged from 0.89 to 0.98, with mean and median equal to 0.93.

$$\Theta = \left((SO_4^=) - (Cu^{2+}) - (Ni^{2+}) - (Co^{2+}) - (Zn^{2+}) \right) / (SO_4^=) \qquad (6.25)$$

The mole fraction of sulfide present as iron sulfide was 86%.

6.6 Summary

The acid producting potential of the Duluth gabbro is dependent on the relative rates of dissolution of iron sulfides and silicate minerals. These rates can be monitored by aqueous concentrations of sulfate and Me^{z+}- (Cl^-) respectively. The theoretical acid production for waters of low alkalinity can be represented by

$$\frac{d(H^+)}{dt} = \frac{2\Theta\, d(SO_4^=)}{dt} + \frac{d(Cl^-)}{dt} - \Sigma \frac{d(Me^{z+})z}{dt} \qquad (6.26)$$

If the rate of iron sulfide dissolution exceeds that of metal silicate dissolution, acid will be produced. The rate of acid production from leaching reactions depends on the composition of the solid leached. The acid producing potential increases with the iron sulfide content; the acid consumption capacity increases with silicate mineral content. If the rate of silicate dissolution decreases with time as was the case in the batch reactor system, the rate of net acid production will increase with time.

Acid leachate has been observed in the copper-nickel study area at the U.S. Steel bulk sample site and the Amax test pile FL-5. The pH at Amax test pile FL-6 has decreased and varies between 6 and 7. The iron sulfide content in rock at these sites is 1.5, 3.4 and 1.6%, respectively, which is higher than at other sites studied.

Precise prediction of acid generation rates involves determination of the iron sulfide and silicate mineral dissolution rates. Nine types of iron sulfides and numerous silicate minerals have been identified in the Duluth gabbro (Stevenson et al, 1979). Determination of dissolution rates of these minerals under conditions of variable pH would be required to accurately quantify the rate of acid production presented in equation 6.26. Additional study of the generation of acid leachate from the Duluth gabbro will provide additional insight for estimating rates from an empirical approach. The study of dissolution rates of individual minerals under controlled conditions would also contribute useful information for assessing the potential for acid production.

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