

CN 043

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PROGRESS REPORT

to

COPPER-NICKEL REGIONAL TASK FORCE

MECHANISM AND CONTROL OF METAL SULFIDE IN

GABBRO MINING-RELATED SOLIDS

JANUARY 10, 1977

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GABBRO MINING-RELATED SOLIDS

Dr. Steven J. Eisenreich  
Dr. Michael R. Hoffmann  
Mr. Kim Lapakko  
Environmental Engineering Program  
Department of Civil & Mineral  
University of Minnesota  
Minneapolis, MN 55455

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## Field Leaching Studies

1. Sampling. Water samples were collected by the Cu-Ni staff at various locations in Unnamed Creek, at Seepages 1, 2 and 3, in the connecting bog area and from surface waters of Bob Bay in Birch Lake from July-September, 1976. Samples were transported to the Kawishiwi River Laboratory (U.S. Forest Service) and filtered where appropriate. Samples were separated into aliquots for analysis of selected metals, calcium, magnesium, dissolved inorganic and organic carbon, dissolved reactive silica, chloride, sulfate and hardness (deleted after initial analyses). After acidifying metal fractions, samples were transported to the University of Minnesota for analysis.

## 2. Analytical Procedures.

a. General Parameters. The following techniques were applied to general parameter analysis:

<u>Parameter</u>	<u>Technique</u>
Hardness	EDTA Titration
Si	Molybdosilicic Acid (Colorimetric)
Cl	Ion Specific Electrode
SO <sub>4</sub>	Turbidimetric
DOC, DIC	Infrared Analyzer

b. Metals. Aqueous samples have been analyzed for heavy metals, calcium and magnesium with a Perkin-Elmer Model 360 Atomic Absorption Spectrophotometer (AAS) fitted with a Deuterium Background Corrector and an HGA 2100 Graphite Furnace when operated in the flameless mode. Calcium (Ca) and magnesium (Mg) were measured in the flame mode in samples (diluted where necessary with DDW) containing ~1 % La(NO<sub>3</sub>)<sub>3</sub>. Fe, Cu, Ni and Zn were determined using an air-acetylene flame with sample responses compared to a standard curve which was prepared daily. Blanks, standards and EPA analyzed water samples were run frequently to check metal results.

Metals analyzed in the flameless mode using the HGA 2100 Graphite Furnace were Cu, Ni, Fe, Co, Cd, Pb and Zn with Mn and Al to be added. Settings for programmed operation of the graphite furnace are listed in Table I.

Table II details the listed detection limits and practical working limits for metal analyses by flameless AAS. The practical working limits were obtained by two different approaches. In the first case, the practical working limit was determined as the concentration of standard exceeding the background noise level by a factor of two. In the second case, the practical working limit was determined as the standard deviation of a series of metal measurements

Table I.

Instrumental Settings for Programmed Operation of HGA 2100<sup>a</sup>

<u>Metal</u>	<u>Drying</u>		<u>Charring</u>		<u>Atomization</u>	
	Time (sec)	Temp. (°C)	Time (sec)	Temp. (°C)	Time (sec)	Temp. (°C)
Cd	30	125	10	350	7	1500
Co	30	125	10	850	10	2600
Cu	30	125	10	800	9	2500
Fe	30	125	10	900	10	2500
Ni	30	125	10	1000	10	2500
Pb	30	125	10	500	7	2000
Zn	30	125	10	400	7	2000

<sup>a</sup>A 50  $\mu$ l sample is assumed.

Table II.

Detection and Practical Working Limits  
for Metal Analysis by AAS (Flameless)

<u>Metal</u>	<u>Detection Limit</u> (pg)	<u>Working Limit</u> (pg)	<u>Conc.</u> (ppb)
Cu	50	25	0.5
Ni	140	200	1.0
Fe	30	25	0.5
Zn	1	2	0.04
Cd	2	2	0.04
Pb	50	50	1.0
Al	120	100	2.0

Table III.

Precision of Metal Analyses by AAS (Flameless)

Metal	Rel. Std. Dev. (%)	Concentration (ppb)
Zn	1.5	1
	2.9	2
Cu	3.7	5
	2.5	25
Ni	7.8	25
	2.3	100
Fe	5.4	25
	0.8	50
Cd	2.4	5
Pb	4.3	10
	3.7	25
Al	3.7	50

at 10 ppb (10  $\mu\text{g}/\text{l}$ ) with a 50  $\mu\text{l}$  injection and 5 mV full scale on the Perkin-Elmer Model 56 Recorder. The stated working limits in pg and  $\mu\text{g}/\text{l}$  (Table I) is the concentration of metal exceeding the background signal by a factor of two. However, both techniques yielded similar results.

Precision of metal determinations in the flameless AAS mode were determined by repetitive analysis of metal standards and EPA samples. Table III lists the precision of metal determination for Zn, Cu, Ni, Fe, Cd, and Pb at one or two concentrations in terms of relative standard deviation.

### 3. Evaluation of Metal Analysis Procedures by Flameless AAS.

A detailed investigation of the optimum operating parameters for metal analysis by flameless AAS was initiated to evaluate anomalies noted in analytical results. Two aspects of that study are reported here because of their relevance to trace metal analysis of Cu-Ni-related aqueous samples.

Three types of natural water samples were obtained to demonstrate the effect of background correction and quantification procedures on metal results. Table IV lists the average concentrations of general parameters for bog, river and leachate samples. Depending on metal concentration, each sample was diluted by factors of 1 to 25x to yield concentrations in the linear response range of the AAS technique. The samples were chosen to demonstrate the variations in natural water which might be encountered: bog (high organic, high Fe, low inorganic), leachate (high inorganic, low organic, high metal) and river (moderate inorganic, organic, and metals; higher suspended solids).

The deuterium background corrector ( $\text{D}_2$ ) is used to correct for non-atomic absorption and furnace emission contributions to peak height. Samples of the bog, leachate and river were analyzed in duplicate for Cu, Ni, Pb, Cd, Fe and Co with and without background correction (Table V). In all cases, the metal concentrations were determined by comparison to standard curves.

With the exception of Fe, all metals studied exhibited different behavior with and without  $\text{D}_2$  correction. In general, the metal concentrations determined with the  $\text{D}_2$  were significantly lower than those without the  $\text{D}_2$  indicating intense non-atomic absorption and/or furnace emission contributions to absorbance. The bog matrix with high organic concentrations and the river matrix affects Cu, Ni and Co response the greatest while all metals studied except Fe, exhibit similar behavior in the leachate. The data clearly points out that background correction is necessary for accurate trace metal analysis in natural water samples. Some deviations in response in standards was also noted suggesting that background correction is necessary for all sample matrices.

Quantification of metal levels in aqueous samples is commonly performed by comparison of peak heights to a standard curve. Calculation of metal concentrations by comparison of sample response to that of sample plus single

Table V.

Comparison of FAAS Analyses of Trace Metals  
With and Without Deuterium Background Correction

	<u>BOG</u>		<u>LEACHATE</u>		<u>RIVER</u>	
	<u>D<sub>2</sub></u>	<u>NoD<sub>2</sub></u>	<u>D<sub>2</sub></u>	<u>NoD<sub>2</sub></u>	<u>D<sub>2</sub></u>	<u>NoD<sub>2</sub></u>
Cu	8.2	23.2	11.2	31.3	7.3	12.0
Ni	41.1	57.0	47.8	54.5	12.7	42.5
Pb	11.8	11.5	3.8	12.0	3.4	2.6
Cd	0.24	0.37	0.55	0.82	0.16	0.23
Fe	26.1	25.3	32.6	35.1	18.8	17.1
Co	7.1	31.7	11.5	26.0	1.2	9.3

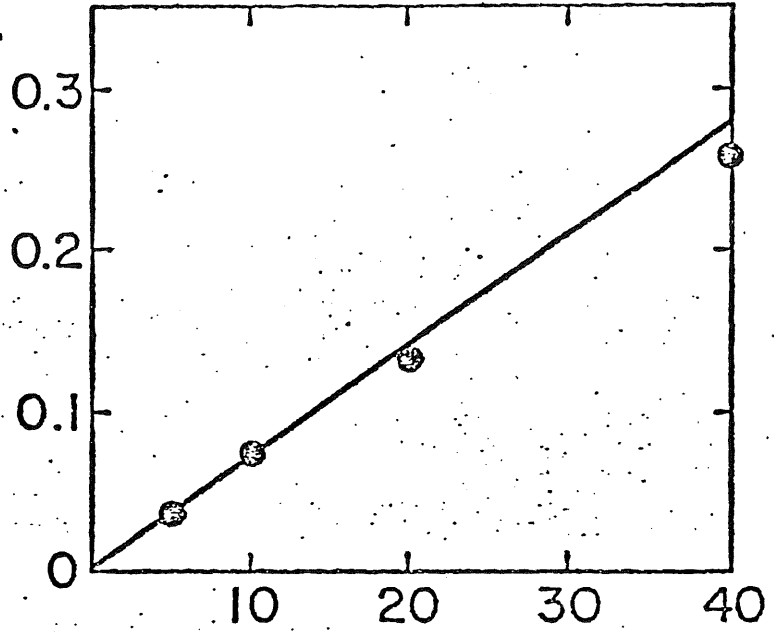
All values given in  $\mu\text{g/l}$  (ppb)



Figure I.

Cu

STANDARD CURVE



STANDARD ADDITION

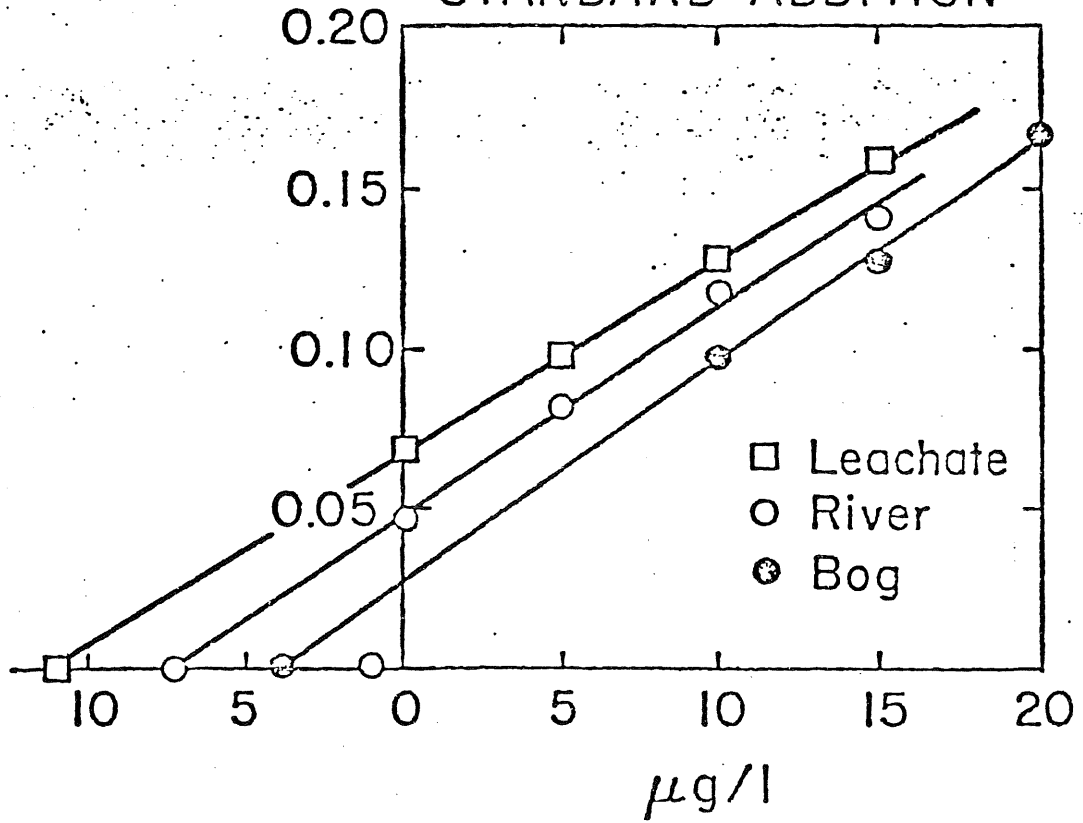
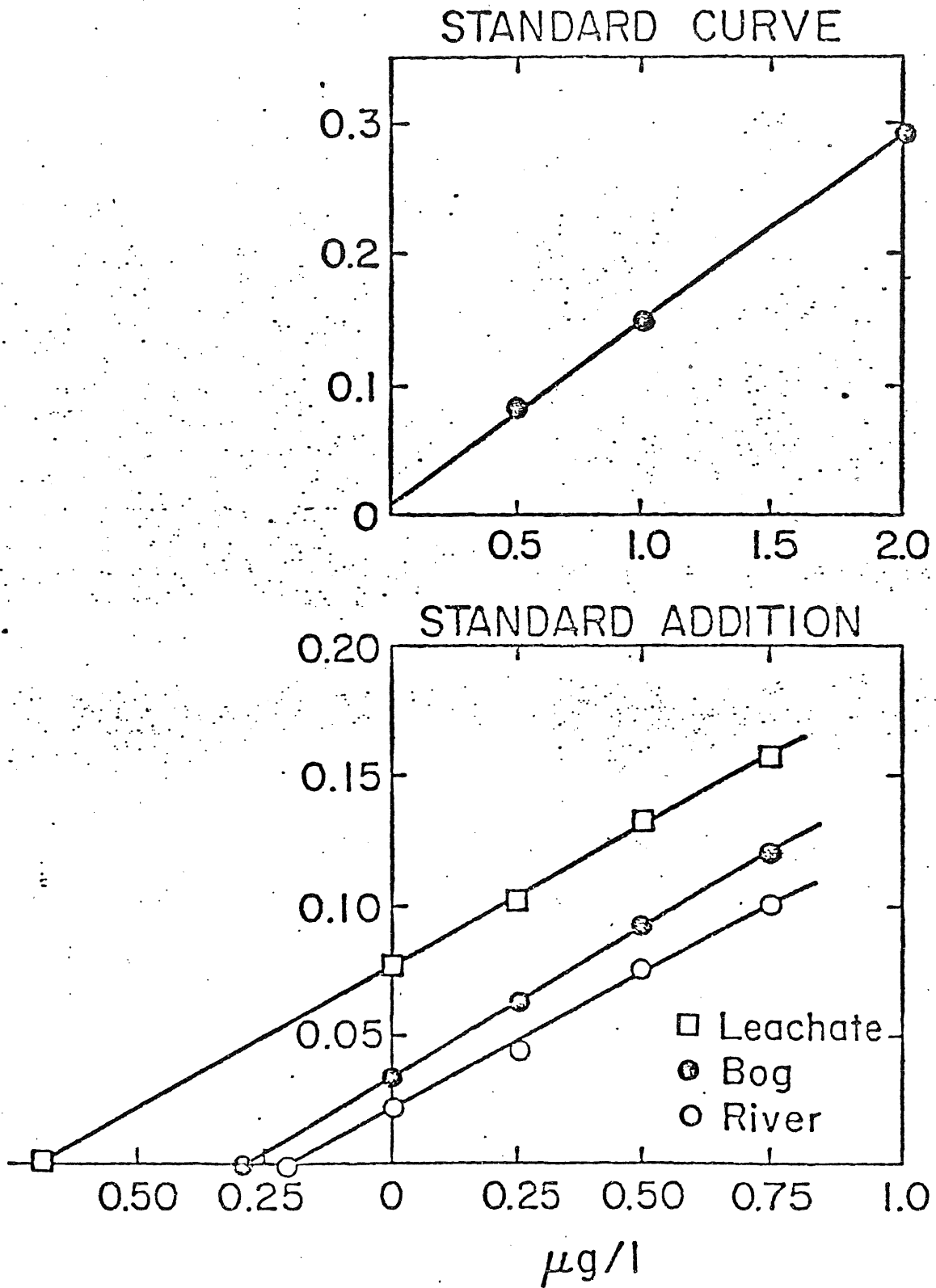


Figure II.

Cd



standard spike response is commonly used in polarographic techniques and has been applied to FAAS analyses. The method most often employed to correct for matrix effects is standard addition whereby successive standard metal additions and measurements are performed on one sample. Although time consuming, the standard addition technique is the standard quantification procedure.

A comparison of the three methods of metal calculation was performed for Cu, Ni, Pb, Cd, Fe and Co in bog, leachate and river matrices with  $D_2$  correction. Results are detailed in Table VI and examples of calculation plots in Figures I and II. In general, the single spike addition technique yields results higher than either the standard curve or standard addition procedures (Figure III). This behavior is likely due to analytical and statistical uncertainty in a single measurement. However, the standard curve and standard addition procedures also yield variable concentrations depending on the metal studied and the sample matrix. In some cases, the standard curve appears to give better results than standard addition because the added metal may not be homogeneously distributed throughout the solution compartments; i.e., the spike metal does not respond as the native aqueous metal. Reasons for this behavior may include stable, strong complex formation and variations in salt volatility. Additional work in this area is required. At the present time, the standard curve or standard addition procedures must be applied selectively depending on metal and sample matrix to yield optimum results. For many situations, the easier and more efficient standard curve comparison is adequate to generate accurate metal concentrations based on analysis of exhaustively-studied samples.

#### 4. Field Leaching Data.

The following tables of data (Tables VII A-L) represent chemical analyses of field samples collected between 7-01-76 and 9-31-76 in Unnamed Creek, nearby seepages, and Bob Bay-Dunka Bay of Birch Lake. In addition to the general parameters and metals listed, a survey of other metal concentrations in selected samples is presently being conducted. Analytical data for samples collected between 10-01-76 and the present is being generated and will be available in the near future.

#### 5. General Observations of Chemical Field Data.

In the absence of flow data at various locations in Unnamed Creek and nearby seepages, several general observations can be made of the chemical data with respect to geochemical cycling and interactive mechanisms.

a. Table VIII lists the average concentrations of general parameters and metals, standard deviations and number of data points considered for EM-1 (mouth of Unnamed Creek), EM-8 (near base of Gabbro pile), EMS-1 and EMS-3 (both Gabbro seepages which eventually drain into Unnamed Creek). The chemical composition of EMS-1 is typified by high alkalinity, specific conductance, inorganic and organic carbon, sulfate and higher pH relative to EMS-3. Concentrations of trace, heavy and alkaline metals are considerably higher in EMS-3 compared to EMS-1 except for Fe which averages  $\sim 10$  x the

Table VI.

## COMPARISON OF QUANTIFICATION PROCEDURES

## IN FAAS

	<u>Bog</u>			<u>Leachate</u>			<u>River</u>		
	S.C.	S.S.	S.A.	S.C.	S.S.	S.A.	S.C.	S.S.	S.A.
Cu	8.2	11.3	3.8	11.2	12.7	12.1	7.3	6.6	9.2
Ni	41.1	129.0	43.9	47.8	40.5	84.5	12.7	17.4	12.3
Pb	11.8	19.0	23.9	3.8	9.1	8.3	3.4	2.4	4.6
Cd	0.24	0.28	0.32	0.55	0.73	0.70	0.16	0.25	0.15
Fe	26.1	20.1	31.1	32.6	86.1	48.9	18.8	13.4	21.7
Co	ND	ND	7.10	7.4	6.9	11.5	ND	ND	1.2

S.C.: Standard Curve

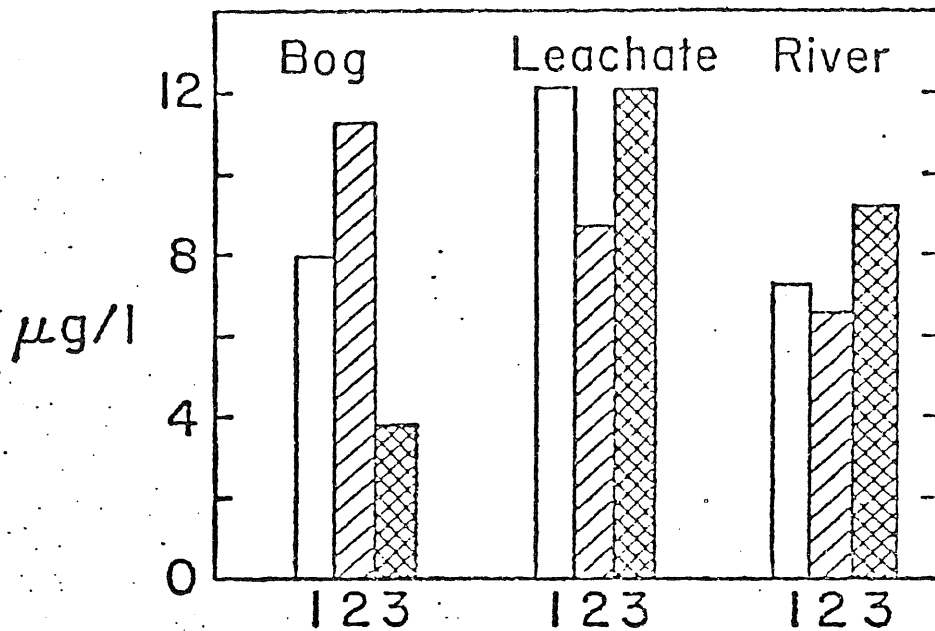
S.S.: Single Spike

S.A.: Standard Addition

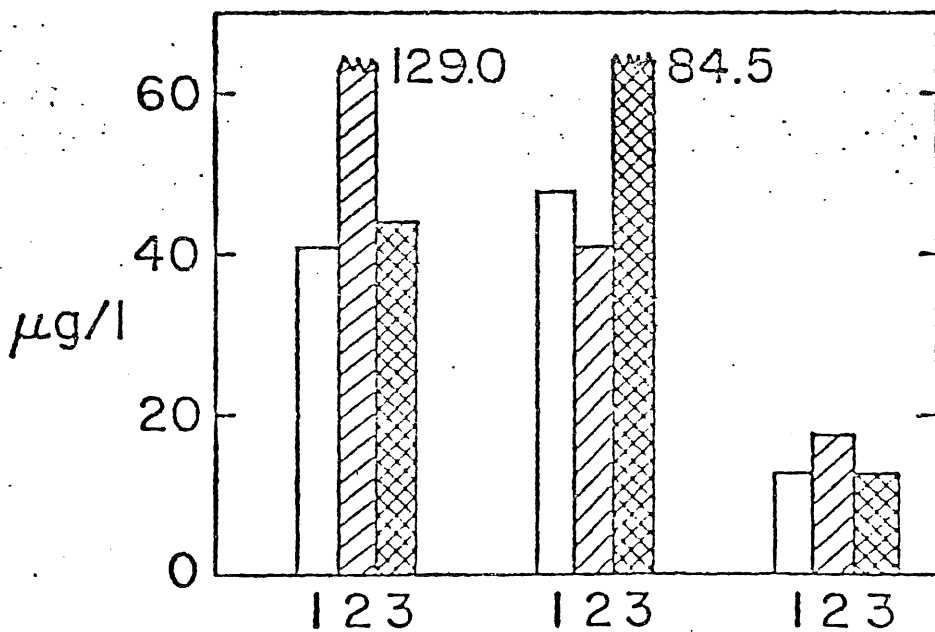
All values are given in  $\mu\text{g/l}$  (ppb)

Figure III.

Cu



Ni



- 1: Standard Curve
- 2: Single Spike
- 3: Standard Addition





Tab VII-C

SAMPLE SITE: Erie Mining Co. DATE: 7-27-76

1 2 3 4 5 6 7 8 9 10 Sep 1 Sep 2 Sep 3

PH	ALK	Spec. Cond	DIST	Cl	SO <sub>4</sub>	DOC	DIC	CU T	CO T	NI T	Fe T	Zn T	CO T	PB T	HN T	Ca T	Mg T	AT T	CD T
7.59	113	787	9.24	43.2	455	18.5	18.0	.007	.007	.171	.250	<.01				69.5			
7.60	108	1130	7.65	52.7	523	15.0	19.5	.005	.006	.171	.097	<.01				62.6			
7.70	97	847	10.3	35.1	317	16.5	15.5	.006	.005	.422	.268	<.01				55.4			
6.8	36	492	6.97	1.41	77.8	30.0	4.5	.001	.001	.042	.097	<.01				5.3			
7.5	97	83	10.4	49.9	132	15.5	15.5	.010	.010	.036	.236	<.01				10.0			
7.55	95	500	10.2	49.9	123	17.0	24.0	.013	.016	.016	.195	<.01				11.1			
7.01	133	2030	9.99	42.7	1409	19.5	26.5	.019	.022	2.00	.099	<.01				177			
7.0	130	2048	9.89	45.3	1337	20.0	28.0	.022	.022	1.97	.090	<.01				200			
7.0	184	3330	9.41	2.2	1095	1.5	28.0	.022	.022	1.89	.114	<.01				ND			
6.80	77	2732	11.3	49.8	2555	28.0	35.5	.019	.022	1.24	.710	<.01				ND			
				58.9	2001	17.5	10.0	.190	.190	20.0	.261	.383				226			
								NS	NS	NS	NS	NS				226			
								NS	NS	NS	NS	NS				226			
								NS	NS	NS	NS	NS				226			
								NS	NS	NS	NS	NS				226			





Table VII-E

SAMPLE SITE: Erie Mining Co. DATE: 8-26-76

	1	2	3	4	5	6	7	8	9	10	EMS-1	EMS-3
pH	7.36	8.3	9.82	-	7.80	8.01	-	7.40	9.32	-	7.34	7.50
ALK	105	108	104	-	103	88	-	130	136	-	188	99
Spec.	-	-	-	-	-	-	-	-	-	-	-	-
DRST	-	-	-	-	-	-	-	-	-	-	-	-
Cl	20.9	33.3	22.5	23.0	20.6	15.5	36.8	29.2	22.8	ND	29.3	38.5
SO <sub>4</sub>	243	368	215	331	-	78.0	1458	1564	1619	ND	2190	1539
DOC	21.0	21.8	21.0	21.6	17.3	16.7	23.8	26.5	24.9	0.6	42.8	23.8
DIC	14.2	14.4	14.4	12.7	14.4	12.4	13.7	19.5	19.8	0.2	25.2	13.7
CU T	.003	.004	.003	.004	.008	.007	.617	.018	.018	ND	.023	.617
F	.003	.004	.003	.003	.008	.005	.538	.016	.016	ND	.023	.617
M T	.105	.055	.194	.054	.191	.086	19.8	2.36	2.36	ND	1.10	19.2
F	.095	.052	-	.039	.666	.008	19.3	2.40	2.32	ND	1.10	19.2
Fe T	.195	.016	.098	.506	.064	.122	.752	.095	.126	ND	3.8	.733
F	-	.020	.091	.223	.023	.570	.057	.063	.063	ND	NS	.733
Zn T	<.01	<.01	<.01	<.01	<.01	<.01	.335	.038	.035	ND	.250	.330
F	<.01	<.01	<.01	<.01	<.01	<.01	.330	.035	.035	ND	.250	.330
CO T												
Pb T												
Mn T												
Ca T	42.3	65.0	46.0	52.4	72.0	21.7	-	230	241	ND	-	-



Table VII-C

SAMPLE SITE: Eric Mining Co. DATE: 9-21-76  
 6 7 8 9 10 EMS-1 EMS-3

	1	2	3	4	5	6	7	8	9	10	EMS-1	EMS-3
pH	8.0	8.05	8.1	-	7.55	8.1	-	7.65	7.35	-	7.30	7.25
ALK	109	118	106	-	107	99	-	145	152	-	220	119
Spec. Cond.	600	1140	617	-	760	346	-	2740	3018	-	3810	2900
DRSI	9.95	6.96	9.10	9.23	10.1	9.83	10.9	13.0	9.65	ND	9.95	9.59
Cl	27.5	34.7	24.0	22.4	20.9	17.4	35.5	39.0	38.0	ND	36.3	50.1
SO4	227	226	63.0	189	236	-	266	1523	1386	ND	2004	1628
DOC	10.0	10.0	7.5	7.5	8.5	8.0	23.0	11.5	12.0	0.5	23.5	15.0
DIC	27.0	27.0	18.0	25.5	25.0	23.5	55.5	37.5	39.5	0.5	56.0	31.0
Cu T	.002	.004	.002	.002	.005	.003	.012	.020	.019	ND	.091	.736
F	.001	.003	.003	ND	.005	.001	.009	.016	.018	ND	ND	.504
Ni T	.100	.054	.127	.113	.316	.004	.872	2.72	2.52	ND	.884	19.5
F	.110	.062	.154	NS	.356	.003	.861	2.52	2.49	ND	.945	20.0
Fe T	.151	.012	.097	.011	.097	.138	2.20	.208	.211	ND	7.07	1.20
F	.101	.016	.033	NS	.034	.034	5.96	.134	.111	ND	5.70	.746
Zn T	4.01	4.01	4.01	4.01	4.01	4.01	.125	.040	.043	ND	.125	.318
F	4.01	4.01	4.01	4.01	4.01	4.01	.091	.053	.044	ND	.101	.329
Co T	.001	.002	.002	.001	.005	ND	.136	.029	.033	ND	.132	.857
F												
Pb T												
F												
Mn T												
F												
Ca T	145.8	69.1	39.4	47.9	57.5	23.1	225	248	244	ND	226	253
Mg T												
Al T												
F												
Cu T	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	550	4.002
F											4.000	











concentration of EMS-3. This behavior is consistent with the leaching of a more mineralized rock in EMS-3 compared to EMS-1; however, sulfate concentrations typical of metal sulfide oxidation and release are significantly lower in the EMS-3 seepage, although still high at 1521 mg/l. Further study of the variable leaching properties of different Gabbro mineralizations is required.

b. Unlike acid mine drainage generally found in mineral mining regions, the leachate pH is comparatively high in the range pH 7-8. Buffering of leachate and creek solution is probably accomplished by weathering of silicate minerals. Weathering effects are further exemplified by high dissolved reactive silicate, alkalinity and dissolved inorganic carbon. High pH likely acts as a master variable in limiting metal release.

c. Based on the operational criteria of 0.45  $\mu$ m membrane filtration for separation of "dissolved" and "particulate" metal most of the Cu, Ni and Zn occurred in the filterable fraction while "dissolved" Fe comprised ~ 40-60% of the total Fe measured. Co concentrations in EMS-1 and EMS-3 were anomalously high and should be considered in future studies. The release of Ca is typical of weathering reactions involving (Ca, Mg, Al) - silicates. Cd concentrations were universally less than 0.1  $\mu$ g/l in all aqueous samples tested.

#### 6. Metal Cycling in Unnamed Creek.

Figures IV-VII detail the temporal variation of DOC, SO<sub>4</sub>, Cu, Ni and Fe at sites EM-8, EMS-1, EMS-3 and EM-1, respectively, for the period of 7-01-76 to 9-30-76. The main discharge to Unnamed Creek occurs upstream of EM-8 but negligible change in chemical concentrations has been noted in traversing ~ 94 meters from the base of the pile to EM-8. At EM-8 (Figure IV) SO<sub>4</sub> concentrations generally build throughout the summer reaching > 1600 mg/l in September. Ni levels follow the same general trend as SO<sub>4</sub> while Fe and DOC fluctuate widely. Cu concentrations remain low (<50  $\mu$ g/l) with little temporal variation noted. The good correlation of Ni with SO<sub>4</sub> suggests that the release and transport of both are related. Natural removal mechanisms such as precipitation as the metal hydroxide or sorption onto sediment are not active apparently in the case of Ni, although mass balance calculations based on flow data will aid in interpretation. Figures V and VI depict the temporal variation in component concentrations for seepages EMS-1 and EMS-3, respectively. As noted earlier, corresponding leachates differ markedly in concentration and behavior, especially with regard to Ni, Cu and Fe release. However, within each seepage, Cu, Ni and Fe release appear interdependent. Components present at site EM-1 (Figure VII) over time are significantly reduced relative to inflowing streams. Low Cu concentrations at EM-1, the input stream to Bob Bay (Birch Lake) are due to sorption, precipitation and for dilution processes in the stream. The bog through which EMS-1 and EMS-3 traverse in flowing to the creek may remove significant quantities of metal. The extent to which Cu levels are reduced from upstream sites and nearby seepages suggest the sediments as a sink.

Table VIII.

Average Chemical Concentrations:  
 Unnamed Creek Area (7-01-76 to 9-31-76)<sup>a</sup>

	EM-1 <sup>b</sup>	EM-8	EMS-1	EMS-3
pH	7.63±0.23(7)	7.27±0.23(7)	7.33±0.20(5)	7.19±0.31(6)
AlK	101±14(7)	140±28(7)	196±27(5)	96±23(6)
S.C.	738±230(8)	1949±848(6)	3468±358(5)	2688±193(5)
Hardness	428±159(4)	1150±247(4)	2641±684(3)	2049±796(3)
Si	9.22±0.48(5)	9.91±1.44(7)	9.62±0.32(5)	11.0±0.98(4)
Cl	33.9±10.5(7)	41.0±7.6(9)	48.2±19.3(6)	58.0±14.1(6)
SO <sub>4</sub>	281±88(7)	1209±337(10)	2230±277(6)	1521±294(7)
DOC	16.6 ±6.5(7)	20.0±6.1(10)	31.0±7.5(6)	18.8±5.1(7)
DIC	19.1±6.2(7)	25.1±8.0(10)	36.5±15.2(6)	18.8±9.2(7)
CuT	.004±.002(7)	.018±.002(10)	.039±0.28(6)	.758±.195(6)
F	.003±.002(7)	.017±.002(10)	.019±--(1)	.552±.063(3)
NiT	.123±.032(7)	1.83±0.70(10)	1.25±0.37(6)	20.4±2.96(7)
F	.118±.033(7)	1.74±0.80(10)	0.87±0.04(2)	19.7±0.52(3)
FeT	.189±.046(7)	.142±.041(10)	4.03±2.21(6)	.462±.221(5)
F	.141±.056(5)	.068±.035(10)	3.39±3.27(2)	.256±.128(2)
CoT	.001±--(1)	.029±--(1)	.132±--(1)	.857±--(1)
ZnT	<.01--(1-)	.031±.010(6)	.226±.056(5)	.345±.030(6)
F	<.01--(1)	.033±.012(6)	.106±.007(2)	.350±.031(3)
CaT	48.4±10.1(7)	173±61.9(10)	220±17.4(4)	246±13.2(5)

<sup>a</sup>All values are given in mg/l except pH.

<sup>b</sup>Numbers represent average ± standard deviation with number of data points considered in parentheses.

Figure IV

Variable FM-8 (7.50-7.60) (7.50-7.60)



Figure V

DATA FROM 140 WAYS TO 100 WAYS  
(7-9-36 / 9-30-76)

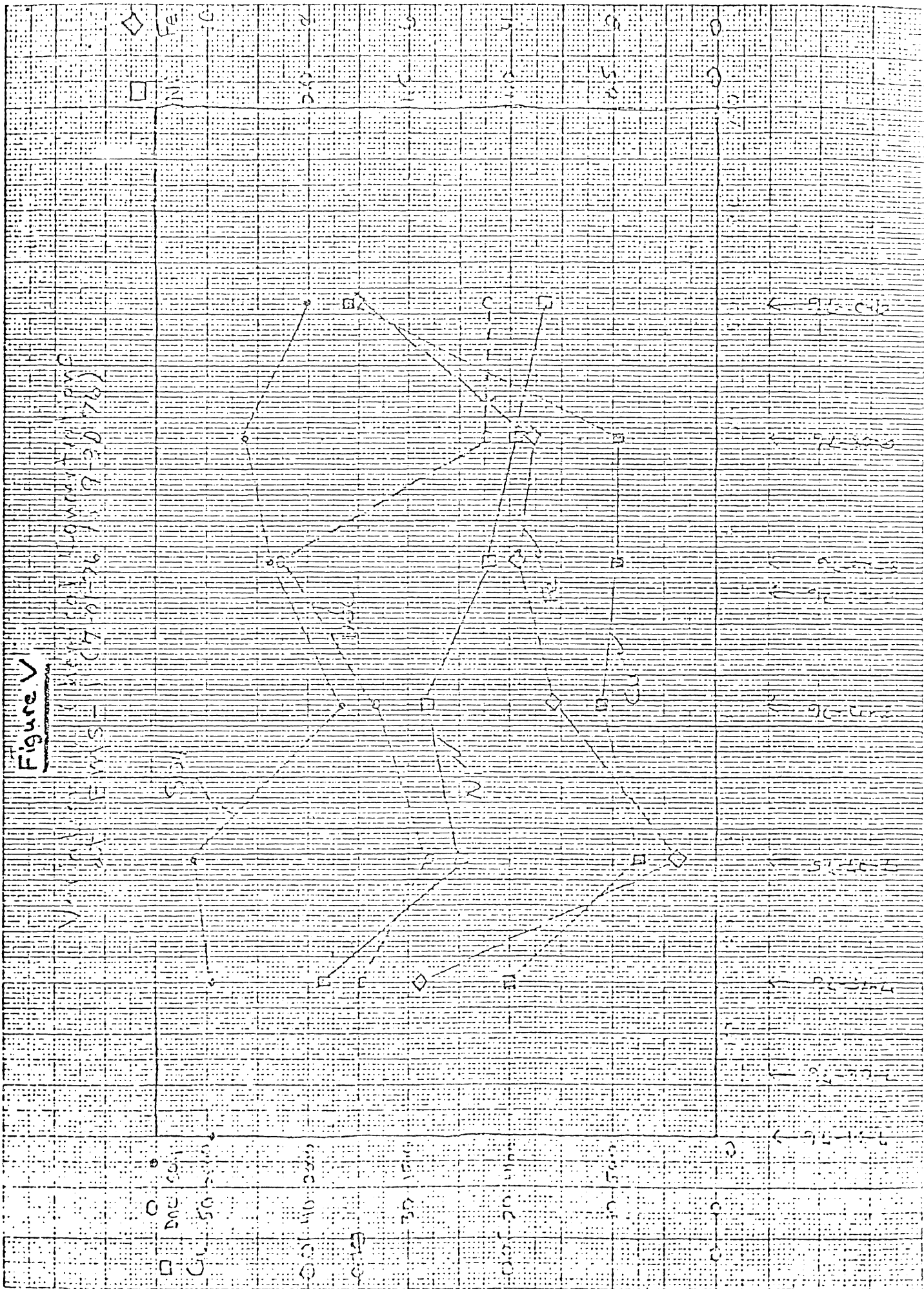
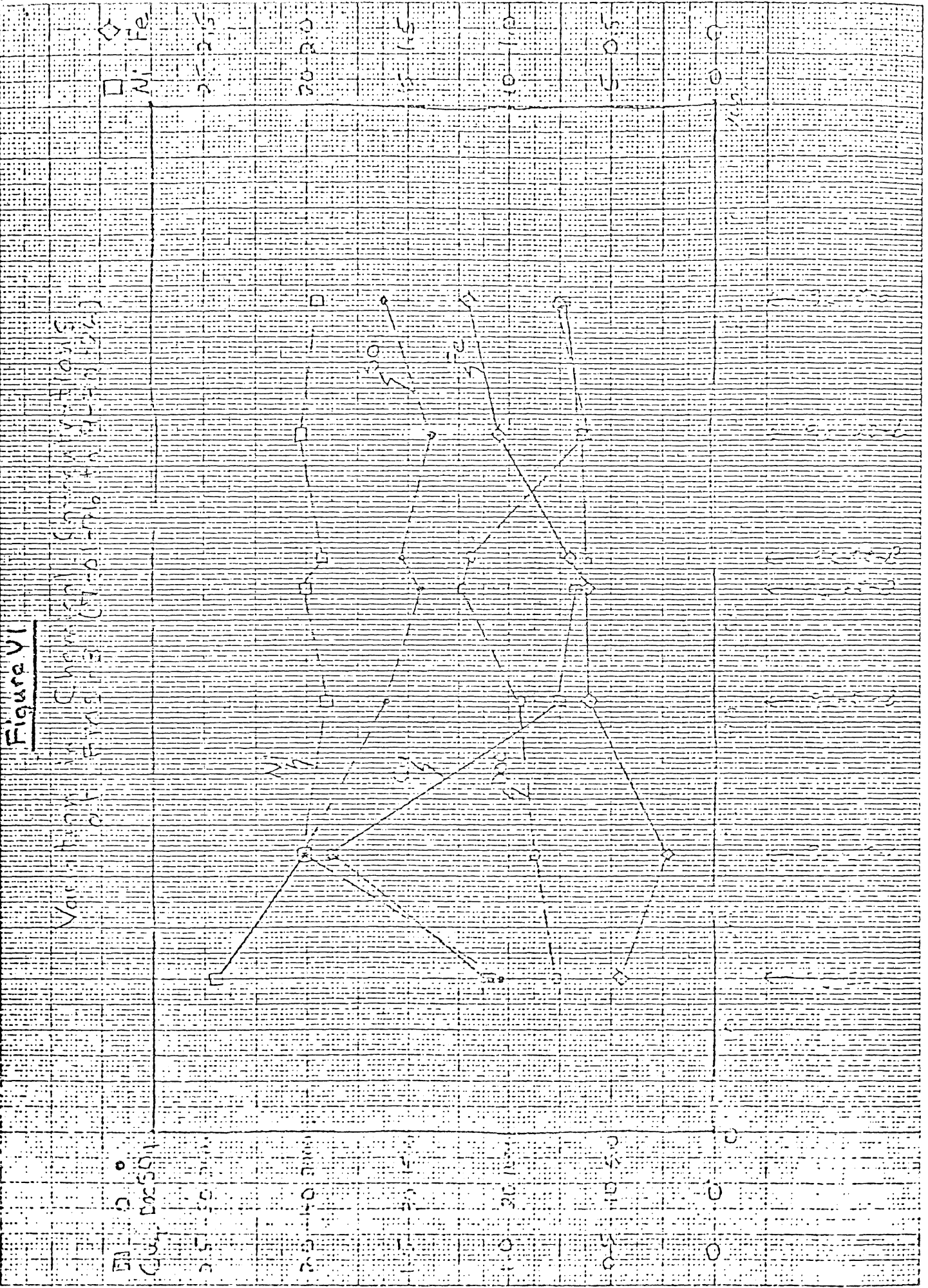


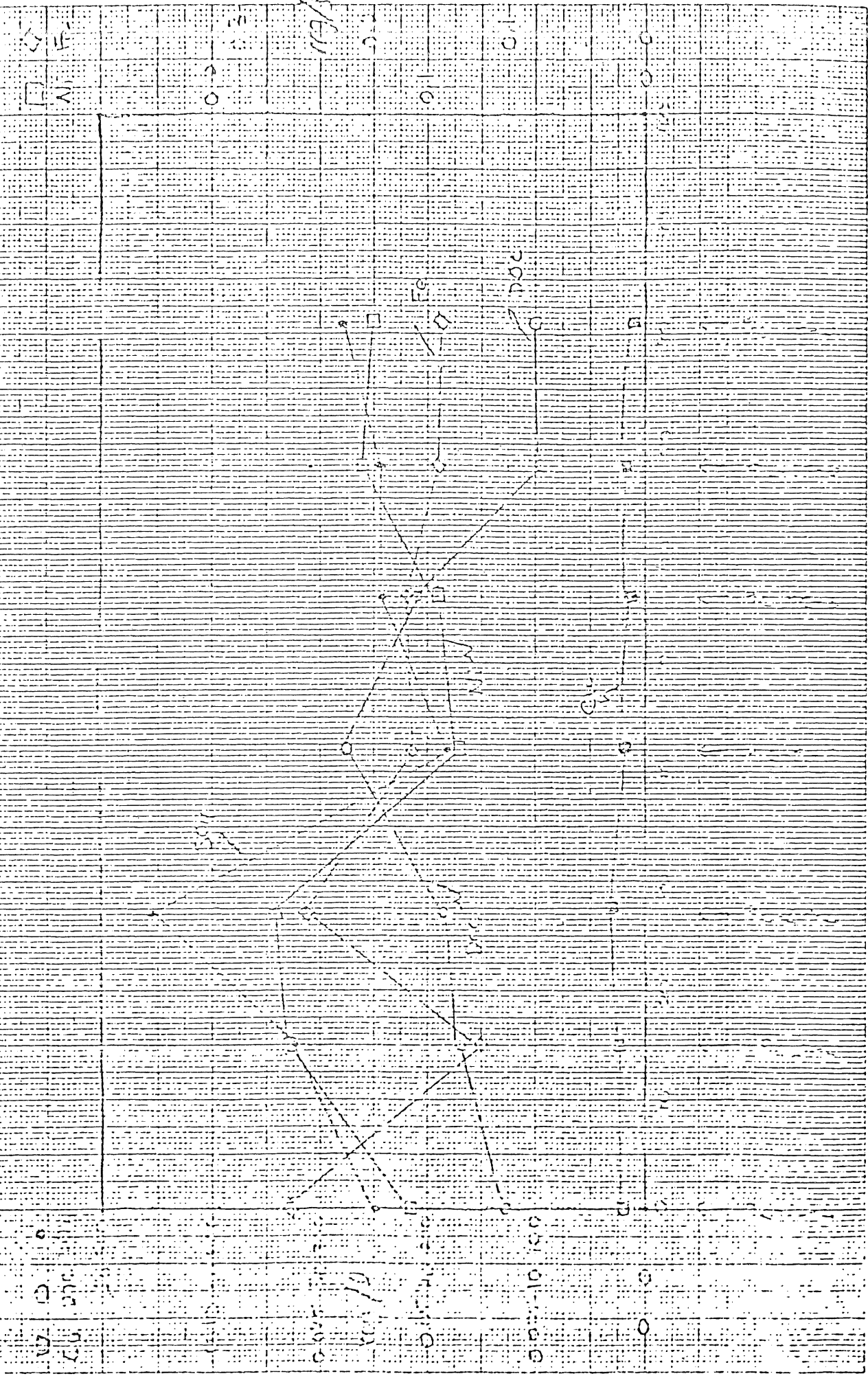
Figure VI

Var. of  $\log \frac{C_{Ni}}{C_{Fe}}$  vs.  $\log \frac{C_{Ni}}{C_{Fe}}$  (7-0-1776 + 4-11-1776)



### Figure VII

Various Views of a Ship's Hull (See page 10 for details)  
E.M. 1 (17-51) (See page 10 for details)



Concentrations of other components fluctuated in early and mid-summer due to variable pumping practices but leveled in late summer. Comparison of EM-1 data with Bob Bay values indicates that Unnamed Creek flows into the bay in a stratified, dense layer near the sediments which mixes slowly with the fresh water. Again, sediments represent the likely sink for metals such as Cu, Ni, Fe, Mn and others. Additional study of suspended and deposited sediments of Unnamed Creek and Bob Bay are required to furnish data on natural sinks and removal mechanisms for metal species derived from metal sulfide leachates.

## 7. Chemical Equilibrium Models of Metal Speciation

Two related approaches were used to model aqueous metal behavior in Unnamed Creek and the seepage EMS-3. Both modeling efforts utilize the computational assistance of the chemical equilibrium computer program, REDEQL2, which uses the stability constant approach and the Newton-Raphson method for digital calculations of equilibrium speciation. REDEQL2 has the capability of computing chemical equilibria in aqueous systems involving acid-base, coordination, solubility, redox and adsorption phenomena. Data for EM-1, EM-8 and EMS-3 collected from Unnamed Creek on 8-12-76 was selected for typical speciation studies. Concentrations of measured components in unfiltered samples used as input data to the computer program which calculated the equilibrium distribution of metals and ligands in inorganic and organic models.

Figures VIII-X depict the equilibrium speciation (Cu, Ni) for EM-8, EMS-3 and EM-1 in the inorganic model. Metals considered were Ca, Fe, Cu, Cd, Zn, Ni, Pb and Co while ligands were represented by  $\text{CO}_3$ ,  $\text{SO}_4$ , Cl,  $\text{PO}_4$  and  $\text{SiO}_3$ . Tables IX-XI show input and calculated equilibrium concentrations of metal and ligand species. In general, Cu is controlled by  $\text{CuCO}_3$  formation in either the solid or soluble state at all three sites. Ni is distributed primarily between the soluble species  $\text{Ni}^{2+}$ ,  $\text{NiSO}_4$  and  $\text{NiCO}_3$ . The elevated concentrations of Ni over Cu in stream and seepage samples may be due to increased release rates from Gabbro rock and lack of efficient removal mechanisms. However, unfiltered and filtered metal, especially Cu and Fe do not conform to an inorganic model strictly because the majority of metal occurs in the  $<0.45\mu\text{m}$  fraction. Consequently, an organic model superimposed on the inorganic components was constructed in which added organic ligands were citrate, acetate, tartrate, cysteine and phthalate. These ligands were chosen to represent organic functional groups known or thought to exist in aquatic organics but not yet identified. Ligand concentrations were determined by dividing the DOC by 100 giving a better value for ligand concentration and then distributed, on an equivalent carbon basis, between the selected ligands.

The resulting superimposition of the organic ligands on the inorganic model as shown in Figures XI-XIII clearly indicates that Ni speciation is negligibly affected by reasonable concentrations of strong organic ligands. Cu speciation, on the other hand, is controlled effectively by formation of a Cu-citrate complex in EM-1 and EM-8 while inorganic complexes and solids still predominate in the more concentrated EMS-3 seepage. Tables XII-XIV show that Fe becomes bound with cysteine in about the same percentage of

Figure X . EM-1, Inorganic Model

- $Cu^{+2}$  7.20    ×  $CuOH^+$     I  $NiSO_4$
- △  $CuCO_3$     ◇  $Ni^{+2}$  5.83    — organic model
- +  $CuSO_4$     †  $NiCO_3$     - - - - -

(8-12-76)

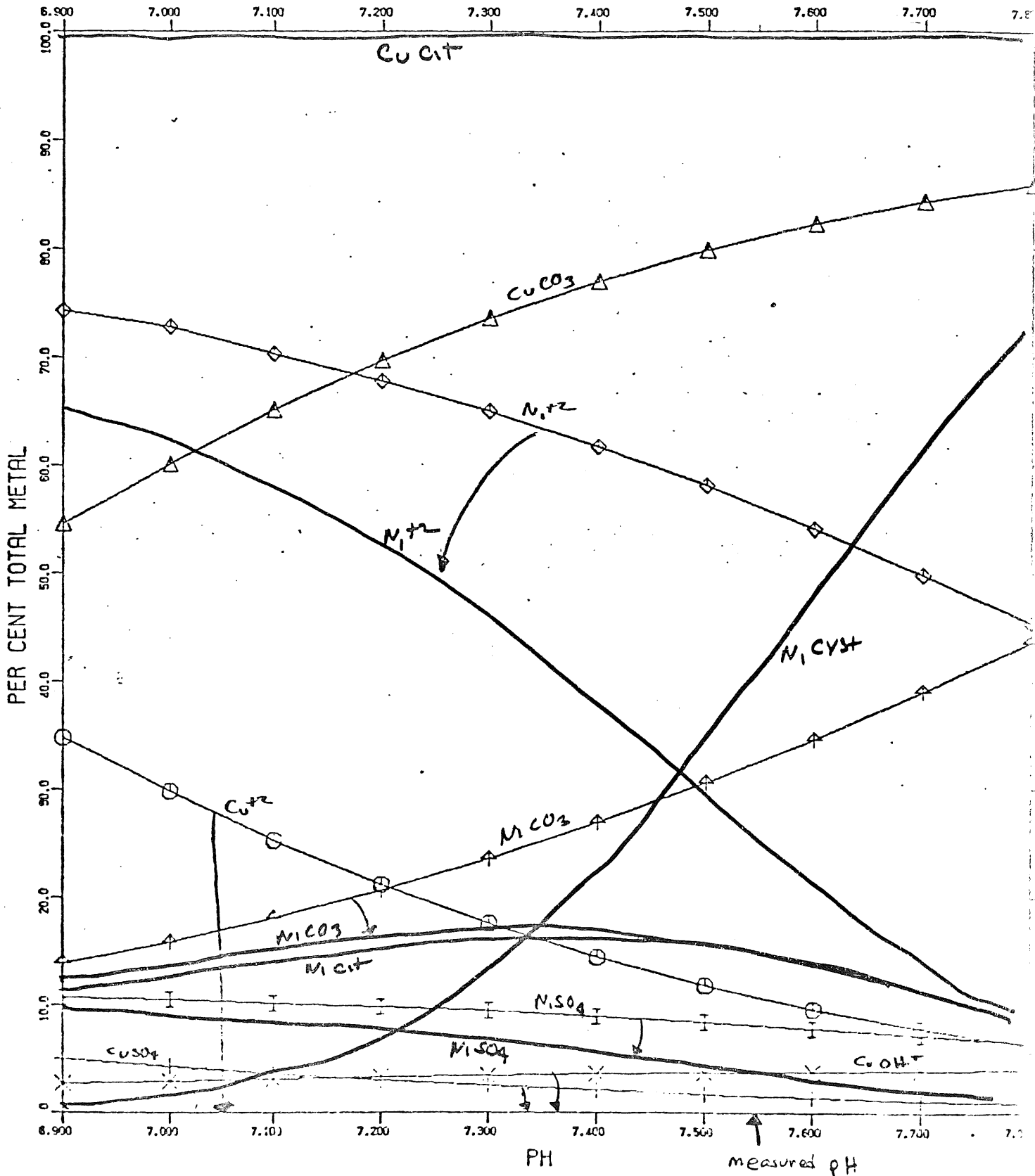
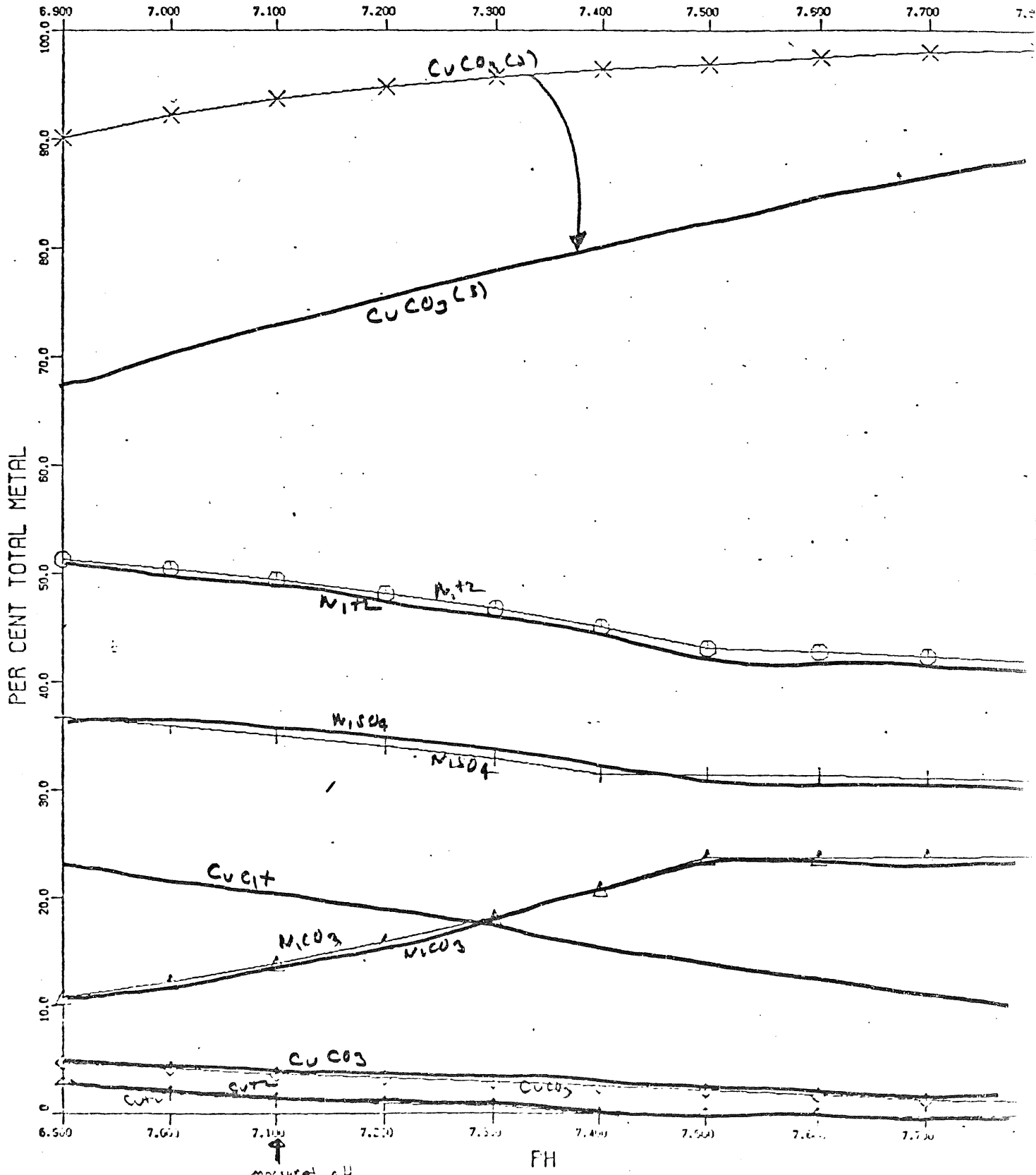




Figure IX. EMS-3, Inorganic Model

○ NI(+2)3.49    ×    CUCO3S  
 △    NiCO3        ◇    CUCO3  
 +    NiSO4        †    CU(+2)4.93  
 (8-12-76)

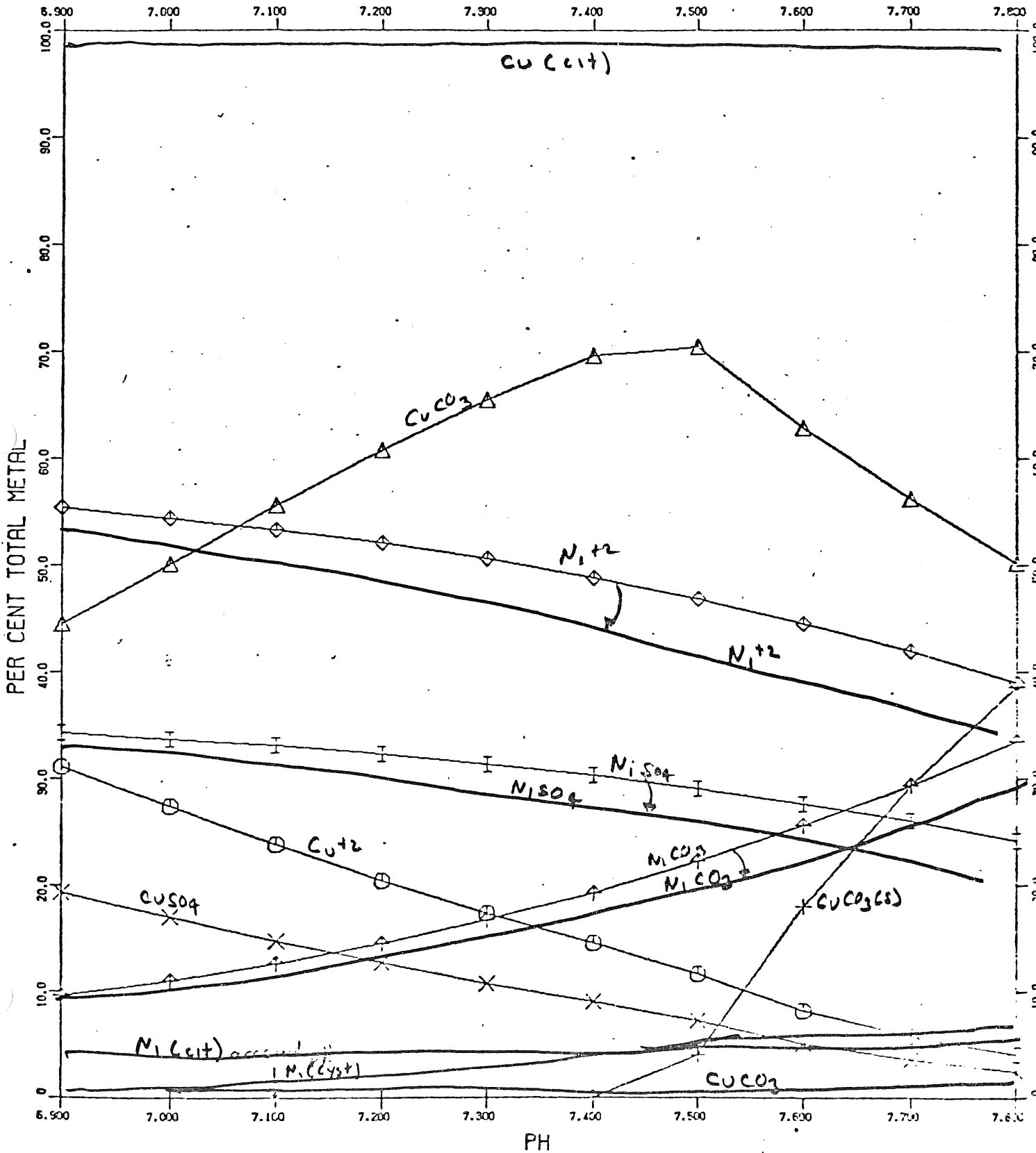


12/13F006185REVEUHEX'440MEUWLLZ FLUIJF S-3

Figure VIII. EM-8, Inorganic Model

- $Cu(+2)6.48$     ×  $CuSO_4$     I  $NiSO_4$
- △  $CuCO_3$       ◇  $Ni(+2)4.39$     — organic model
- +  $CuCO_3(s)$     †  $NiCO_3$

(8-12-76)



100.0  
90.0  
80.0  
70.0  
60.0  
50.0  
40.0  
30.0  
20.0  
10.0  
0

6.900 7.000 7.100 7.200 7.300 7.400 7.500 7.600 7.700 7.800

PER CENT TOTAL METAL

PH

EM-8

IONIC STRENGTH= .3800000E-01

EM-8

Inorganic

1 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	INMAT	GUESS	TOTCC $\bar{i}$	TOTCC
CA	1	8.000	2.840	
FE3	6	8.000	5.620	
CU2+	9	8.000	6.480	
CD	11	8.000	8.050	
ZN	12	8.000	6.270	
NI	13	8.000	4.390	
PB	15	8.000	6.810	
CO2+	16	8.000	6.310	
CO3+	17	8.000	8.000	

LIGAND	INMAT	GUESS	TOTCC $\bar{i}$	TOTCC
CO3-	1	8.000	2.840	
SO4	2	8.000	1.850	
CL	3	8.000	2.800	
PO4	9	8.000	6.210	
SI03	12	8.000	3.450	

FIXED PH 7.020

REDOX POTENTIAL 12.000

THE FOLLOWING REDOX REACTIONS ARE CONSIDERED

PH02  
CO2/CO3  
FE304

C03-	6.50	1 1 0	4.88	1 1 1						
S04	3.5	1 1 0								
P04	8.15	1 1 1								
OH	8.42	1 0-1								
S04	16.30	1 1 0	16.98	1 2 0						
CL	19.45	1 1 0	21.87	1 2 0	25.63	1 3 0				
P04	16.89	1 1 1								
S103	13.56	1 1 1								
OH	13.10	1 0-1	10.28	1 0-2	13.16	1 0-4	24.07	2 0-2		
C03-	6.80	1 1 0	9.40	1 2 0	7.98	1 1 1	12.05	1 1-2		
S04	7.26	1 1 0								
CL	8.57	1 1 0	10.93	1 2 0	14.03	1 3 0	17.17	1 4 0	8.08	1 1-1
P04	10.75	1 1 1	12.43	1 1 2						
OH	8.12	1 0-1	10.54	1 0-2	12.90	1 0-3	18.71	1 0-4	10.60	2 0-2
C03-	9.37	1 1 0	9.55	1 1 1						
S04	8.53	1 1 0								
CL	9.25	1 1 0	11.71	1 2 0	15.11	1 3 0	18.25	1 4 0	11.16	1 1-1
P04	17.00	1 1 0								
OH	11.50	1 0-1	14.92	1 0-2	20.68	1 0-3	27.59	1 0-4	18.91	2 0-1 37.9
C03-	7.66	1 1 0	7.74	1 1 1						
S04	6.73	1 1 0								
CL	8.24	1 1 0	10.90	1 2 0	14.60	1 3 0	9.65	1 1-1	16.84	1 4 0
P04	11.02	1 1 1								
OH	9.19	1 0-1	13.97	1 0-3	19.48	1 0-4	9.61	1 0-2	14.90	2 0-1
C03-	5.60	1 1 0	5.68	1 1 1						
S04	4.86	1 1 0								
CL	7.28	1 1 0	9.44	1 2 0						
P04	9.45	1 1 1								
OH	6.53	1 0-1								
C03-	6.95	1 1 0	9.35	1 2 0	8.13	1 1 1	9.18	1 2 2		
S04	7.71	1 1 0								
CL	9.32	1 1 0	11.38	1 2 0	13.98	1 3 0	17.42	1 4 0	10.63	1 1-1
OH	8.77	1 0-1	11.19	1 0-2	15.05	1 0-3	14.97	2 0-1	22.00	3 0-4 35.1
C03-	7.68	1 1 0	7.76	1 1 1						
S04	6.65	1 1 0								
CL	8.36	1 1 0	11.02	1 2 0						
P04	11.34	1 1 1								
OH	9.01	1 0-1	11.13	1 0-2	16.89	1 0-3				
C03-	2.90	0 1 1	3.74	0 1 2						
S04	6.97	0 1 1								
P04	6.57	0 1 1	6.47	0 1 2	11.61	0 1 3				
S103	5.91	0 1 1	3.45	0 1 2						

191731

CA

AS A FREE METAL/	61.2 PERCENT
BOUND WITH CO3-/	.9 PERCENT
BOUND WITH SO4 /	37.9 PERCENT

FE3

IN SOLID FORM WITH OH / 100.0 PERCENT

CU2+

AS A FREE METAL/	26.6 PERCENT
BOUND WITH CO3-/	51.2 PERCENT
BOUND WITH SO4 /	16.5 PERCENT
BOUND WITH CL /	3.3 PERCENT
BOUND WITH OH /	2.3 PERCENT

CD

AS A FREE METAL/	52.8 PERCENT
BOUND WITH CO3-/	7.9 PERCENT
BOUND WITH SO4 /	32.8 PERCENT
BOUND WITH CL /	6.5 PERCENT

ZN

AS A FREE METAL/	56.4 PERCENT
BOUND WITH CO3-/	7.4 PERCENT
BOUND WITH SO4 /	34.9 PERCENT
BOUND WITH CL /	1.1 PERCENT

NI

AS A FREE METAL/	54.2 PERCENT
BOUND WITH CO3-/	11.3 PERCENT
BOUND WITH SO4 /	33.6 PERCENT
BOUND WITH OH /	.7 PERCENT

PB

AS A FREE METAL/	8.0 PERCENT
BOUND WITH CO3-/	78.0 PERCENT
BOUND WITH SO4 /	12.5 PERCENT
BOUND WITH OH /	1.1 PERCENT

CO2+

AS A FREE METAL/	46.1 PERCENT
BOUND WITH CO3-/	7.6 PERCENT
BOUND WITH SO4 /	45.3 PERCENT
BOUND WITH CL /	.9 PERCENT

CO3+

CO3-

BOUND WITH CA /	.9 PERCENT
BOUND WITH H /	98.6 PERCENT

SO4

AS A FREE LIGAND/	96.0 PERCENT
BOUND WITH CA /	3.9 PERCENT

CL

AS A FREE LIGAND/ 100.0 PERCENT

PO4

THESE COMPUTATIONS INVOLVE 10 METALS, 6 LIGANDS, 71 COMPLEXES AND 24

Table IX

IONIC STRENGTH= .7600000E-01

EMS-3

Inorganic

1 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	INMAT	GUESS	TOTCC $\bar{i}$	TOTCC
NI	13	8.000	3.490	
FE3	6	8.000	4.970	
ZN	12	8.000	5.270	
CD	11	8.000	7.570	
PB	15	8.000	6.810	
CO2+	16	8.000	4.840	
CO3+	17	8.000	8.000	
CA	1	8.000	2.190	
CU2+	9	8.000	4.930	

LIGAND	INMAT	GUESS	TOTCC $\bar{i}$	TOTCC
CO3-	1	8.000	2.650	
SO4	2	8.000	1.570	
CL	3	8.000	2.700	
PO4	9	8.000	5.490	
SI03	12	8.000	3.410	

FIXED PH 7.100

REDOX POTENTIAL 12.000

THE FOLLOWING REDOX REACTIONS ARE CONSIDERED



CO3-	4.58	1 1 0	4.73	1 1 1						
SO4	3.73	1 1 0								
CL	6.41	1 1 0	8.52	1 2 0						
PO4	9.15	1 1 1								
OH	5.65	1 0-1								
SO4	16.39	1 1 0	16.92	1 2 0						
CL	19.56	1 1 0	21.97	1 2 0	25.67	1 3 0				
PO4	17.59	1 1 1								
SI03	13.62	1 1 1								
OH	13.20	1 0-1	10.35	1 0-2	13.05	1 0-4	24.08	2 0-2		
CO3-	7.27	1 1 0	7.42	1 1 1						
SO4	6.42	1 1 0								
CL	7.99	1 1 0	10.60	1 2 0	14.20	1 3 0	9.34	1 1-1	16.29	1 4 0
PO4	11.33	1 1 1								
OH	8.93	1 0-1	13.53	1 0-3	18.87	1 0-4	9.28	1 0-2	14.31	2 0-1
CO3-	8.77	1 1 0	9.02	1 1 1						
SO4	8.02	1 1 0								
CL	8.79	1 1 0	11.20	1 2 0	14.50	1 3 0	17.49	1 4 0	10.64	1 1-1
PO4	16.97	1 1 0								
OH	11.03	1 0-1	14.38	1 0-2	20.03	1 0-3	26.77	1 0-4	17.91	2 0-1
CO3-	6.92	1 1 0	8.99	1 2 0	8.17	1 1 1	9.10	1 2 2		35.8
SO4	7.78	1 1 0								
CL	9.45	1 1 0	11.46	1 2 0	13.96	1 3 0	17.25	1 4 0	10.70	1 1-1
OH	8.89	1 0-1	11.24	1 0-2	14.99	1 0-3	15.12	2 0-1	22.23	3 0-4
+ CO3-	7.40	1 1 0	7.55	1 1 1						35.4
+ SO4	6.45	1 1 0								
+ CL	8.23	1 1 0	10.84	1 2 0						
+ PO4	11.77	1 1 1								
+ OH	8.07	1 0-1	10.92	1 0-2	16.57	1 0-3				
CO3-	5.72	1 1 0	4.17	1 1 1						
SO4	2.57	1 1 0								
PO4	8.08	1 1 1								
OH	7.78	1 0-1								
+ CO3-	6.39	1 1 0	8.65	1 2 0	7.64	1 1 1	11.37	1 1-2		
+ SO4	6.94	1 1 0								
+ CL	8.31	1 1 0	10.62	1 2 0	13.62	1 3 0	16.61	1 4 0	7.76	1 1-1
+ PO4	11.05	1 1 1	12.79	1 1 2						
+ OH	7.85	1 0-1	10.20	1 0-2	12.45	1 0-3	18.09	1 0-4	10.01	2 0-2
CO3-	2.72	0 1 1	3.68	0 1 2						
SO4	6.88	0 1 1								
PO4	6.93	0 1 1	6.99	0 1 2	12.24	0 1 3				
SI03	5.76	0 1 1	3.42	0 1 2						

NI

AS A FREE METAL/ 49.4 PERCENT  
BOUND WITH CO3-/ 13.9 PERCENT  
BOUND WITH SO4 / 35.9 PERCENT  
BOUND WITH OH / .7 PERCENT

FE3

IN SOLID FORM WITH OH / 100.0 PERCENT

ZN

AS A FREE METAL/ 9.7 PERCENT  
BOUND WITH CO3-/ 1.7 PERCENT  
BOUND WITH SO4 / 7.1 PERCENT  
IN SOLID FORM WITH SI03/ 81.2 PERCENT

CD

AS A FREE METAL/ 48.6 PERCENT  
BOUND WITH CO3-/ 9.9 PERCENT  
BOUND WITH SO4 / 35.4 PERCENT  
BOUND WITH CL / 6.1 PERCENT

PB

AS A FREE METAL/ 5.9 PERCENT  
BOUND WITH CO3-/ 82.3 PERCENT  
BOUND WITH SO4 / 10.7 PERCENT  
BOUND WITH OH / .8 PERCENT

CO2+

AS A FREE METAL/ 2.1 PERCENT  
IN SOLID FORM WITH CO3-/ 95.0 PERCENT  
BOUND WITH SO4 / 2.4 PERCENT

CO3+

CA

AS A FREE METAL/ 57.2 PERCENT  
BOUND WITH CO3-/ 1.1 PERCENT  
BOUND WITH SO4 / 41.6 PERCENT

CU2+

AS A FREE METAL/ 1.3 PERCENT  
BOUND WITH CO3-/ 3.7 PERCENT  
IN SOLID FORM WITH CO3-/ 93.7 PERCENT  
BOUND WITH SO4 / 1.0 PERCENT

CO3-

BOUND WITH NI / 2.0 PERCENT  
IN SOLID FORM WITH CO2+/ .6 PERCENT  
BOUND WITH CA / 3.1 PERCENT  
BOUND WITH H / 93.8 PERCENT

SO4

AS A FREE LIGAND/ 89.6 PERCENT  
BOUND WITH CA / 10.0 PERCENT

CL

AS A FREE LIGAND/ 100.0 PERCENT

PO4

IN SOLID FORM WITH CA / 92.9 PERCENT  
BOUND WITH H / 6.8 PERCENT



THESE COMPUTATIONS INVOLVE 10 METALS, 6 LIGANDS, 71 COMPLEXES AND

Table X EM-1

IONIC STRENGTH= .1100000E-01

Inorganic

1 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	INMAT	GUESS	TOTCC $\bar{i}$	TOTCC
CA	1	8.000	2.990	
FE3	6	8.000	5.510	
CU2+	9	8.000	7.200	
CD	11	8.000	8.320	
ZN	12	8.000	7.120	
NI	13	8.000	5.830	
PB	15	8.000	6.810	
CO2+	16	8.000	7.770	
CO3+	17	8.000	8.000	

LIGAND	INMAT	GUESS	TOTCC $\bar{i}$	TOTCC
CO3-	1	8.000	2.940	
SO4	2	8.000	2.730	
CL	3	8.000	3.040	
PO4	9	8.000	7.010	
SI03	12	8.000	3.480	

FIXED PH 7.550

REDOX POTENTIAL 12.000

THE FOLLOWING REDOX REACTIONS ARE CONSIDERED

19173E



9917  
CA

AS A FREE METAL/ 86.0 PERCENT  
BOUND WITH CO3- / 1.6 PERCENT  
BOUND WITH SO4 / 12.4 PERCENT

FE3

IN SOLID FORM WITH OH / 100.0 PERCENT

CU2+

AS A FREE METAL/ 10.6 PERCENT  
BOUND WITH CO3- / 81.1 PERCENT  
BOUND WITH SO4 / 1.5 PERCENT  
BOUND WITH CL / 2.9 PERCENT  
BOUND WITH OH / 3.7 PERCENT

CD

AS A FREE METAL/ 59.3 PERCENT  
BOUND WITH CO3- / 26.2 PERCENT  
BOUND WITH SO4 / 8.6 PERCENT  
BOUND WITH CL / 5.8 PERCENT

ZN

AS A FREE METAL/ 64.6 PERCENT  
BOUND WITH CO3- / 23.6 PERCENT  
BOUND WITH SO4 / 9.3 PERCENT  
BOUND WITH CL / 1.1 PERCENT  
BOUND WITH OH / 1.3 PERCENT

NI

AS A FREE METAL/ 56.2 PERCENT  
BOUND WITH CO3- / 32.6 PERCENT  
BOUND WITH SO4 / 8.1 PERCENT  
BOUND WITH OH / 3.1 PERCENT

PB

AS A FREE METAL/ 2.5 PERCENT  
BOUND WITH CO3- / 95.2 PERCENT  
BOUND WITH SO4 / .9 PERCENT  
BOUND WITH OH / 1.4 PERCENT

CO2+

AS A FREE METAL/ 58.1 PERCENT  
BOUND WITH CO3- / 26.7 PERCENT  
BOUND WITH SO4 / 13.3 PERCENT  
BOUND WITH CL / .9 PERCENT  
BOUND WITH OH / 1.0 PERCENT

CO3+

CO3-

BOUND WITH CA / 1.5 PERCENT  
BOUND WITH H / 98.2 PERCENT

SO4

AS A FREE LIGAND/ 93.2 PERCENT  
BOUND WITH CA / 6.8 PERCENT

CL

AS A FREE LIGAND/ 100.0 PERCENT

PO4

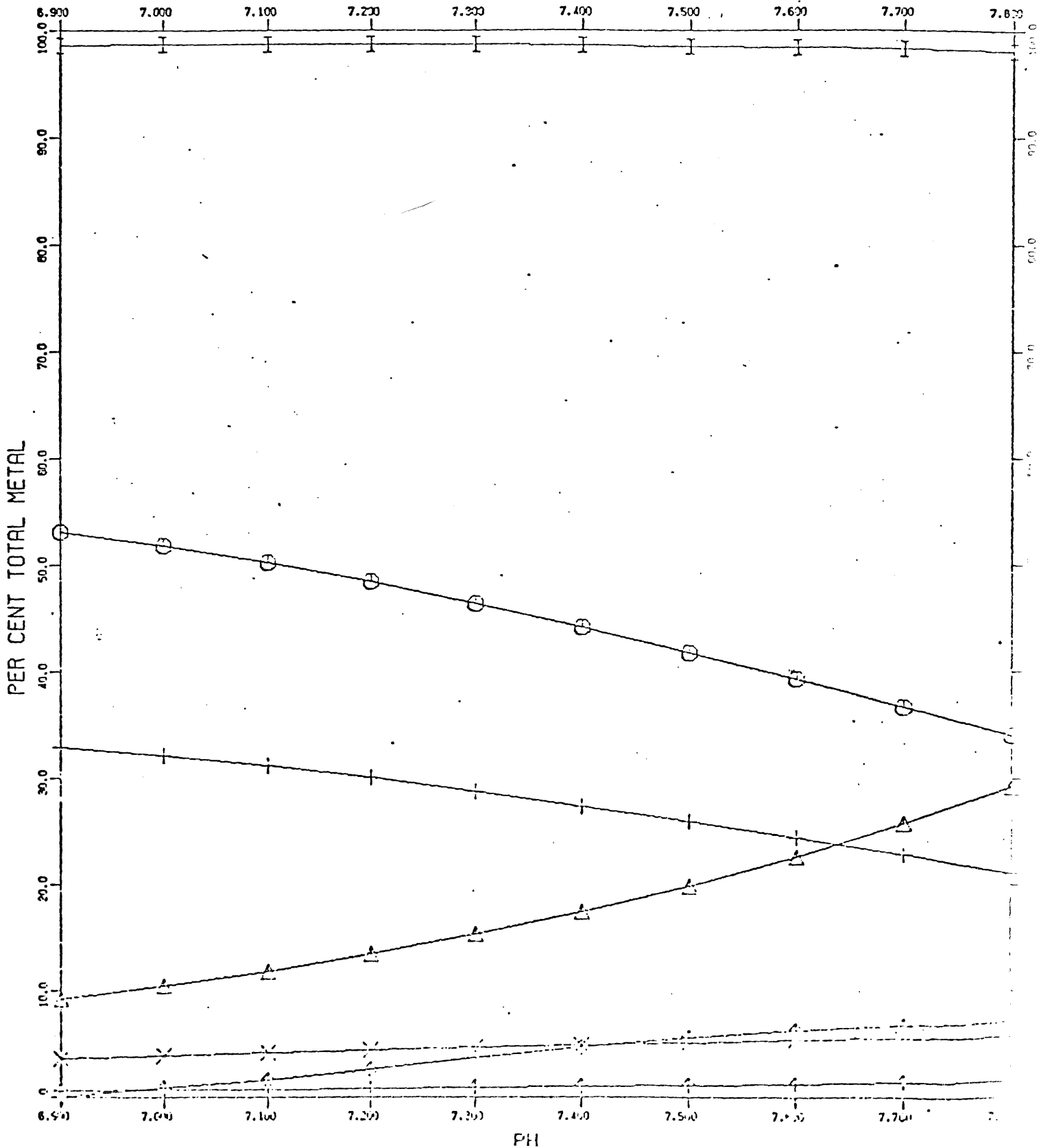
Figure XI. EM-8, Organic Model

○ NI(+2)4.39 X NI(CIT) I CU(CIT)

△ NI(CO3) ◇ NI(CYST)

+ NI(SO4) † CUCO3 6.48

(8-12-76)



12/18FQ06185REDEHJXEXU3/4UNGTMLLN LN 00

Figure XII. EMS-3, Organic Model

○ NI(+2)3.49 X CU(CO3) I CU(+2)4.93

△ NI(CO3) ◇ CU(CO3)S

† NI(SO4) † CU(CIT)

(8-12-76)

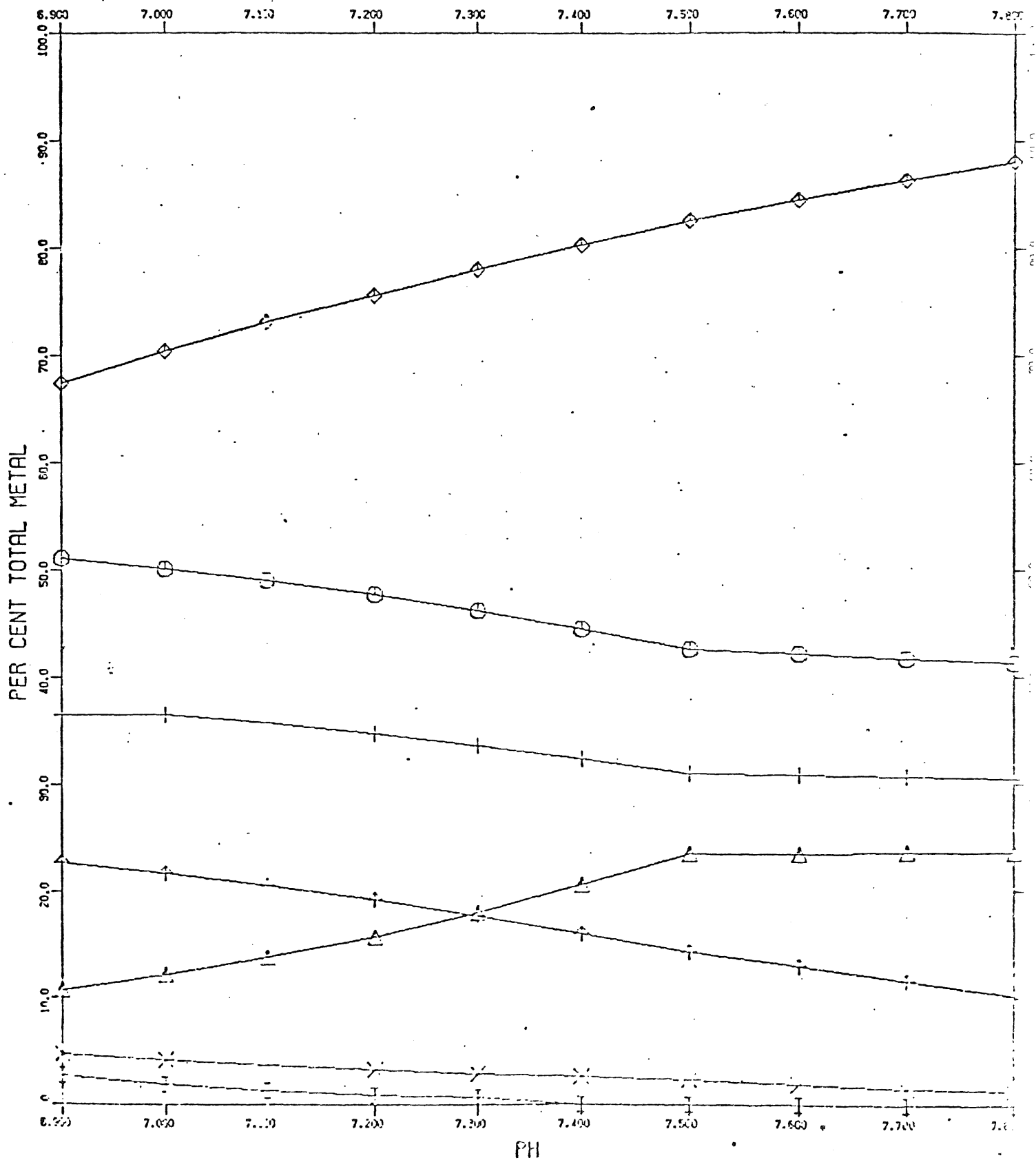


Figure XIII. EM-1, Organic Model

- CUCIT 7.2
- △ NI(+2)5.83
- + NIC03
- × NIS04
- ◇ NICIT
- ⊕ NICYST

(8-12-76)

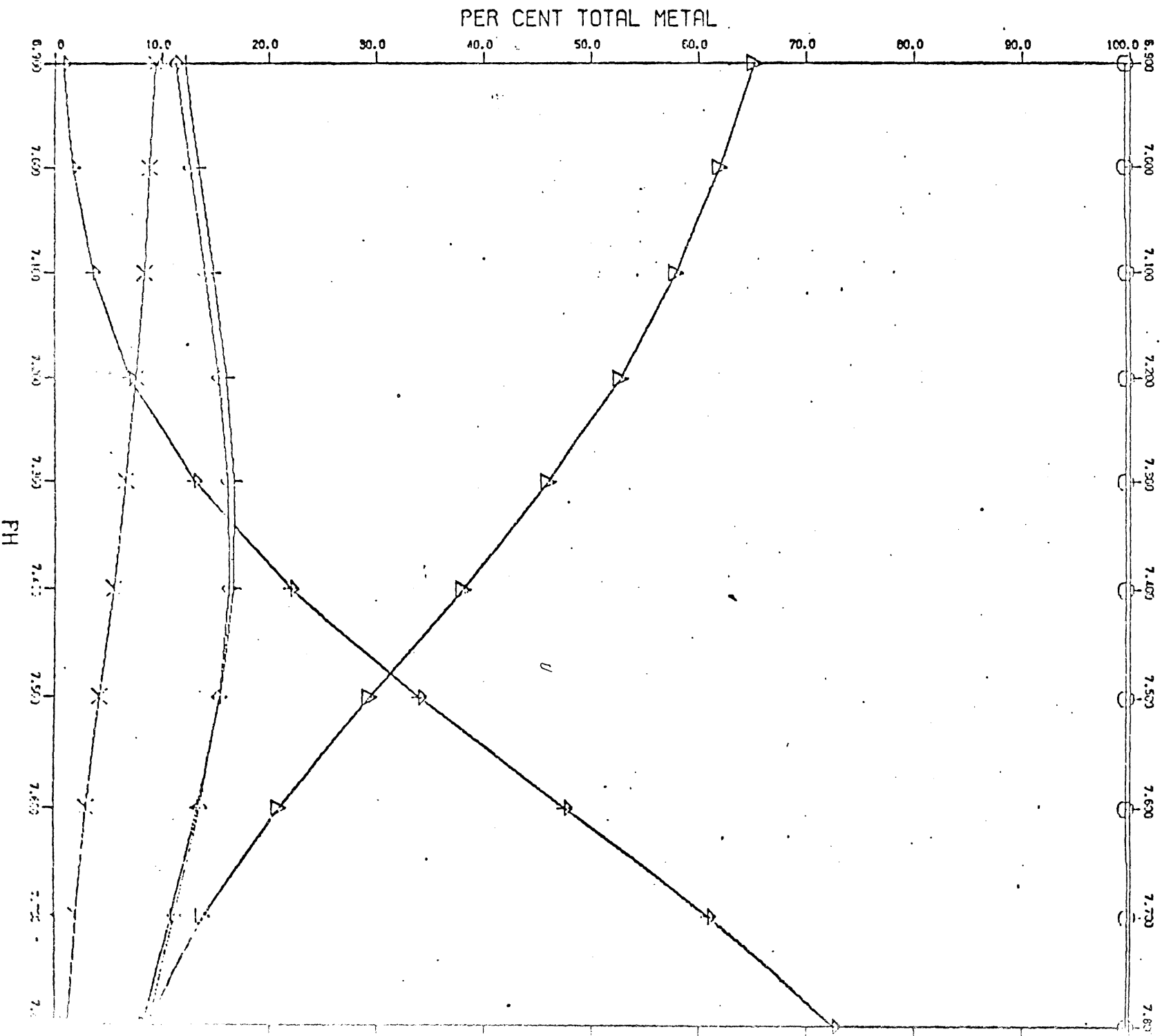


Table XL.<sup>74</sup>

IONIC STRENGTH= .3800000E-01

EM-8

Organic

DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	INMAT	GUESS	TOTCC $\bar{1}$	TOTCC
CA	1	8.000	2.840	
FE3	6	8.000	5.620	
CU2+	9	8.000	6.480	
CD	$\bar{11}$	8.000	8.050	
ZN	$\bar{12}$	8.000	6.270	
NI	$\bar{13}$	8.000	4.390	
PB	$\bar{15}$	8.000	6.810	
CO2+	$\bar{16}$	8.000	6.310	
CO3+	$\bar{17}$	8.000	8.000	

LIGAND	INMAT	GUESS	TOTCC $\bar{1}$	TOTCC
CO3-	1	8.000	2.840	
SO4	2	8.000	1.850	
CL	3	8.000	2.800	
PO4	9	8.000	6.210	
SI03	12	8.000	3.450	
CIT	17	8.000	5.490	
AC	15	8.000	5.010	
TART	20	8.000	5.310	
CYST	30	8.000	5.190	
PHTH	32	8.000	5.610	

CA	CO3-	6.50	1 1 0	4.88	1 1 1				
CA	S04	3.26	1 1 0						
CA	P04	8.15	1 1 1						
CA	CIT	5.93	1 1 1	8.21	1 1 2	12.94	1 1 3		
CA	AC	7.39	1 1 0						
CA	TART	10.24	1 1 1	6.26	1 1 0				
CA	PHTH	6.66	1 1 0						
CA	OH	8.42	1 0-1						
FE3	S04	16.30	1 1 0	16.98	1 2 0				
FE3	CL	19.45	1 1 0	21.87	1 2 0	25.63	1 3 0		
FE3	P04	16.89	1 1 1						
FE3	SI03	13.56	1 1 1						
FE3	CIT	7.59	1 1 0	12.87	1 1 1	18.79	1 1 2		
FE3	AC	18.87	1 1 0	20.90	1 2 0	23.08	1 3 0		
FE3	CYST	6.19	1 2 0						
FE3	OH	13.10	1 0-1	10.28	1 0-2	13.16	1 0-4	24.07	2 0-
CU2+	CO3-	8.68	1 1 0	11.28	1 2 0	9.86	1 1 1	13.93	1 1-
CU2+	S04	9.14	1 1 0						
CU2+	CL	10.46	1 1 0	12.82	1 2 0	15.92	1 3 0	19.06	1 4
CU2+	P04	12.63	1 1 1	14.31	1 1 2				
CU2+	CIT	6.49	1 1 0	11.42	1 1 1	19.03	1 1 3		
CU2+	AC	12.07	1 1 0	15.95	1 2 0	20.56	1 3 0	25.92	1 4
CU2+	TART	10.64	1 1 0	14.10	1 2 0	20.43	1 3 0	25.23	1 4
CU2+	PHTH	11.04	1 1 0	15.40	1 2 0				
CU2+	OH	10.01	1 0-1	12.43	1 0-2	14.79	1 0-3	20.60	1 0-
CD	CO3-	9.38	1 1 0	9.56	1 1 1				
CD	S04	8.54	1 1 0						
CD	CL	9.25	1 1 0	11.71	1 2 0	15.11	1 3 0	18.25	1 4
CD	P04	17.00	1 1 0						
CD	CIT	12.58	1 1 0	10.21	1 1 1	13.19	1 1 2		
CD	AC	11.07	1 1 0	15.24	1 2 0	19.66	1 3 0	26.91	1 4
CD	TART	10.44	1 1 0						
CD	PHTH	10.93	1 1 0						
CD	OH	11.50	1 0-1	14.92	1 0-2	20.68	1 0-3	27.59	1 0-
ZN	CO3-	7.82	1 1 0	7.90	1 1 1				
ZN	S04	6.89	1 1 0						
ZN	CL	8.40	1 1 0	11.06	1 2 0	14.76	1 3 0	9.81	1 1
ZN	P04	11.18	1 1 1						
ZN	CIT	10.83	1 1 0						
ZN	AC	10.21	1 1 0	14.29	1 2 0				
ZN	TART	14.06	1 1 1	9.18	1 1 0				
ZN	CYST	6.80	1 1 0	8.47	1 2 0				
ZN	PHTH	9.68	1 1 0						
ZN	OH	9.35	1 0-1	14.13	1 0-3	19.64	1 0-4	9.77	1 0-
NI	CO3-	5.62	1 1 0	5.70	1 1 1				
NI	S04	4.89	1 1 0						
NI	CL	7.30	1 1 0	9.46	1 2 0				
NI	P04	9.48	1 1 1						
NI	CIT	5.93	1 1 0	6.36	1 1 1	9.14	1 1 2		
NI	AC	8.81	1 1 0	13.09	1 2 0				
NI	CYST	6.37	1 2 0						
NI	PHTH	7.78	1 1 0						
NI	OH	6.55	1 0-1						
PR	CO3-	8.16	1 1 0	10.57	1 2 0	9.34	1 1 1	10.40	1 2
PR	S04	8.93	1 1 0						
PR	CL	10.54	1 1 0	12.60	1 2 0	15.20	1 3 0	16.64	1 4
PR	CIT	11.48	1 1 2	10.40	1 1 1	12.37	1 1 0		
PR	AC	12.06	1 1 0	15.53	1 2 0				
PR	TART	10.22	1 1 0						
PR	CYST	6.84	1 1 0						
PR	PHTH	10.92	1 1 0	16.58	1 2 0				



03130

CO2+	PO4	11.36	1 1 1						
CO2+	CIT	24.34	1 1 1	33.02	1 1 2				
CO2+	AC	10.40	1 1 0	14.77	1 2 0				
CO2+	TAPT	9.46	1 1 0						
CO2+	CYST	7.58	1 1 0	10.76	1 2 0				
CO2+	PTH	13.42	1 2 0						
CO2+	OH	9.03	1 0-1	11.15	1 0-2	16.91	1 0-3		
H	CO3-	2.90	0 1 1	3.74	0 1 2				
H	SO4	6.97	0 1 1						
H	PO4	6.57	0 1 1	6.47	0 1 2	11.61	0 1 3		
H	SiO3	5.91	0 1 1	3.45	0 1 2				
H	CIT	7.05	0 1 1	7.95	0 1 2	10.59	0 1 3	14.57	0 1
H	AC	7.16	0 1 1						
H	TAPT	8.16	0 1 1	12.10	0 1 2				
H	CYST	6.78	0 1 1	5.42	0 1 2	10.40	0 1 3		
H	PTH	7.46	0 1 1	11.60	0 1 2				

334994

CA

AS A FREE METAL/	61.1 PERCENT
BOUND WITH CO3-/	.9 PERCENT
BOUND WITH SO4 /	37.9 PERCENT

FE3

BOUND WITH CIT /	1.1 PERCENT
BOUND WITH CYST/	26.6 PERCENT
IN SOLID FORM WITH OH /	72.3 PERCENT

CU2+

BOUND WITH CO3-/	.7 PERCENT
BOUND WITH CIT /	98.7 PERCENT

CD

AS A FREE METAL/	52.1 PERCENT
BOUND WITH CO3-/	7.8 PERCENT
BOUND WITH SO4 /	32.3 PERCENT
BOUND WITH CL /	6.4 PERCENT
BOUND WITH CIT /	.7 PERCENT

ZN

AS A FREE METAL/	39.1 PERCENT
BOUND WITH CO3-/	5.1 PERCENT
BOUND WITH SO4 /	24.2 PERCENT
BOUND WITH CL /	.8 PERCENT
BOUND WITH CYST/	30.5 PERCENT

NI

AS A FREE METAL/	51.5 PERCENT
BOUND WITH CO3-/	10.7 PERCENT
BOUND WITH SO4 /	31.9 PERCENT
BOUND WITH CIT /	4.0 PERCENT
BOUND WITH CYST/	1.0 PERCENT
BOUND WITH OH /	.7 PERCENT

PB

BOUND WITH CO3-/	4.8 PERCENT
BOUND WITH SO4 /	.8 PERCENT
BOUND WITH CYST/	93.8 PERCENT

CO2+

AS A FREE METAL/	43.6 PERCENT
BOUND WITH CO3-/	7.2 PERCENT
BOUND WITH SO4 /	42.8 PERCENT
BOUND WITH CL /	.8 PERCENT
BOUND WITH CYST/	5.3 PERCENT

CO3+

CO3-

BOUND WITH CA /	.9 PERCENT
BOUND WITH H /	98.6 PERCENT

SO4

AS A FREE LIGAND/	96.0 PERCENT
BOUND WITH CA /	3.9 PERCENT

CL

AS A FREE LIGAND/	100.0 PERCENT
-------------------	---------------

## SI03

BOUND WITH H / 100.0 PERCENT

## CIT

BOUND WITH CA / 36.7 PERCENT

BOUND WITH FE3 / .8 PERCENT

BOUND WITH CU2+ / 10.1 PERCENT

BOUND WITH NI / 49.9 PERCENT

BOUND WITH H / 3.1 PERCENT

## AC

AS A FREE LIGAND / 98.8 PERCENT

BOUND WITH H / .7 PERCENT

## TART

AS A FREE LIGAND / 88.5 PERCENT

BOUND WITH CA / 11.3 PERCENT

## CYST

BOUND WITH FE3 / 19.8 PERCENT

BOUND WITH ZN / 2.6 PERCENT

BOUND WITH NI / 13.1 PERCENT

BOUND WITH PB / 2.3 PERCENT

BOUND WITH H / 61.8 PERCENT

## PHTH

AS A FREE LIGAND / 88.9 PERCENT

BOUND WITH CA / 9.0 PERCENT

BOUND WITH NI / .7 PERCENT

BOUND WITH H / 1.4 PERCENT

THESE COMPUTATIONS INVOLVE 10 METALS, 11 LIGANDS, 151 COMPLEXES AND

Table XIII

IONIC STRENGTH = .1100000E-01

EM-1  
Organic

1 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	INMAT	GUESS	TOTCC $\bar{i}$	TOTCC
CA	1	8.000	2.990	
FE3	6	8.000	5.510	
CU2+	9	8.000	7.200	
CD	$\bar{11}$	8.000	8.320	
ZN	$\bar{12}$	8.000	7.120	
NI	$\bar{13}$	8.000	5.830	
PB	$\bar{15}$	8.000	6.810	
CO2+	16	8.000	7.770	
CO3+	$\bar{17}$	8.000	8.000	

LIGAND	INMAT	GUESS	TOTCC $\bar{i}$	TOTCC
CO3-	1	8.000	2.940	
SO4	2	8.000	2.730	
CL	3	8.000	3.040	
PO4	9	8.000	7.010	
SIO3	$\bar{12}$	8.000	3.480	
CIT	17	8.000	5.410	
AC	15	8.000	4.940	
TART	20	8.000	5.240	
CYST	30	8.000	5.110	
PHTH	22	8.000	5.540	
F I Y F D P H			7.550	



	CO2+	PO4	13.15	1 1 1					
	CO2+	CIT	25.28	1 1 1	34.51	1 1 2			
	CO2+	AC	11.61	1 1 0	15.85	1 2 0			
	CO2+	TART	10.58	1 1 0					
	CO2+	CYST	7.91	1 1 0	10.26	1 2 0			
	CO2+	PHTH	14.48	1 2 0					
	CO2+	OH	9.83	1 0-1	11.41	1 0-2	16.69	1 0-3	
	H	CO3-	2.97	0 1 1	4.29	0 1 2			
	H	SO4	8.28	0 1 1					
	H	PO4	7.19	0 1 1	7.51	0 1 2	13.13	0 1 3	
	H	SI03	5.46	0 1 1	3.48	0 1 2			
	H	CIT	6.83	0 1 1	8.15	0 1 2	11.27	0 1 3	15.80
	H	AC	7.57	0 1 1					
	H	TART	8.55	0 1 1	12.97	0 1 2			
	H	CYST	6.37	0 1 1	5.49	0 1 2	11.02	0 1 3	
	H	PHTH	7.84	0 1 1	12.46	0 1 2			

63503

635006

CA  
 AS A FREE METAL/ 85.5 PERCENT  
 BOUND WITH CO3- / 1.6 PERCENT  
 BOUND WITH SO4 / 12.3 PERCENT

FE3  
 BOUND WITH CYST/ 43.7 PERCENT  
 IN SOLID FORM WITH OH / 56.2 PERCENT

CU2+  
 BOUND WITH CIT / 99.6 PERCENT

CD  
 AS A FREE METAL/ 57.1 PERCENT  
 BOUND WITH CO3- / 25.3 PERCENT  
 BOUND WITH SO4 / 8.2 PERCENT  
 BOUND WITH CL / 5.6 PERCENT  
 BOUND WITH CIT / 2.3 PERCENT  
 BOUND WITH TART/ .9 PERCENT

ZN  
 AS A FREE METAL/ 8.3 PERCENT  
 BOUND WITH CO3- / 3.0 PERCENT  
 BOUND WITH SO4 / 1.2 PERCENT  
 BOUND WITH CYST/ 87.1 PERCENT

NI  
 AS A FREE METAL/ 25.1 PERCENT  
 BOUND WITH CO3- / 14.5 PERCENT  
 BOUND WITH SO4 / 3.6 PERCENT  
 BOUND WITH CIT / 14.6 PERCENT  
 BOUND WITH CYST/ 40.7 PERCENT  
 BOUND WITH OH / 1.4 PERCENT

PB  
 BOUND WITH CO3- / 1.6 PERCENT  
 BOUND WITH CYST/ 98.3 PERCENT

CO2+  
 AS A FREE METAL/ 31.3 PERCENT  
 BOUND WITH CO3- / 14.4 PERCENT  
 BOUND WITH SO4 / 7.2 PERCENT  
 BOUND WITH CYST/ 46.0 PERCENT  
 BOUND WITH OH / .6 PERCENT

CO3+

CO3-  
 BOUND WITH CA / 1.4 PERCENT  
 BOUND WITH H / 93.2 PERCENT

SO4  
 AS A FREE LIGAND/ 93.2 PERCENT  
 BOUND WITH CA / 6.8 PERCENT

CL  
 AS A FREE LIGAND/ 100.0 PERCENT

PO4

100-007-100

BOUND WITH H / 100.0 PERCENT

CIT

BOUND WITH CA / 88.7 PERCENT

BOUND WITH CU2+ / 1.6 PERCENT

BOUND WITH NI / 5.5 PERCENT

BOUND WITH H / 4.0 PERCENT

AC

AS A FREE LIGAND / 99.2 PERCENT

BOUND WITH CA / .6 PERCENT

TART

AS A FREE LIGAND / 81.2 PERCENT

BOUND WITH CA / 18.7 PERCENT

CYST

BOUND WITH FE3 / 34.8 PERCENT

BOUND WITH ZN / 1.0 PERCENT

BOUND WITH NI / 15.5 PERCENT

BOUND WITH PB / 2.0 PERCENT

BOUND WITH H / 46.6 PERCENT

PHTH

AS A FREE LIGAND / 84.1 PERCENT

BOUND WITH CA / 15.4 PERCENT

BOUND WITH H / .5 PERCENT



metal which passes a 0.45  $\mu\text{m}$  membrane filter. The data indicates that complexing agents present at natural levels may be important in maintaining metals in solution promoting transport and affecting toxicity to aquatic organisms. Natural ligands such as those present in surface and bog water may also affect the rate and extent of metal sulfide leaching processes. Thus, total metal measurements, although informative, would be even more so if detailed metal distribution between species was known. At the present time, suspended and total metal in conjunction with realistic computer equilibrium models is the most effective approach to understanding environmental metal cycling.

## LABORATORY LEACHING

The objective of the laboratory leaching program is to determine the rate and mechanism(s) of metal and other chemical contaminant release from mining-derived solids under the influence of variable aqueous conditions. The rates of metal release will contribute to the modeling of contaminant release, transport and cycling associated with the mining of metal sulfide ores from the Duluth Gabbro Complex. Solids of particular importance for leaching studies are lean ore and waste rock which may be stockpiled near mining sites under the influence of natural weathering conditions. Understanding the mechanism of metal release in field and laboratory studies will promote procedures to inhibit or minimize environmental degradation. Specific stockpiling procedures and/or water treatment processes will be suggested.

### 1. Experimental

- a. Sample Handling: Samples of waste rock and lean ore (~ 0.27% combined Cu-Ni) were collected by Paul Eger in the fall of 1976 from the Gabbro stockpiles adjacent to the Erie Mining Co. Dunker Pit (south). Samples were ground at MRRRC (University of Minnesota; Dr. Iwao Iwasaki) to minus 200 mesh in particle size. This corresponds to a particle-size of <70  $\mu\text{m}$  particle diameter. Ground samples were stored in clean, polyethylene containers closed to the atmosphere. An unknown quantity of surface oxidation undoubtedly occurred in the grinding step by generating fresh surface in contact with air.
- b. Batch Reactor Design and Procedures: All batch experiments were performed in 4-liter borosilicate glass reaction cells (reactors) with tight fitting Plexiglass covers fitted with

polyethylene liners. The plexiglass cover was constructed with three sealable holes to permit sample collection and introduction of pH and ion-specific electrodes for in-situ analysis. Compressed air was bubbled through the reaction cells from gas dispersion tubes after passing through a filter.  $N_2$  gas was bubbled directly from purified tank  $N_2$  by means of dispersion tubes. All experiments were conducted in a constant temperature room maintained at  $20.0 \pm 0.5^\circ C$ . After bubbling compressed air or  $N_2$  through 3500 ml. of de-ionized, distilled water (DDW) for  $\approx$  2 hours, 2.0 to 100.0g of crushed and ground rock (-200 mesh) was added to the reaction cells per liter of DDW. The solutions were continuously stirred to maintain the solid in suspension and keep the slurry homogenized. Stirring was performed with polyethylene-coated paddle mixers suspended from above the reactor.

One-hundred and fifty-ml aliquots of the well-mixed suspension were withdrawn periodically from the reaction cell with an acid-cleaned glass pipette and immediately filtered through acid-rinsed  $0.4 \mu m$  pore-size Nuclepore membranes. A portion ( $\approx$ 30 ml) was then used for pH determination on an Orion 801A digital pH meter with a glass and saturated calomel electrode. The pH meter was calibrated with commercial pH buffer solutions at pH 4.0, pH 7.0 and pH 9.0. The remaining sample volume was stored in a 250-ml. acid-cleaned polyethylene bottle and acidified with 4 drops of concentrated  $HNO_3$ . A filter and acid blank were carried through the entire procedure. The

acidified sample was analyzed for Cu, Ni, Fe, and  $\text{SO}_4$  by procedures described previously.

## 2. Preliminary Results

- a. Experiment 1: A preliminary experiment was performed to gain information on optimal experimental loading rates and to observe whether leaching did occur. Three reactors loaded at 16.7, 33.3 and 100.0 g of crushed rock (Erie) per liter of DDW respectively, were maintained well-mixed with air diffusion up to 343 hours. Initial data indicated Ni and Cu release was substantial. Final pH of the reaction mixture was 7.63, 7.86 and 8.12, respectively for 16.7, 33.3 and 100.0g/l loading. A fourth reaction cell was studied with no air diffusion but constant mixing at 25 g/l loading. Final pH was 7.44 with significant Cu and Ni release.

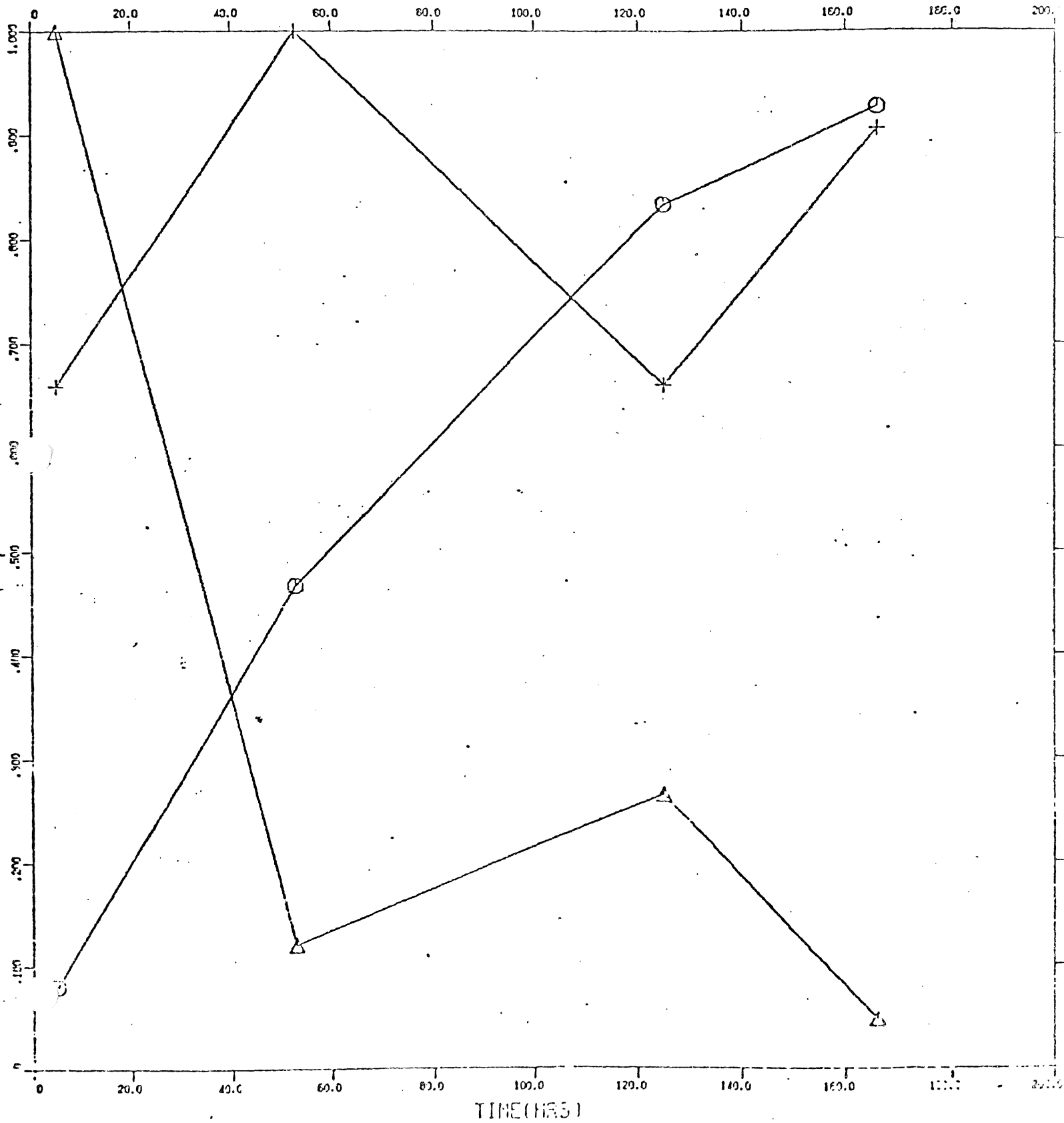
Figure XIV is a kinetic plot for the reaction cell with a loading of 100.0 g/l. The y-axis ( $C/C_{\text{max}}$ ) is the concentration of a component at time,  $t$ , divided by the maximum concentration of the component measured in the course of the reaction. The kinetic plot indicates that sulfate undergoes a buildup in the cell solution with an estimated rate constant ( $k$ ) of  $0.06 \text{ sec}^{-1}$ . Ni and Cu undergo a relatively rapid release; however, Cu levels decrease with time suggesting sorption onto suspended solids probably as the hydroxide or carbonate. Ni levels remain elevated over the time period studied indicating a paucity of effective removal mechanisms (i.e., strong complexation by  $\text{H}_2\text{O-Ni}(\text{H}_2\text{O})_6^{+2}$  aqueous species). This pattern repeats itself often in subsequent experiments.

Figure XIV Leaching Exp. 1-5.

○ SO<sub>4</sub> (C<sub>MAX</sub>=15.0PPM)

△ CU (C<sub>MAX</sub>=12.5PPB)

+ NI (C<sub>MAX</sub>=35PPB)



b. Experiment 2: This experiment was designed to further study the influence of solids loading on chemical release as well as demonstrate the contribution of  $O_2$  to leaching. Also, careful attention was paid to delineating which chemical parameters could most effectively furnish overall leaching rates. Six reaction cells were run simultaneously in which cells 1-4 had  $O_2$  bubbled through them while 5 and 6 had  $N_2$  as the purging gas. Dissolved oxygen (D.O.) levels were maintained at  $> 9.0$  mg/l in reactors 1-4 while D.O. concentrations of  $< 0.3$  mg/l were maintained in 5-6 until late in the experiment. Table XV lists the measured components as a function of time for the kinetic run. In performing the experiment, sampling frequency emphasized the rapidly-released components as well as long-term leaching. Reaction cells 1-4 had solids loadings (-200 mesh) of 2, 10, 50 and 100 g/l respectively, while 5 and 6 were duplicates of reactors 1 and 3 except  $N_2$  was the purging gas. All reaction cells were well-mixed and maintained at  $20.0 \pm 0.5^\circ C$  for the experiment. Solution components measured were Cu, Ni, Fe,  $SO_4$ , and D.O. and pH.

Kinetic plots ( $C/C_{max}$  vs time (hrs.)) for reaction cells 1-6 are shown in Figure XV-XX and experimental data given in Table XV. The kinetic plot for reactor 1 shows the time-release behavior of Cu, Ni, Fe and  $SO_4$  at a loading of 2.0 g/l crushed rock. Solution pH decreased rapidly on equilibration of DDW with the solids to 3.66 and slowly rose to 4.58 over 748 hours. Concurrent with the low pH values were high Fe,

Cu and Ni concentrations but low  $\text{SO}_4$ . The low pH may be due to a combination of sulfide oxidation to sulfate releasing  $\text{H}^+$  or the hydrolysis of rapidly-released  $\text{Fe}^{+3}$  releasing  $\text{H}^+$ . Titration of 10.0 g quantities of the crushed rock with 1.0N  $\text{H}_2\text{SO}_4$  yielded a buffering capacity of  $\sim 0.4$  meq  $\text{H}^+$ /g. Initial estimates indicate that the  $\text{H}^+$  released should not have exceeded the buffering capacity of the rock; however, further study is required.  $\text{SO}_4$  and Fe release show similar trends although the low  $\text{SO}_4$  levels generate a high analytical uncertainty. Ni and Cu release follow the same general trend with rapid release initially followed by a slower release stage. Cu, Ni and Fe release are apparently related with each exhibiting 1st order-like kinetics. Kinetic rate constants were not calculated because of the preliminary nature of the data but the release pattern suggests that at the low pH conditions observed, significant amounts of each metal are in a free or soluble, complexed form which do not compete effectively with  $\text{H}^+$  for available sorption sites. Precipitation of Cu and Ni-hydroxides is not predicted in acid solutions.

Comparison of reactors 1 and 5 is informative because the latter reactor is low in D.O. Fe and  $\text{SO}_4$  exhibit similar concentrations and release trends in both reactors but Cu and Ni differ. Cu and Ni levels are reduced in reactor 5 as compared to 1 but are influenced by both pH and oxygen concentrations. Solution pH for reactor 5 ranged from 4.27 to 5.04 with the

Figure XV. Leaching Expt. 2-1.

- SO<sub>4</sub> (C<sub>MAX</sub> 3.6 PPM)
- △ NI (C<sub>MAX</sub> 326.6 PPB)
- + CU (C<sub>MAX</sub> 378.0 PPB)
- × FE (C<sub>MAX</sub> 7500 PPB)

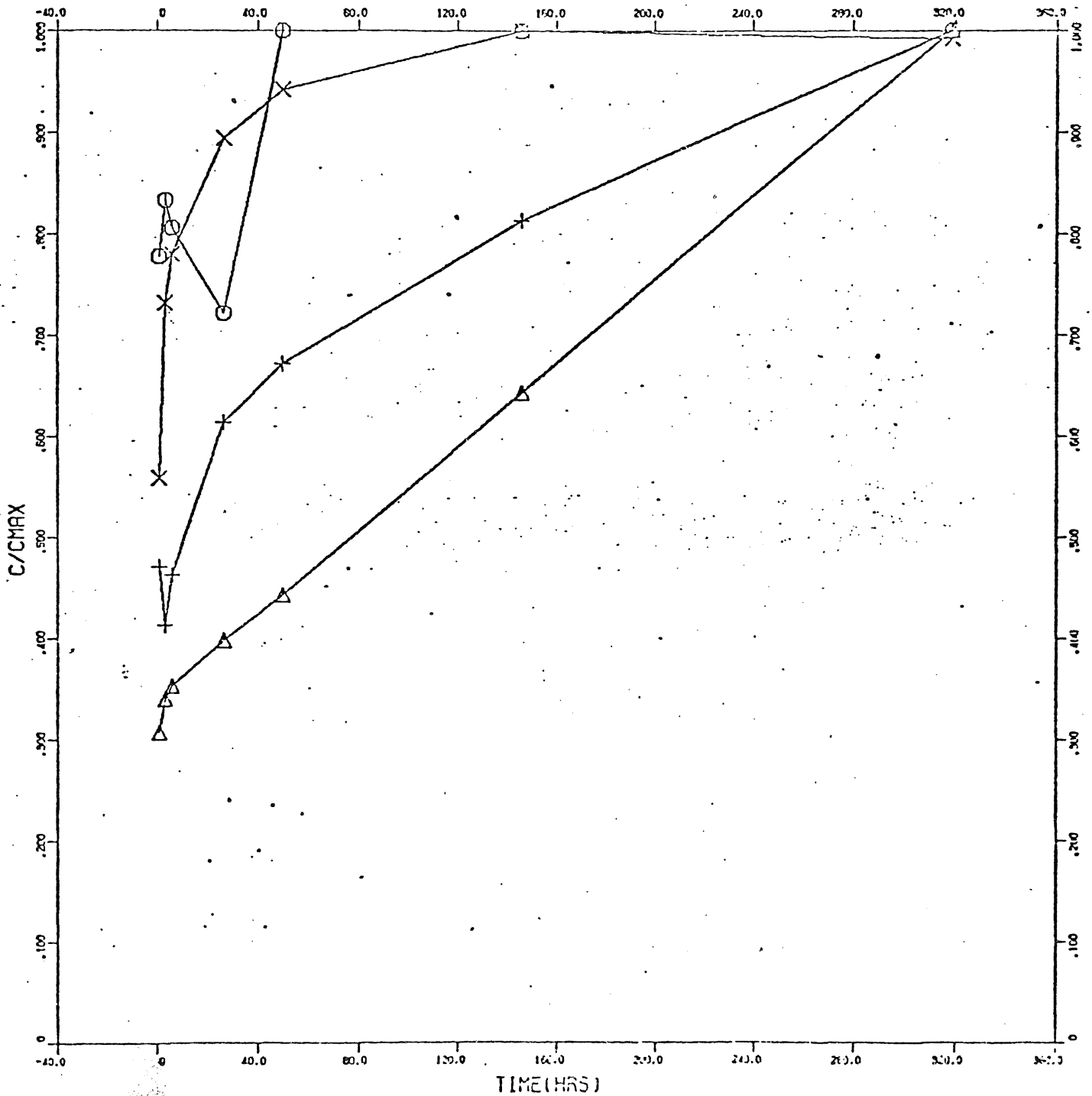
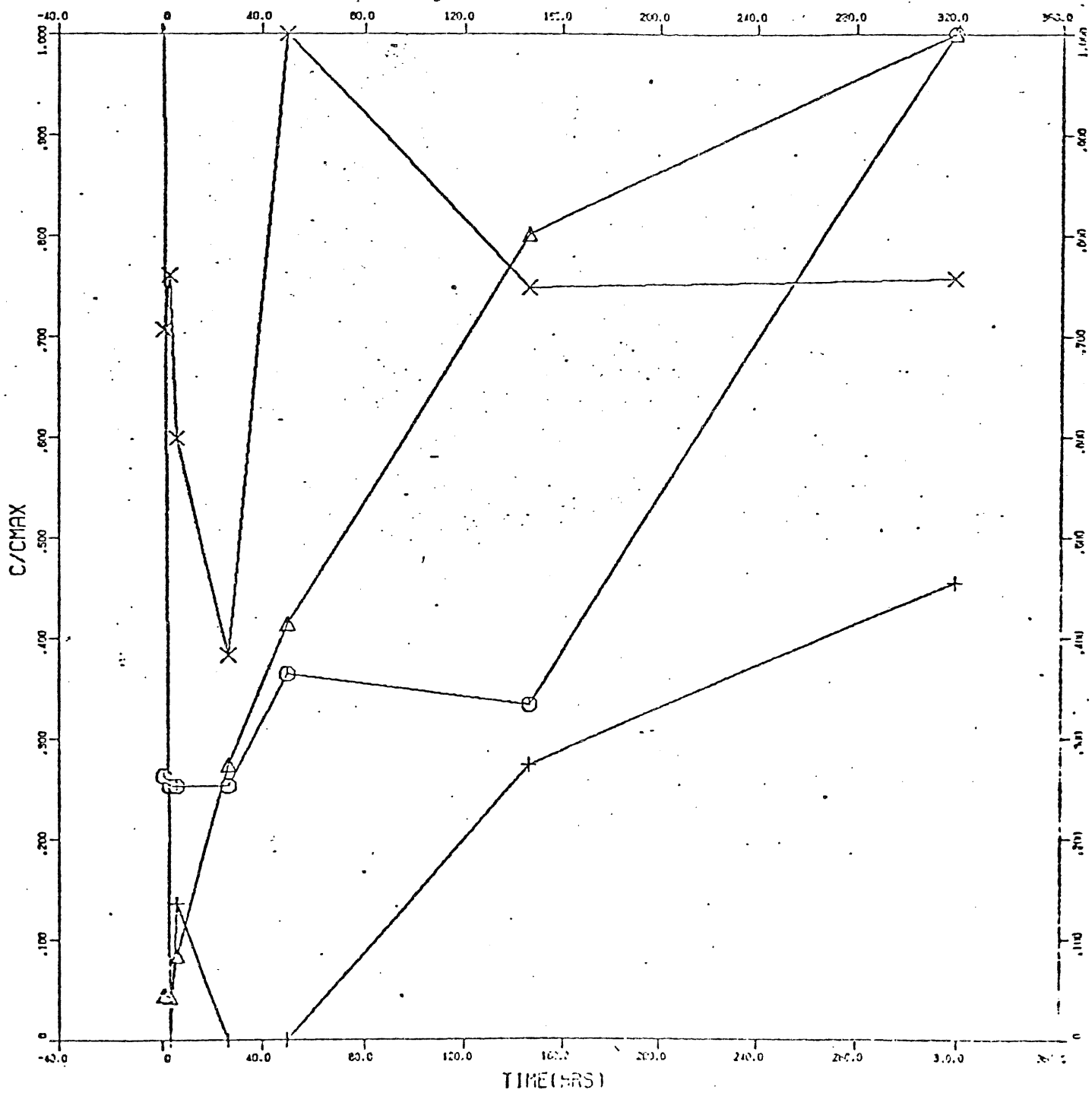




Figure XVI. Leaching Expt. 2-2.

○ SO4(CMAX 9.9 PPM)      × FE(CMAX 22.2 PPB)  
△ NI(CMAX 373 PPB)  
+ CU(CMAX 2.2 PPB)



2-2 LEACHING EXPERIMENT 2-2

Figure xvii. Leaching Expt. 2-3.

- SO4(CMAX 20.4 PPM)
- △ NI(CMAX 110.8 PPB)
- +
- CU(CMAX 3.70 PPB)
- × FE(CMAX 22.3 PPB)

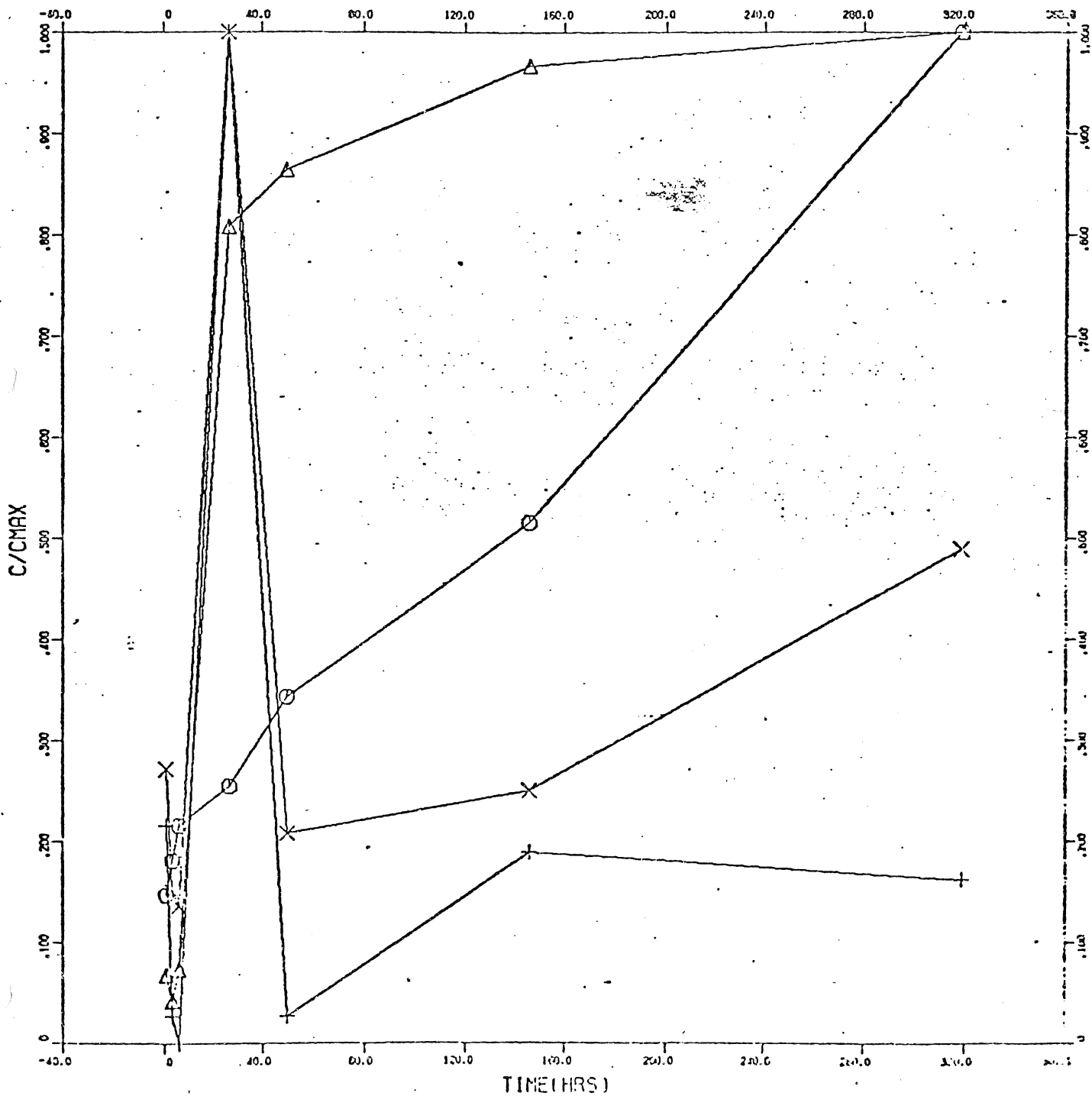
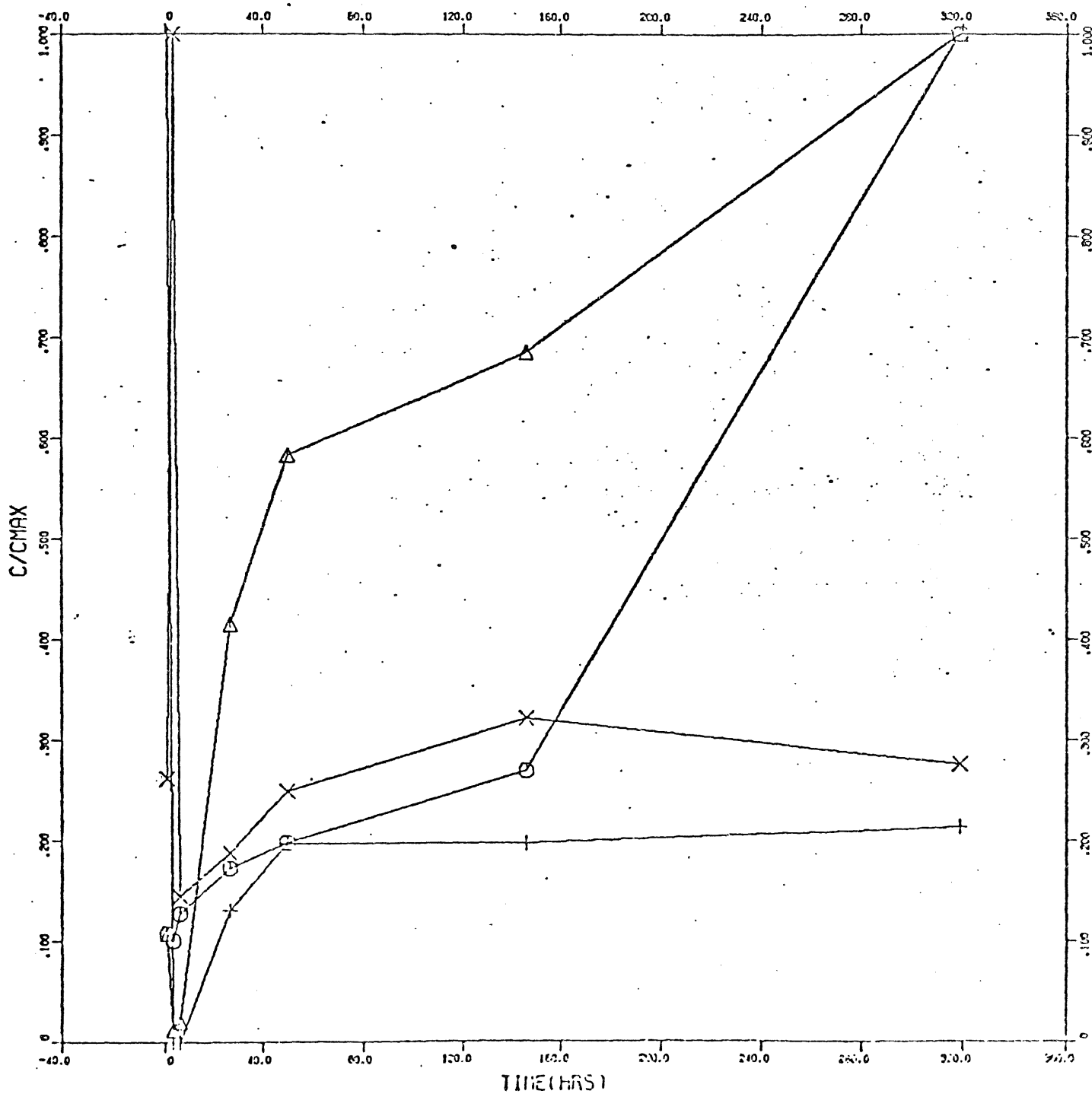


Figure XVIII. Leaching Expt. 2-4.

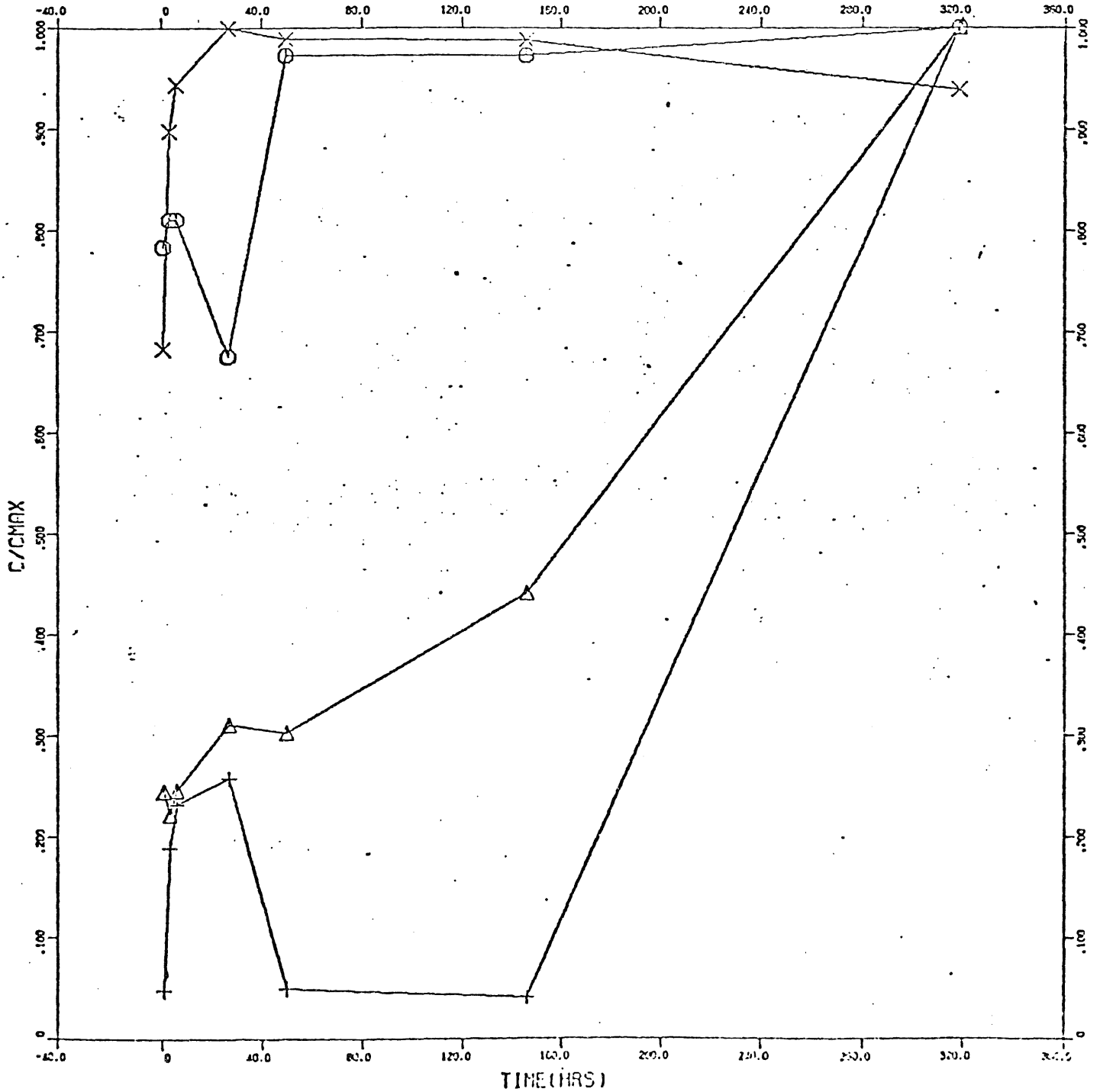
- SO<sub>4</sub>(C<sub>MAX</sub> 59.5 PPM)
- △ NI(C<sub>MAX</sub> 113.5 PPB)
- + CU(C<sub>MAX</sub> 6.1 PPB)
- × FE(C<sub>MAX</sub> 44.2 PPB)



EXPT 2-4

Figure XIX. Leaching Expt. 2-5.

- SO4 (C<sub>MAX</sub> 3.7 PPM)
- △ NI (C<sub>MAX</sub> 230.6 PPB)
- + CU (C<sub>MAX</sub> 41.8 PPB)
- × FE (C<sub>MAX</sub> 7330 PPB)



5-72 EXP. LEACHING SUBSTITUTIONAL LEAD

777 U17 U31 W10 T03 NEU EPHAZEXUZLEHUNG EXPZ-6

Figure XX. Leaching Expt. 2-6.

50%  
1/2  
pH > 9

- SO4 (C<sub>MAX</sub> 10.1 PPM)
- △ NI (C<sub>MAX</sub> 17.1 PPB)
- + CU (C<sub>MAX</sub> 1.6 PPB)
- × FE (C<sub>MAX</sub> 48.2 PPB)

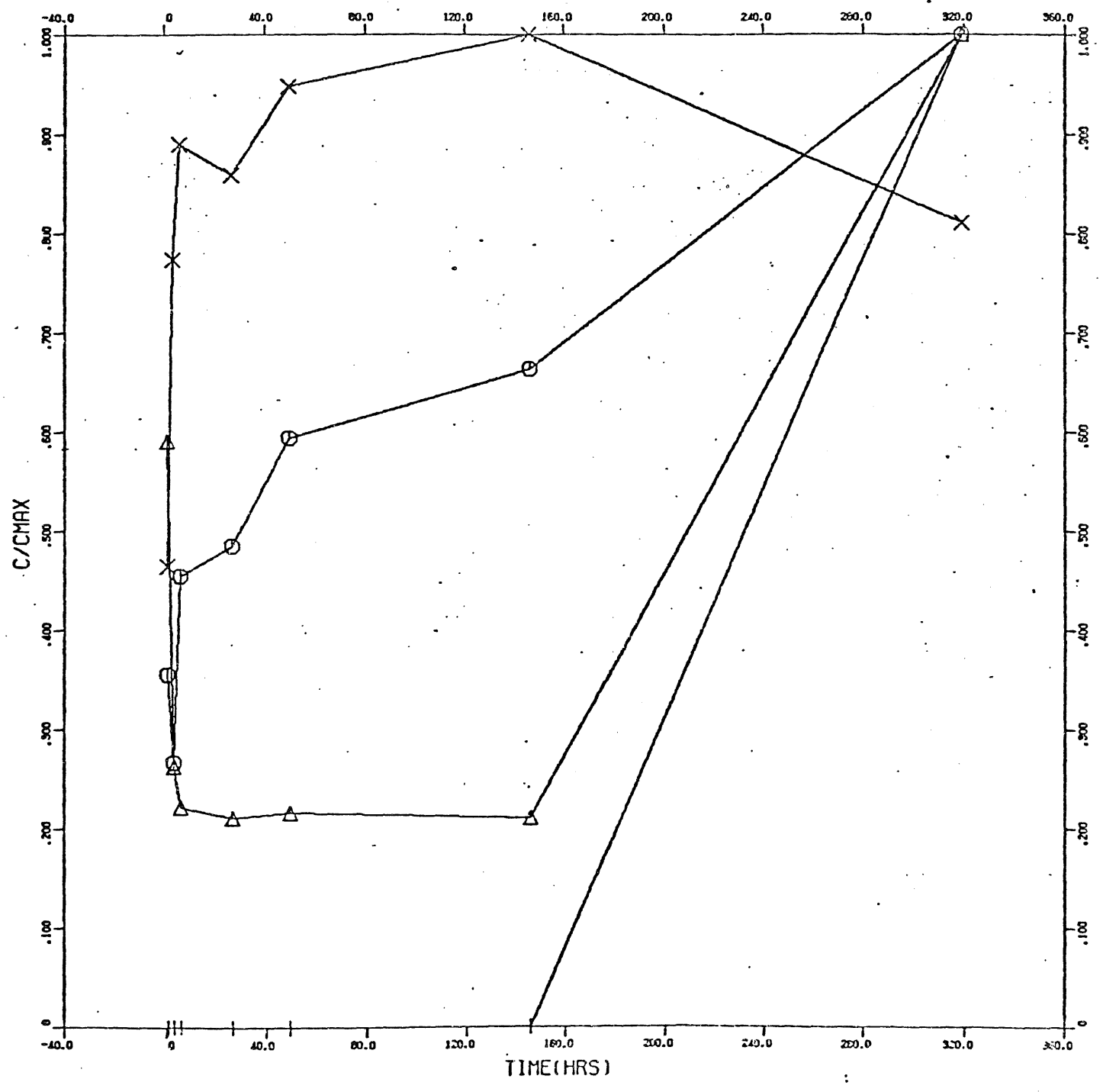


Table XV

## LEACHING OF ERIE ROCK-EXPERIMENT 2

Effect of Solid: Solution Ratio

Reactor	Time (hrs.)	SO <sub>4</sub> (mg/l)	pH	Ni (μg/l)	Ni (μg/g)	Cu (μg/l)	Cu (μg/g)	Fe (μg/l)
1	0.75	2.8	3.66	100.4	50.2	178.2	89.1	4240
r Diffusion	3.25	3.0	3.82	111.2	55.6	156.2	78.1	5550
g/l	6.00	2.9	3.89	115.3	57.65	174.9	87.5	5910
	26.75	2.6	4.00	---	---	232.1	116.1	6780
	49.50	3.6	4.20	144.8	72.4	254.1	127.1	7140
	146.0	3.6	4.41	210.0	105.0	307.3	153.7	7580
	319.3	3.6	4.42	326.6	163.0	378.0	189.0	7520
	507		4.51					7980
AD-a	748	4.8	4.48					8000
		0						440
	0.75	2.6	7.10	16.6	1.66	2.2	0.2	15.
2	3.25	2.5	7.19	16.0	1.6	ND	--	16.
r Diffusion	6.00	2.5	7.18	31.4	3.14	0.3	0.03	13.
	26.75	2.5	7.21	102.2	10.22	ND	--	8.
g/l	49.50	3.6	7.41	154.4	15.44	ND	--	22.
	146.0	3.3	7.39	298.8	29.88	0.6	0.06	16.
	319.3	9.9	7.11	373-0	37.30	1.0	0.1	16.
	507.	12.9	7.12					17.
	748.	13.7	6.90					
-AD-2		3.8						1650

(Continued)

	Time (hrs.)	SO <sub>4</sub> (mg/l)	pH	Ni (µg/l)	Ni (µg/g)	Cu (µg/l)	Cu (µg/g)	Fe (µg/g)
3	0.75	3.0	8.19	7.47	0.15	0.8	0.4	12
Air Diffusion	3.25	3.7	7.88	4.55	0.09	0.1	0.02	6
	6.00	4.4	7.92	8.14	0.16	ND	--	6
	26.75	5.2	7.89	89.5	1.79	3.7	0.07	45
50 g/l	49.5	7.0	8.01	95.7	1.90	0.1	0.002	9
	146.0	10.5	8.02	107.1	2.14	0.7	0.014	11
	319.3	20.4	7.81	110.8	2.22	0.6	0.012	22
	507	53.3	7.49					19
3-AD-2	748	110	7.55					
		3.8						5660
4		6.4	8.80	12.3	0.12	6.1	0.06	17
Air Diffusion		6.0	8.50	1.4	0.01	ND	--	44
		7.6	8.41	2.3	0.02	ND	--	6
		10.3	8.12	47.1	0.47	0.8	0.008	8
100 g/l		11.8	8.22	66.2	0.66	1.2	0.012	11
		16.0	8.21	77.8	0.78	1.2	0.012	14
		59.5	8.04	113.5	1.14	1.3	0.013	12
		128	8.02					9
4-AD-2		148	7.87					
		3.7						

(Continued)

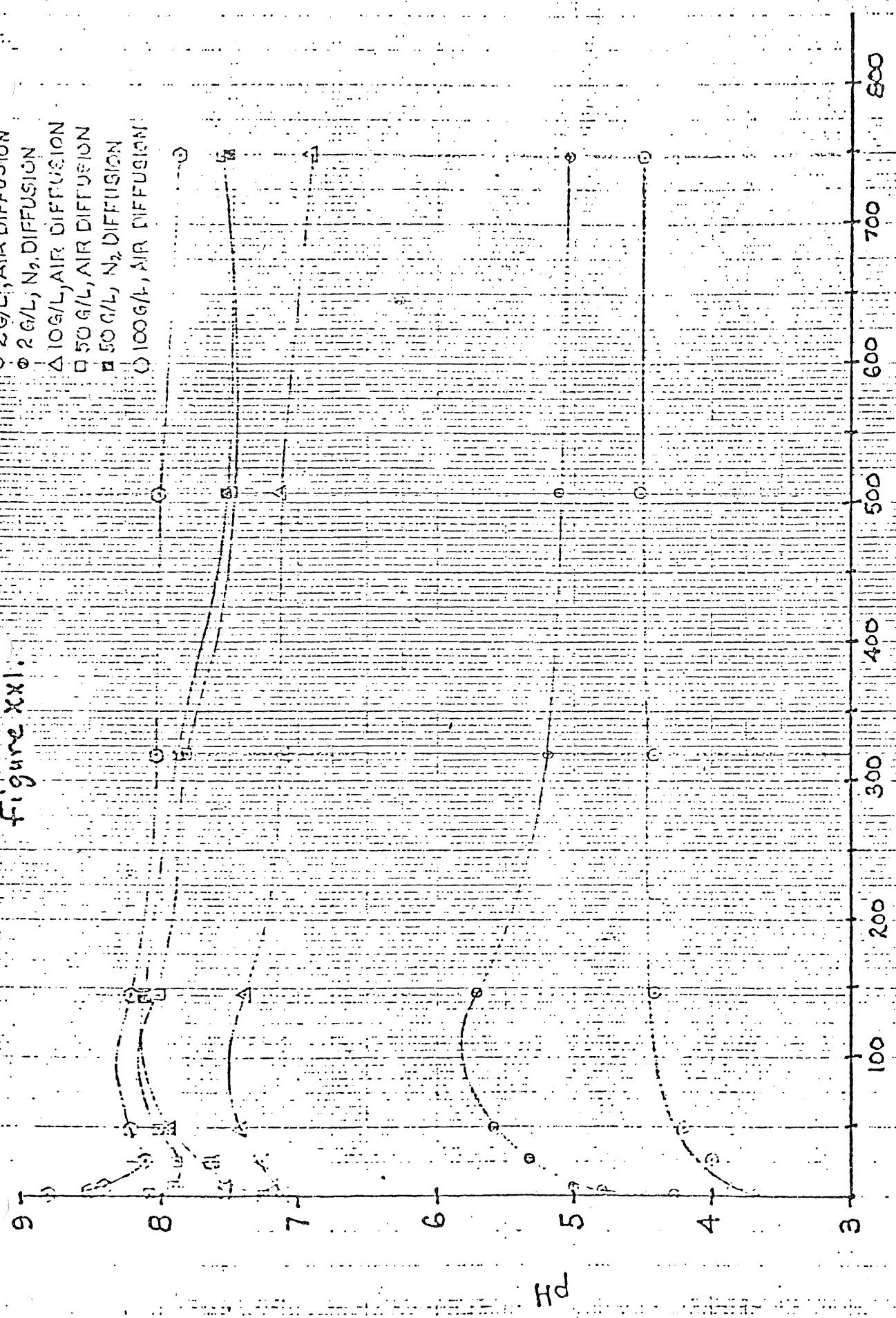
	Time (hrs.)	SO <sub>4</sub> (mg/l)	pH	Ni (µg/l)	Ni (µg/g)	Cu (µg/l)	Cu (µg/g)	Fe (µg/l)
5	0.75	2.9	4.27	56.5	28.3	2.0	1.0	5010
Diffusion	3.25	3.0	4.79	51.1	25.6	7.9	39.5	6580
	6.00	3.0	5.00	56.8	28.4	9.7	4.85	6920
g/l	26.75	2.5	5.32	71.8	35.9	10.8	5.4	7330
	49.5	3.6	69.8	34.9	34.9	2.1	1.05	7250
	146.0	3.6	5.72	101.8	50.9	1.7	1.35	7240
	319.3	3.7	5.18	230.6	114.3	41.8	20.9	6880
	507	3.5	5.12					6910
	748	3.8	5.04					7240
-AD-2		0						760
6		3.6	7.21	10.1	0.2	ND	--	22.4
Diffusion		2.7	7.51	4.5	0.09	ND	--	37.3
		4.6	7.51			ND	--	42.9
		4.9	7.61	3.6	0.07	ND	--	41.4
50 g/l		6.0	7.93	3.7	0.07	ND	--	45.7
		6.7	8.12	3.6	0.07	ND	--	48.2
		10.1	7.85	17.1	0.34	1.6	0.032	39.1
		25.1	7.51					31.1
		29.1	7.48					
-AD-2		3.5						5150



# PH VS TIME: EXPERIMENT 2

Figure XXI.

- 2 G/L, AIR DIFFUSION
- ◐ 2 G/L, N<sub>2</sub> DIFFUSION
- △ 10 G/L, AIR DIFFUSION
- ◑ 50 G/L, AIR DIFFUSION
- ◒ 50 G/L, N<sub>2</sub> DIFFUSION
- 100 G/L, AIR DIFFUSION



TIME IN HOURS

KL 12/13/76

difference in pH between 1 and 5 likely due to sulfide oxidation. The higher pH for reactor 5 may have influenced final metal concentrations but the anoxic conditions are also important. The decreased Cu concentrations for reactor 5 may be a result of Cu sorption following initial release. pH variations with time are shown in Figure XXI for all reactors.

The quantity of information generated on the leaching behaviour of the crushed rock precludes drawing firm conclusions at this time but several observations can be made by examining the data from all six reactors.

- 1). Except for the low solid loading reaction cells, high pH values were maintained typical of buffering by silicate minerals.
- 2).  $\text{SO}_4$  accumulation in solution was proportional to surface area available for leaching while Cu exhibited an inverse relationship.
- 3). The kinetic plots can be divided into at least two and perhaps more stages; an initial fast release followed by a linear or parabolic buildup or a decrease (sorption?).
- 4).  $\text{SO}_4$  and Ni as measurable parameters may serve as indicator components for determining reaction rates due to their apparent conservative behavior.
- 5). Reactions carried out in the presence of  $\text{O}_2$  yielded greater metal and  $\text{SO}_4$  concentrations in solution as compared to  $\text{N}_2$  being used as a purge gas.

The buffering effect of the crushed rock is demonstrated in Figure XXII. When the final solution pH in all experiments

is plotted versus the loading in g/l, a parabolic function results. The equilibrium solution pH of 7.5 to 8.0 for loadings > 20 g/l is typical of silicate mineral buffering. pH is a master variable in aqueous solutions and may be the controlling factor in metal release. Figure XXIII is a plot of all data for Ni release in all experiments given in  $\mu\text{g Ni/g}$  rock versus pH at sampling time. The plot yields a decreasing exponential function with increasing pH (i.e., higher concentrations at low pH). Although preliminary in nature, the data does portray in real terms the potential dangers to the environment if drainage through mineralized areas is permitted to become acidic.

### 3. Future Experiments.

a. Batch Reactions: Future experiments will be conducted to determine the effect of particle size,  $\text{O}_2$  tension, pH, temperature, solution composition, solid's chemical composition and mineral phases on rates and mechanism of metal release. A survey of metals leached into solution will be performed and will include Cd, Pb, Mn, Al, Zn and Co plus Ca, Mg and Si.

b. Column Studies: Column experiments are currently being set-up to determine the long-term release potential of Erie rock and AMAX rock under the influence of a slow-flowing (0.1 ml/mix), continuous stream of simulated or real rainwater, groundwater and surface water. Column experiments will be performed in 5 x 90 cm borosilicate

*how to handle  
effect of organics*

*H<sub>2</sub>O<sub>2</sub>*