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FINAL REPORT
to
MINNESOTA ENVIRONMENTAL QUALITY BOARD
COPPER-NICKEL STUDY

MINERAL PROCESSING STUDIES

July 31, 1978

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to

Minnesota Environmental Quality Board
Copper-Nickel Study

Mineral Processing Studies
Hydrometallurgical Processing of Concentrates

by

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ABSTRACT

Some hydrometallurgical and environmental aspects of processing Duluth copper-nickel concentrate are examined in this study. A literature review of six hydrometallurgical techniques pertinent to this study revealed that hydrolysis of iron, oxidation behavior of sulfur, and solubility characteristics of silicates merit further study, and hence an in-depth review was undertaken on each of the above areas. Characterization and environmental studies on acid and ammonia leach residues of the copper-nickel concentrate showed that hydronium jarosite and ferric oxide respectively were the chief iron products in the leach residues, which equilibrated in distilled water at different pH's, and possessed different morphologies. Further studies were conducted on pure hydrolysis products and their precipitation conditions, equilibration pH's, release of ions, and morphologies have been reported.

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INTRODUCTION

The copper-nickel deposits in Northeastern Minnesota hold great potential for emerging as a major producer of copper and nickel in the U.S.A. In this study some metallurgical and environmental aspects of hydrometallurgical treatment of the copper-nickel concentrates of the Duluth gabbro are examined. In any hydrometallurgical process, the discard of the treatment has to be carefully examined and safely disposed of. Hydrometallurgy is often hailed as a non-polluting extractive technique, but in fact it could pollute the ground water with hazardous consequences if the process waste is not adequately inspected and treated.

This investigation was carried out as a part of the Mineral Processing Studies sponsored by the Minnesota Environmental Quality Council. Various hydrometallurgical processes applicable to copper-nickel concentrates have been reviewed in this study. From this review, three major areas of interest in all processes have been identified and reviewed in depth. Areas of interest for experimentation have been evolved out of these reviews. The experimental investigation broadly consists of two areas: that of metallurgical leaching and environmental leaching tests on the acid and ammonia leach residues, and of preparation of hydrolysis products of iron and study of their equilibration in distilled water. The two separate experimental studies have then been compared and general conclusions drawn.

The experimental techniques adopted include pressure leaching, environmental leaching, x-ray diffraction analysis, electron microscope analysis, etc. The equilibration tests with distilled water in the case of copper-nickel leach residues have been termed "environmental leaching tests" on account of their closely resembling an actual plant discard. Similar treatment on the pure hydrolysis products have been termed "equilibration tests".

II. LITERATURE REVIEW

A. HYDROMETALLURGICAL EXTRACTION TECHNIQUES POTENTIALLY APPLICABLE TO COPPER-NICKEL CONCENTRATES OF THE DULUTH GABBRO

Six hydrometallurgical extraction techniques are discussed in the following chapters. Their selection out of the many techniques proposed is based on current commercial practice and possible development into a full-fledged plant operation.

The ammoniacal leaching technique is an established commercial process for copper and nickel sulfide concentrates. The sulfuric acid pressure leach with oxygen as the oxidant is an attractive process with the possibility of developing into a viable commercial operation. Ferric ion leaching in the sulfate medium is a subject that has held the interest of investigators for many years, and is considered to be the effective leaching agent in dump and in situ leaching. Another technique that is becoming very attractive and promising is the ferric chloride leaching technique. Several alternative processes have been proposed based on this technique and presently a commercial plant is in operation. The ferric chloride leaching technique continues to attract more research in this area. Though nitric acid leaching technique has been known a long time, recently there has been a revival of interest in this extraction method. Bacterial leaching has continued to interest investigators especially with respect to its effectiveness in treating mine wastes and low-grade deposits. Table 1 gives a list of commercial plants currently in operation based on the above extraction techniques.

TABLE 1. LIST OF COMMERCIAL PLANTS CURRENTLY IN OPERATION

Company	Location	Process	Major Process Steps	Products	Capacity tons/year	Year of Startup
Sherritt Gordon Mines Ltd.	Port Saskatchewan, Canada	Sherritt Gordon Process	NH_3 leaching H_2 reduction	Ni, Co	15,000 (Ni)	1954
Western Mining Corporation	Kwinana, Western Australia	Sherritt Gordon Process	NH_3 leaching H_2 reduction	Ni	15,000	1970
*Anaconda Company	Anaconda, Montana U.S.	Arbiter Process	NH_3 leaching, liquid-liquid extraction, electrowinning	Cu	36,000	1974
Duval Corporation	Tucson, Arizona U.S.	CLEAR Process	$FeCl_3$ leaching, electrolysis	Cu	32,500	1976

*Closed in December 1977.[18]

Ammonia Pressure Leaching

The two well known techniques of pressure leaching of sulfides using ammoniacal solutions are the Sherritt Gordon process and the Arbiter process. The Sheritt Gordon process yields ammonium sulfate as the chief by-product, and it is known that for each ton of nickel produced 8 tons of ammonium sulfate are also produced.[1] Hence, in spite of the excellent extraction efficiencies that the Sherritt Gordon process claims, the application of the process to sulfide concentrates is limited by the marketability of ammonium sulfate. The disposal of sulfur thus plays an important role in the economic feasibility of the above processes.

Leaching of sulfide ores by ammoniacal solutions has been suggested as early as 1905.[2] The first commercial application of the technique was to the copper oxide tailings at Kennecott, Alaska,[3] and to tailings containing metallic copper at Calumet, Michigan.[4] In 1953, Forward and the investigators at the research department of the Sherritt Gordon Mines Ltd., at Fort Sasketchewan, Alberta, developed the Sherritt Gordon process, which was primarily applied to nickel sulfide concentrates. The chemistry of this process has been investigated and fairly well established.[5,6]

The Sherritt Gordon process can be outlined as follows. The flotation concentrate is leached in autoclaves with ammoniacal ammonium sulfate solution under 120-130 psi and at temperatures between 80 and 95°C for about 8 1/2 hours. In the case of pentlandite, for example, the nickel forms a soluble ammine complex and the iron is oxidized to an insoluble hydrated iron oxide.

$$NiS \cdot FeS + 3FeS + 7O_2 + 10NH_3 + 4H_3O \rightarrow Ni(NH_3)_6SO_4 + 2Fe_2O_3 \cdot H_2O + 2(NH_4)_2S_2O_3 \qquad \ldots.(1)$$

The sulfide sulfur is at first oxidized to thiosulfate, then undergoes further oxidation to yield trithionate which oxidizes finally to give sulfamate and sulfate

$$2(NH_4)_2S_2O_3 + 2O_2 \rightarrow (NH_4)_2S_3O_6 + (NH_4)_2SO_4 \qquad \ldots.(2)$$

$$(NH_4)_2S_3O_6 + 2O_2 + 4NH_3 + H_2O \rightarrow NH_4 \cdot SO_3 \cdot NH_2 + 2(NH_4)_2SO_4 \qquad \ldots.(3)$$

Any pyrite present in the feed remains relatively unaffected by the leaching and reports in the residue. The leach liquor is filtered and the filtrate is boiled to evolve excess ammonia, which is recycled, and to remove copper as copper sulfide precipitate, which is sent to copper smelters. The solution obtained after separating the precipitate is subjected to oxidation and hydrolysis in order to convert all other forms of sulfur to sulfate. Nickel and cobalt are then recovered by hydrogen reduction and the ammonium sulfate produced is sold a fertilizer. The flowsheet for the above process is given in Figure 1.

Leaching copper sulfides with ammoniacal solutions yields similar results. The reactions of copper sulfide concentrates during ammonia leaching can be divided into two groups, namely, those in which ammonium sulfate is formed and those in which ammonium sulfate is consumed. To illustrate, ammonia leaching of chalcopyrite yields ammonium sulfate whereas that of chalcocite and bornite consumes ammonium sulfate since they contain insufficient sulfur to combine with all of the copper as cupric ammine sulfate,

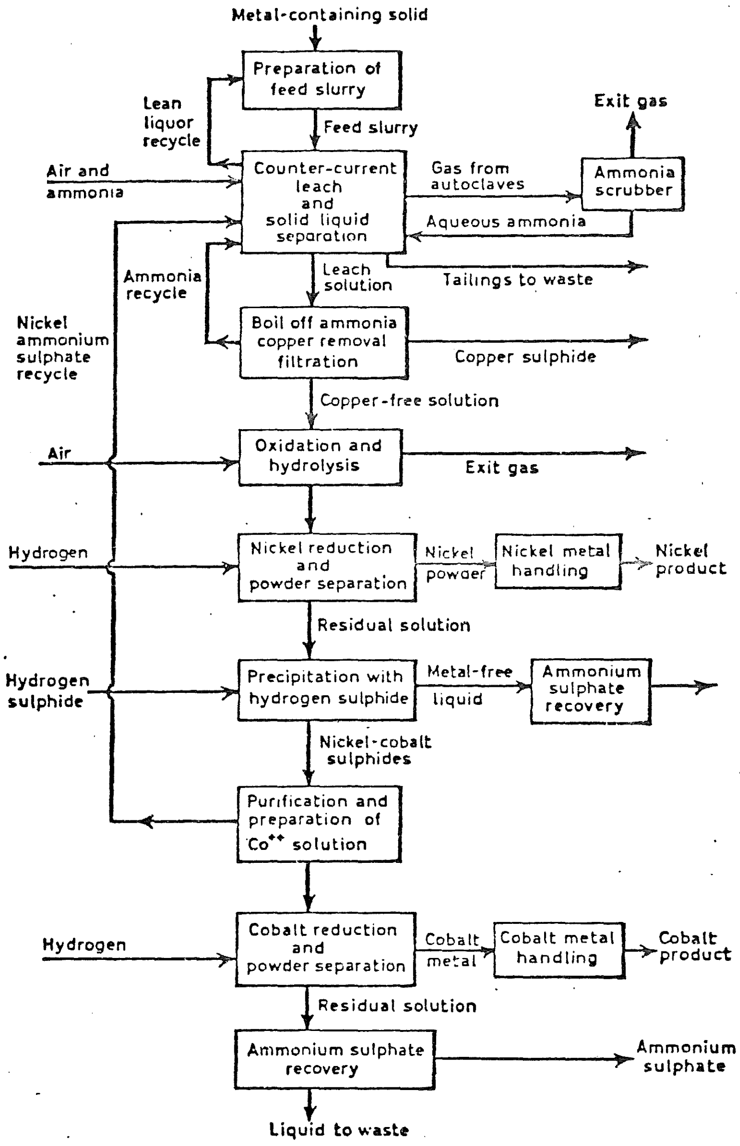


Fig. 1. Flowsheet for Sherritt Gordon process for production of nickel and cobalt metals from sulfide ore.[158]

Chalcopyrite:

$$2CuFeS_2 + 12NH_3 + 8\ 1/2\ O_2 + (2+n)H_2O = 2Cu(NH_3)_4SO_4 + 2(NH_4)_2SO_4 + Fe_2O_3 \cdot nH_2O \quad \ldots.(4)$$

Chalcocite:

$$Cu_2S + 6NH_3 + (NH_4)_2SO_4 + 2\ 1/2\ O_2 = 2Cu(NH_3)_4SO_4 + H_2O \quad \ldots.(5)$$

Bornite:

$$2Cu_5FeS_4 + 36NH_3 + 2(NH_4)_2SO_4 + 18\ 1/2\ O_2 + (n-2)H_2O = 10Cu(NH_3)_4SO_4 + Fe_2O_3 \cdot nH_2O \quad \ldots.(6)$$

All other process details of ammonia leaching of copper sulfides are similar to that of nickel sulfides. Sulfides in the concentrates are oxidized to sulfates through various intermediate sulfur oxidation products as in the case of nickel sulfides. Pyrites remain unattacked and report in the residue. Table 2 gives the results of tests conducted by various investigators based on this process.

The oxidation reactions of the sulfide sulfur is one of the unique features in the ammoniacal leaching of sulfides. Sulfate is the chief end product of the oxidation sequence, and this fact is supported both by the potential -pH diagram of the S-H_2O system (Figure 2) and by experience. Sulfide sulfur oxidizes to sulfate through a series of intermediate sulfur species. The sequence of oxidation of sulfide sulfur in an ammoniacal solution may be written as follows:

sulfide → thiosulfate → trithionate → sulfamate, sulfate

Other polythionates may also be formed during the oxidation but are rapidly converted to stable products. The sulfamate formed in the

TABLE 2. RESULTS OF INVESTIGATIONS ON AMMONIA PRESSURE LEACHING

	Feed			Leaching Conditions					Results, % Extraction				
Author(s)	Mineralogy	Mesh Size		Conc of Leach Solution g/ℓ		Retention time, hrs	Temp °C	O_2 pressure, psi	Cu	Ni	Fe	S	Co
Stanczyk, M.H. and Rampacek, C.[9]	Chalcopyrite	92.2%	-325	59.45	NH_3	1	75	100	95.8	-	-	-	-
*Forward, F.A.[14]	Lynn-Lake Ni-Co Concentrate	-	-	-	-	>24	65-104	>125	88-92	90-95	-	60-75	50-75
**The Anaconda Company[17]	Minnesota Cu-Ni Concentrate	99+%	-400	-	-	7.5	60-90	5	93.11	85.67	0.10	78.20	74.61
Totlani and Balachandra[159]	Cu-Ni Concentrate	100%	-200	~70	NH_3	5	88	150***	>99	95.5	-	-	-
Pearce, et al.[41]	Ni-Cu Matte	98%	-200	85-90 300-335	NH_3 $(NH_4)_2SO_4$	-	80	100	98.5	98.5	-	-	95
Naboichenko, S.S. and Khudyakov, I.F.[20]	Ni-Cu Matte	-	-	80 180	NH_3 $(NH_4)_2SO_4$	4	100	120	-	97-98	-	18-19	80

* Sherritt Gordon Process
** Arbiter Process
***Total pressure

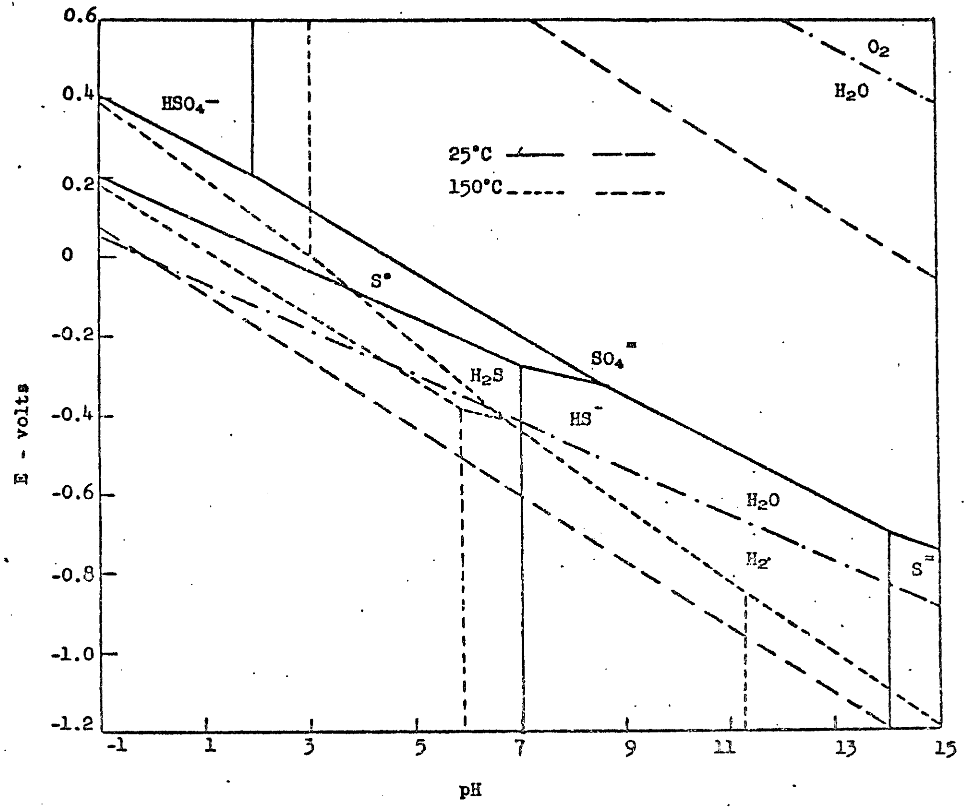


Figure 2. pH-Potential Diagram for Sulfur.[10]

final solution accounts for about a third of the sulfur extracted. Sulfamates have herbicidal properties and hence they have to be completely eliminated so that they will not contaminate the ammonium sulfate which may eventually be used as a fertilizer.[8] Therefore, the solution containing sulfate, sulfamate and small amounts of thiosulfates and thionates is subjected to oxidation and hydrolysis respectively at 245°C and 600 psi air for about half an hour, by which all the sulfur forms are converted to sulfate. A detailed discussion of the oxidation behavior of sulfur species is given in a subsequent section.

The behavior of iron during leaching is worthy of attention. The iron present in the concentrate is oxidized to an insoluble hydrated ferric oxide. This is pseudomorphic with the original mineral and is formed as a layer on the sulfide particles. No other converted form of iron has been reported. Pyrite, and to a lesser extent pyrrhotite, are incompletely leached and report as such in the tailings.[11] Presumably, this is due to the inhibitive coating of ferric oxide on these particles, which considerably slows down their decomposition rate. Fine grinding of the concentrates and extra agitation may essentially resolve the above difficulty and increase extraction rates, and this has been demonstrated by the Arbiter process.[12] Any nickel or cobalt in the pyrite and pyrrhotite also remains undissolved and reports in the leach residue.

A typical feed, product and tailings analysis of the ammonia leach by the Sherritt Gordon process is given in Table 3.[13] It can be seen that considerable amounts of iron and sulfur report in the tailings as well as copper, nickel, and cobalt. Sulfur in the tailings, as well as some amounts of nickel, copper and cobalt, may arise from the pyrite

TABLE 3. CHEMICAL ANALYSIS OF THE FEED, PRODUCTS, AND THE TAILINGS IN THE SHERRITT GORDON PROCESS[13]

Constituent	Feed Conc (Typical) (%)	Ni Product (ppm)	Copper Sulfide (%)	Cobalt Product (ppm)	Tailings * (%)
Quantity Metric TPY	*	12769.37	11267.33	290.43	*
Cu	1.00	30	30	20	0.1
Ni	14.00	99.9%	1	1000	1
Fe	20.00	100	0.5	100	40
S	25.00	250	60	300	10
Pb	0.001	0.05	-	0.08	-
Zn	0.005	3	-	2.0	-
Co	0.20	1000	0.1	99.9%	0.2
As	0.01	1	-	1.3	-
Cd	0.001	30	-	-	-
Se	0.001	4	-	0.4	-
Ti	0.02	0.5	-	0.8	-
Va	0.001	0.05	-	0.1	-
Cr	0.005	1	-	7	-
SiO_2	8.00	9	-	120	-
Al_2O_3	0.05	31	-	5	-
CaO	0.01	0.02	-	4	-
MgO	7.00	0.1	-	5	-
MnO	0.005	0.1	-	1	-
Ag	0.001	0.05	-	0.05	-
Au	-	-	-	-	-
Pt	-	-	-	-	-

Note: Nickel and Cobalt Analysis are given in ppm's of which their main constituent being Ni and Co are presented in percentages.

* Quantities vary depending on the type of feed

and pyrrhotite present in the concentrate. Iron content in the tailings is primarily contributed by ferric oxide, and secondarily by pyrite and pyrrhotite. The tailings may also contain small amounts of insoluble silicates. The final tailings are not gelatinous and they thicken and filter easily, but if agitated vigorously, the friable particles become too fine and make filtering more difficult.[14]

The Sherritt Gordon process, being an ammoniacal leaching process, has the advantage of selective complexation of metals. Also, iron is not complexed, and hence does not enter the purification and recovery circuits. But, as mentioned earlier, the marketability of ammonium sulfate is a constraint in the implementation of this process. As an alternative, ammonia can be regenerated from ammonium sulfate using lime, but the calcium sulfate thus produced must be disposed of. The Sherritt Gordon process has been in practice since 1954 at Fort Sasketchewan, Alberta, by the Sherritt Gordon Mines Ltd. Also, Western Mining Corporation at Kwinana, Western Australia and Impala Platinum Ltd. at Springs, TVL, South Africa, operate on the basis of this process.[15,16]

Another process, named the Arbiter process, was developed in 1973 by The Anaconda Company as a modification to the Sherritt Gordon process. It uses ammonia leaching but at much lower pressures (~5 psi). Tonnage oxygen is employed instead of air. Efficient gas-solid contact is brought about by special agitation techniques and proper control of the reaction is maintained by some unspecified means. The extra agitation is employed in order to divest the mineral particle of the ferric oxide coating and thus present a fresh mineral surface to the leaching agent. Copper is recovered by liquid-liquid extraction and electrowinning. Excellent copper dissolution has been reported.[12] Figure 3 gives a simplified flowsheet of the Arbiter process.

The feed and residue analysis of the Arbiter process on a Minnesota copper-nickel concentrate is given in Table 4.[17] It should be noted that almost all of the iron, calcium oxide and magnesium oxide reports in the residue. Iron occurs in the residue mainly in the form of ferric oxide. In the Arbiter process currently in operation on copper sulfide concentrates, the leach residue is further treated by flotation where almost all the copper is recovered and sent to the smelter. Perhaps the Minnesota copper-nickel concentrates could also be treated in a similar manner to recover the copper, nickel and cobalt from the leach residue.

The advantages of the Arbiter process lie in simpler equipment, lower ammonia loss and the introduction of the liquid-liquid extraction/ electronwinning step for copper recovery, but the chief limitation still remains the economical and proper disposal of the sulfur as ammonium sulfate or calcium sulfate. The process is also dictated by the availability of cheap oxygen, lime and ammonia. It has been reported, however, that the Arbiter plant of the Anaconda Company which began operation in Anaconda, Montana in October 1974, has ceased operation on account of unfavorable market conditions and shortage of sufficient feedstock for capacity operation of the plant.[18]

Naboichenko and coworkers[19, 20] have investigated and reported ammonia leaching of nickel mattes. Mineral-petrographic analyses of the mattes studies showed the main constituents to be sulfides, including sulfides of individual metals as well as $FeS \cdot Ni_3S_2$-type com-

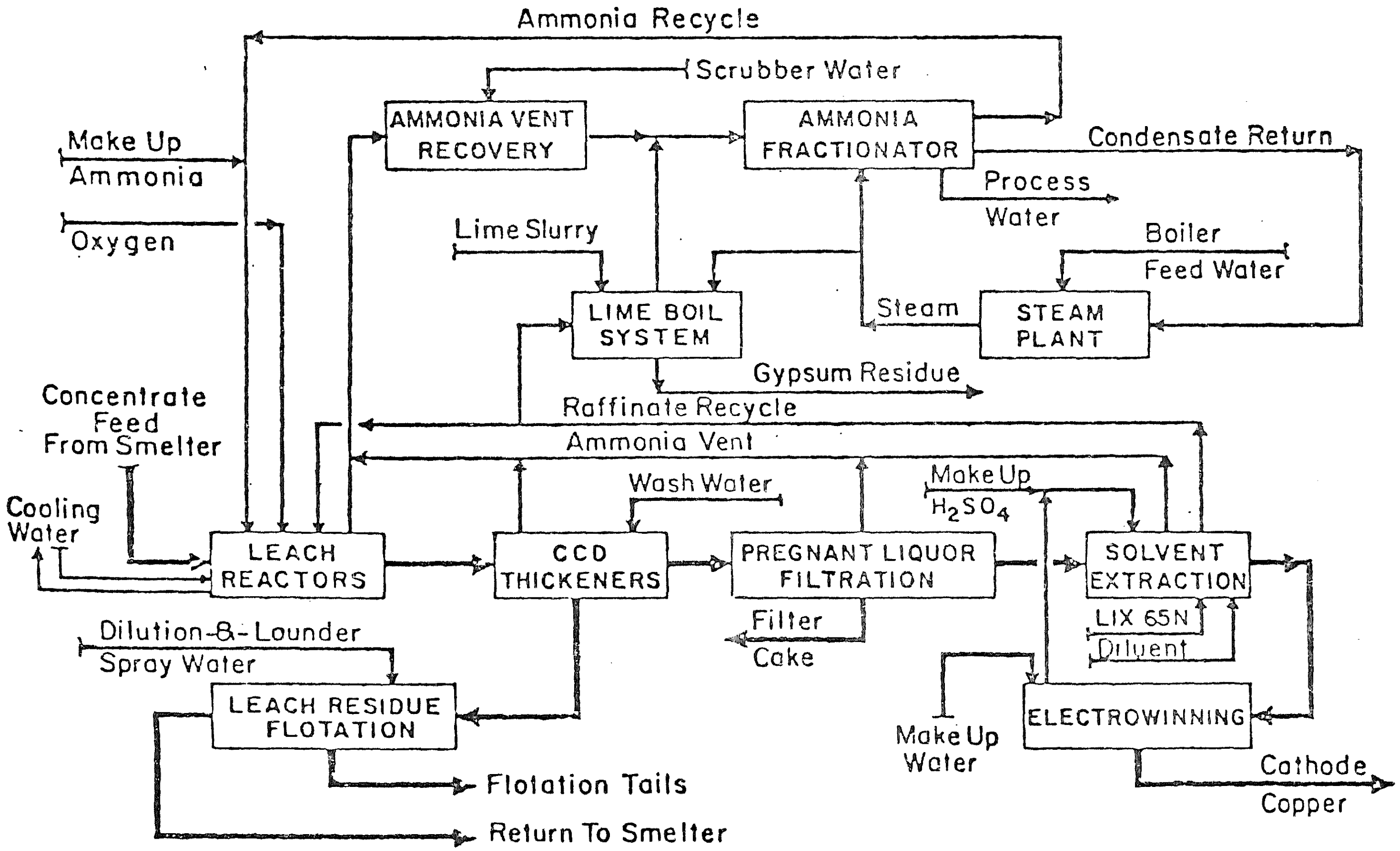


FIGURE 3.— Anaconda Arbiter Plant — block flow diagram.[12]

TABLE 4. THE FEED, LEACHATE AND RESIUDE ANALYSIS OF THE ARBITER PROCESS ON A MINNESOTA COPPER-NICKEL CONCENTRATE[17]

	Feed	Leachate	Residue	Distribution	
	%	%	%	Leachate %	Residue %
Cu	9.80	18.3	0.85	93.11	6.89
Ni	2.05	3.54	0.37	85.67	14.33
Fe	27.60	0.016	32.5	0.10	99.90
S	18.10	53.0	4.6	78.20	21.80
Co	0.11	0.19	0.04	74.61	25.39
SiO_2	19.0	NF**	23.34	-	-
Al_2O_3	5.28	<0.001	6.3	-	-
CaO	2.80	0.088	2.7	3.32	96.68
MgO	5.30	0.040	5.7	0.89	99.11
Ag	0.84*	<0.0001	1.15*	-	-
Au	0.005*	NF	0.006*	-	-

* ounces/ton
**not found

pounds, metallics and oxidized species. The oxidized constituents included slag inclusions and compounds of the magnetite and spinel types, in which nickel and cobalt isomorphically replace the iron. Autoclave ammonia leaching of the nickel mattes yielded nickel, cobalt and copper in solution in the form of complex ammines, sulfur in the form of polythionates and ammonium sulfate, and iron in the form of hydroxide and basic salts.[19] Table 2 shows the data on autoclave ammonia leaching of nickel mattes.

Various parameters on ammonia leaching have been examined and reported by the above-mentioned authors. Increasing the operating temperature and the O_2 pressure of the leach leads to increasing extractions of nickel, cobalt and sulfur to the solutions.[20] The ammonium sulfate concentration in the initial solution has a strong influence on the extraction behavior of different constituents. An increase in the amount of ammonium sulfate in the initial solution leads to increases in metals and sulfur extraction to solution (Figure 4). During leaching, only the sulfur that is combined with nickel, cobalt and sulfur passes into solution. The sulfur combined with iron is used up in the formation of refractory compounds like basic salts, and as a result very little of this sulfur goes into solution. This is also one of the sources of nickel losses into the residue, since nickel that is isomorphically combined with the iron sulfide is practically nonextractable into solution during ammonia leaching of the nickel mattes.[19]

Ammoniacal pressure leaching at 80-95° can be used for high nickel-iron and nickel-copper mattes. At the Sherritt Gordon refinery, nickel mattes mixed with concentrates are processed under varying leaching

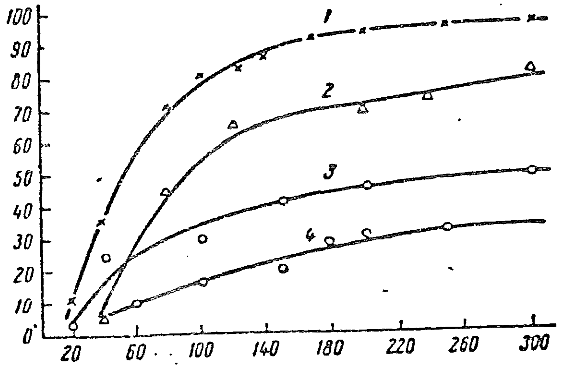


Fig. 4. Effect of ammonium sulfate concentration in the starting solution on metal and sulfur extraction to solution (S_S- degree of oxidation for sulfide sulfur; P_{O_2} = 8.10 n/m^2; t=100°C; time= 6 hours; matte 1):
1-Ni; 2- Co; 3- S_S; 4- $S_{SO_4{}^{2-}}$

conditions dictated by the particular matte. Figure 5 shows a simplified flowsheet of the Sherritt Gordon Nickel Refinery.

Sulfuric Acid Pressure Leaching

Leaching in the sulfuric acid (sulfate) medium is generally distinguished by the type of oxidant employed. In the sulfuric acid pressure leaching, the oxidant is oxygen, and is discussed in this chapter. The next chapter deals with leaching in sulfate medium using ferric ion as the oxidant.

Investigations into the dissolution of copper sulfides by sulfuric acid in the presence of air (oxygen) were carried out as early as 1930 by John D. Sullivan at the Southwest Experiment Station of the U.S. Bureau of Mines.[21-23] In 1955 Forward and Halpern published the results of the pioneering work on autoclave leaching of sulfidic minerals.[24] Significant development in the field occurred in the 1960's with most of the investigations focusing on copper sulfides.[25-30] In addition, leaching studies on copper-nickel sulfides have been reported by Vezina in the early part of this decade.[31,32]

The chemistry of this technique has been discussed by several investigators.[26,31,33] Chalcopyrite, for example, when treated with sulfuric acid under elevated pressure and temperature undergoes dissolution in the following sequence. The sulfide sulfur first gets oxidized to elemental sulfur while copper and iron react with sulfuric acid to form their sulfates.

$$CuFeS_2 + 2H_2SO_4 + O_2 \rightarrow CuSO_4 + FeSO_4 + 2S^\circ + 2H_2O \quad ....(7)$$

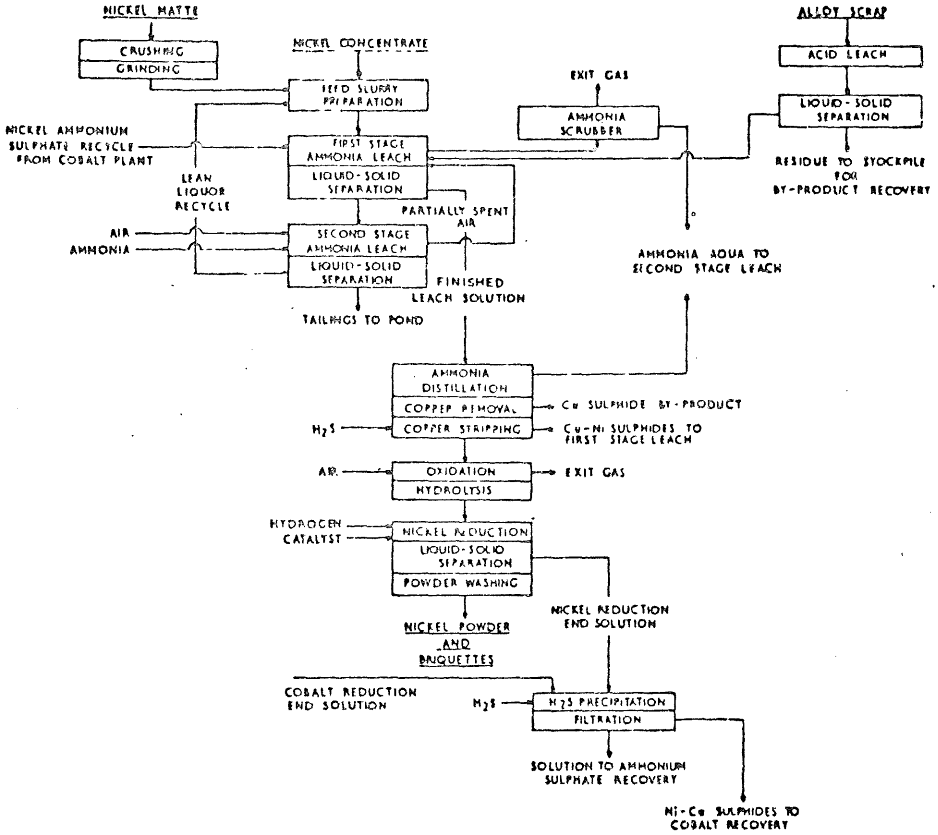


FIG. 5 SHERRITT GORDON MINES, LTD., SIMPLIFIED NICKEL REFINERY FLOW DIAGRAM (FROM ADVANCES IN EXTRACTIVE METALLURGY. 1967, I.M.M.)

Ferrous sulfate is then oxidized to ferric sulfate which raises the pH to 1.0-1.5 at which the ferric sulfate hydrolyzes and regenerates sulfuric acid.

$$FeSO_4 + 1/2\ H_2SO_4 + 1/4\ O_2 \rightarrow 1/2\ Fe_2(SO_4)_3 + 1/2\ H_2O \qquad \ldots.(8)$$

$$1/2\ Fe_2(SO_4)_3 + 3H_2O \rightarrow Fe(OH)_3 + 1\ 1/2\ H_2SO_4 \qquad \ldots.(9)$$

The fresh regenerated acid reacts with more chalcopyrite. An idealized overall equation for chalcopyrite dissolution can be obtained by adding the above equations.

$$CuFeS_2 + H_2SO_4 + 1\ 1/4\ O_2 + 1/2\ H_2O \rightarrow CuSO_4 + Fe(OH)_3 + 2S^\circ \qquad \ldots.(10)$$

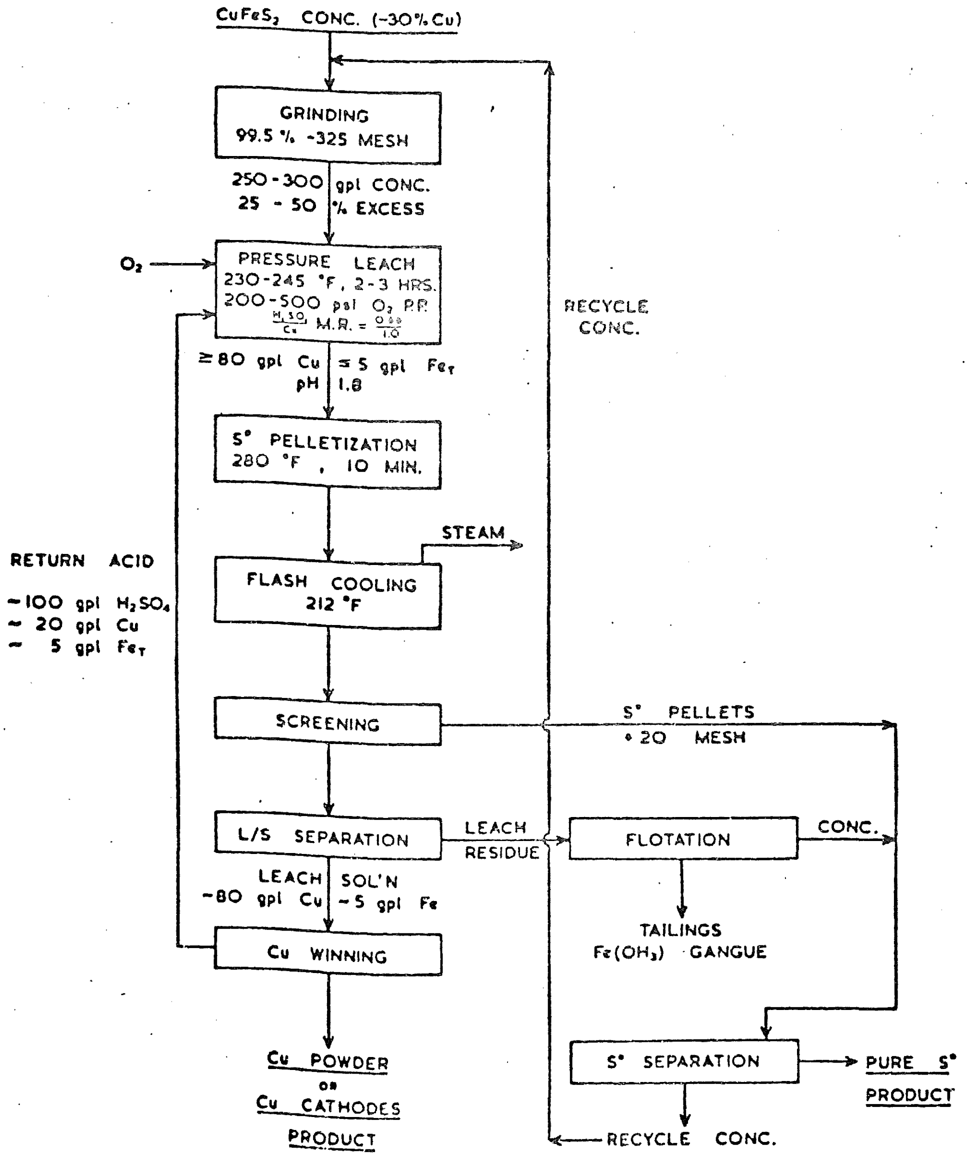
When concentrates contain sulfides of other metals in addition to that of copper, acid leaching yields their sulfates

$$(Fe,Ni)_9S_8 + 4\ 1/2\ O_2 + 9H_2SO_4 \rightarrow 4\ 1/2\ NiSO_4 + 4\ 1/2\ FeSO_4 + 8S^\circ + 9H_2O \qquad \ldots.(11)$$

Figure 6 gives the flow diagram of sulfuric leach for chalcopyrites proposed by Vizsolyi et al.[26]

When two or more sulfides are leached together, the dissolution rates of the minerals differ. Investigation of acid leaching on chalcopyrite-pentlandite-pyrrhotite concentrates has revealed that pyrrhotite is self-sufficient in sulfuric acid for decomposition while chalcopyrite and pentlandite require additional sulfuric acid.[31] In general, the extraction of copper from the mixed concentrates is more difficult than the extractions of nickel and cobalt from the mixed concentrates. Also it is noted that nickel and cobalt attained maximum extractions

FIG. 6. EXAMPLE OF PRESSURE LEACHING SCHEME FOR CHALCOPYRITE.[26]



even at low levels of sulfuric acid additions, while copper required significantly higher levels of sulfuric acid additions to attain high extractions.

Results obtained from various leaching studies have been tabulated (Table 5). Roman and Benner[34] and Subramaniam and Jennings[35] have provided excellent reviews on copper hydrometallurgy. The effect of various parameters on the extraction efficiency have been investigated by several researchers previously cited. Increasing the pressure, temperature and the fineness of grind of the concentrates generally results in better extraction of the metal values.

The formation and behavior of elemental sulfur during the leach dictates the leaching conditions. The elemental sulfur forms a uniform porous coating around the sulfide particle, and further sulfide-oxidant contact takes place through this coating. When the temperature of leaching exceeds the melting point of sulfur, the molten sulfur film on the surface of the sulfide mineral acts as a barrier against further rapid oxidation, and hence the leachability of the sulfide sharply decreases. Therefore the leaching temperature is normally kept below the melting point of sulfur (119°C).

Control of iron content in the pregnant liquor is essential for efficient recovery of copper by electrowinning or hydrogen reduction. To maintain a high copper-to-iron ratio in the liquor, it is preferable to remove as much iron as possible during leaching so that it reports in the residue. Iron hydrolyzes into jarosite, basic iron sulfate or ferric oxide depending on the conditions of leaching. If leaching temperature is maintained below the melting point of sulfur, it is

TABLE 5. RESULTS OF INVESTIGATIONS ON SULFURIC ACID PRESSURE LEACHING

Author(s)	Feed			Leaching Conditions				Results, % Extraction			
	Mineralogy	Mesh Size		Conc of H_2SO_4 g/ℓ	Retention time hrs	Temp °C	O_2 pressure, psi	Cu	Ni	S°*	Co
Stanezyk, M.H. and Rampacek, C.[27]	Chalcopyrite	100%	-270	0	0.5	200	115	97.6	-	-	-
Veltman, H., et al.[25]	Chalcocite concentrate	80%	-325	106	2	107	50	97.3	-	9.8	-
Vizsolyi, A., et al.[26]	Chalcopyrite concentrate	99.5%	-325	95	2.5	115	500	98	-	85	-
Vezina, J.A.[31]	Complex $CuFeS_2$ + (NiFe)S + pyrrhotite concentrate	100%	-325	37.54	14	115	400	95.1	99.2	-	98.2
Vezina, J.A.[32]	"	93%	-20 μ		8	115	80	90.6	99.0	-	97.8
MRRC[36]	Complex chalcopyrite + cubanite + pentlandite + pyrrhotite (Duluth gabbro bulk sulfide concentrate)	100%	-150	20.24	3	115	300	37.0	52.4	-	-
Haas, L.A., et al.[37]	"	100%	-325	50	4	100	400	62	82	-	-
Kawulka, P., et al.[39]	Chalcopyrite + bornite concentrates	-	-	250	3	102	150	98.4	-	-	-
Totlani and Balachandra[160]	Cu-Ni concentrates	-	-	30.6	6	113	500	24.4	83.4	-	-
Pearce, et al.[41]	Ni-Cu-Co matte	84%	-200	1.65	8-10	121	95-100***	90	98.5	-	98
Haas, L.A., et al.[37]	Cu-Ni matte	-	-	100	6	180	450***	>98	>98	-	-

* S° represents sulfur in elemental form

** Sherritt-Cominco Copper Process

***Air pressure

likely that jarosite is formed along with lesser quantities of basic ferric sulfate. A detailed discussion on the behavior of iron during acid leaching is given in a later section.

Stanczyk and Rampacek of the U.S. Bureau of Mines have reported another technique in which the leaching is carried out at 200°C under oxidizing conditions.[27] These investigators have found that chalcopyrite, for example, gives very low extractions at temperatures just above the melting point of sulfur, but the extractions rapidly increase at higher temperatures (Table 6). Also, the sulfur reports chiefly as sulfate. Table 7 gives a typical feed and residue analysis of copper sulfides, when leached with sulfuric acid at 200°C under 115 psi for 30 minutes. Haas et al.,[37] based on studies of a Minnesota copper-nickel sulfide concentrate, have reported that the leach residue of acid leaching treatment on these concentrates at 100°C, contain small quantities of copper, nickel and cobalt, besides considerable quantities of basic ferric sulfates, ferric oxides and elemental sulfur. Under suitable conditions jarosite also may be formed during leaching, and report in the residue. It has been suggested that the copper, nickel and cobalt reporting in the leach residue could have been originally dissolved into the leach liquor and subsequently coprecipitated with the hydrous ferric oxide and basic ferric sulfate.[31] These metal values are thus not available for recovery becasue they are locked with the iron compounds.

Another sulfuric acid leach process was developed in 1976, jointly by Sherritt Gordon Mines and Cominco, with the chief objective of treating concentrates having a wide range of composition with respect to both copper and secondary metals content.[38] The process has been successfully

TABLE 6. - Effect of temperature on copper extraction[27]

Reaction temperature, ° C	Copper extraction, percent		
	Bornite[1]	Chalcocite[2]	Chalcopyrite
125	46.4	63.7	10.8
150	72.5	84.2	32.0
175	91.0	97.8	79.0
200	98.8	99.8	97.6
225	99.0	99.8	97.8

[1] Tests made with 0.5 lb H_2SO_4 per lb bornite.
[2] Tests made with 1.0 lb H_2SO_4 per lb chalcocite.

Test conditions: Pulp density - 5 pct solids; oxygen partial pressure - 115 psig; and reaction time - 30 min.

TABLE 7. [27]

Chemical analysis of minerals

Mineral	Analysis, percent			
	Cu	Fe	S	Insoluble
Chalcocite	74.02	3.08	18.53	0.85
Covellite	66.32	.70	30.00	.50
Bornite	64.73	9.30	24.10	.20
Chalcopyrite	32.69	29.25	33.09	1.51

Chemical analysis of leach residues

Mineral	Residue analysis, percent			
	Cu	Fe	S as sulfide	S as sulfate
Bornite	1.6	47.4	1.8	0.8
Chalcocite	2.1	41.3	.5	.3
Chalcopyrite	1.5	56.2	1.1	2.0

tested in a \$5.2 million pilot plant processing 9 tons of pyritic copper concentrates per day. The first stage of the Sherritt-Cominco Copper Process involves thermal activation wherein the concentrate is heated to about 650°C in a roaster in a current of hydrogen. Due to the combined effect of heating and hydrogen reduction, chalcopyrite and pyrite transform to bornite and troilite respectively with the elimination of a considerable amount of sulfur.

$$5CuFeS_2 \rightarrow 5CuFeS_{1\cdot8} + 1/2\ S_2 \quad ....(12)$$

$$5CuFeS_{1\cdot8} + H_2 \rightarrow Cu_5FeS_4 + 4FeS + H_2S \quad ....(13)$$

$$7FeS_2 \rightarrow Fe_7S_8 + 3S_2 \quad ....(14)$$

$$Fe_7S_8 + H_2 \rightarrow 7FeS + H_2S \quad ....(15)$$

The calcine from the above treatment is subjected to an acid leach, where the troilite dissolves.

$$FeS + H_2SO_4 \overset{80^\circ C}{=} FeSO_4 + H_2S \quad ....(16)$$

The solution containing the dissolved iron is subjected to oxydrolysis with ammonia to precipitate jarosite. The residue from the acid leach containing the chalcopyrite is then subjected to an activation leach removing zinc, other base metals and iron. The residue from the activation leach enters the oxidation leaching stage where the leaching takes place for about 3 hours at 110°C and 100-200 psi oxygen overpressure.

$$Cu_5FeS_4 + 6H_2SO_4 + 3O_2 \rightarrow 5CuSO_4 + FeSO_4 + 4S^\circ + 6H_2O \quad ....(17)$$

The residue from the above leaching is sent for recovery of elemental sulfur by flotation and for precious metals recovery. The pregnant liquor is purified by high temperature oxydrolysis. The copper is then recovered by electronwinning as wire grade product. A simplified flow diagram of the process is given in Figure 7.

The Sherritt Cominco Copper Process claims several advantages. It enables the treatment of relatively low grade concentrates, with high recoveries of copper as well as associated zinc, molybdenum, nickel and cobalt. Sulfur is recovered in the elemental form and iron is rejected as jarosite. Excellent precious metals recovery has been reported.[39] On the whole, the S-C Process claims to be a safe, hygienic, and commercially viable hydrometallurgical process for the treatment of a wide range of copper concentrates.

Acid leaching of mattes has been examined in the laboratory, tested in the pilot plants and is commercially practiced. From their investigations on acid leaching of white matte, which is related to the natural mineral chalcocite, Dobrokhotov and Maiorova[40] have reported the following two main reactions to be taking place simultaneously and in parallel:

$$Cu_2S + 2.5O_2 + H_2SO_4 = 2CuSO_4 + H_2O \qquad ....(18)$$

$$Cu_2S + O_2 + 2H_2SO_4 = 2CuSO_4 + S^\circ + 2H_2O \qquad ....(19)$$

Pearce et al.[41] at the Sherritt Gordon Research Laboratories have reported the studies of acid leach on a high cobalt matte containing nickel, copper, iron and sulfur. Leaching at 121°C at 95-100 psi pressure with air for 8-10 hours extracted more than 98% of the nickel and cobalt and 90% of the copper. Figure 8 shows the flowsheet of the acid leach for the nickel-copper-cobalt matte as proposed by Pearce et al. Working on mattes obtained by smelting bulk flotation concentrates of the Duluth complex ore, Haas et al.[37] have reported copper and nickel

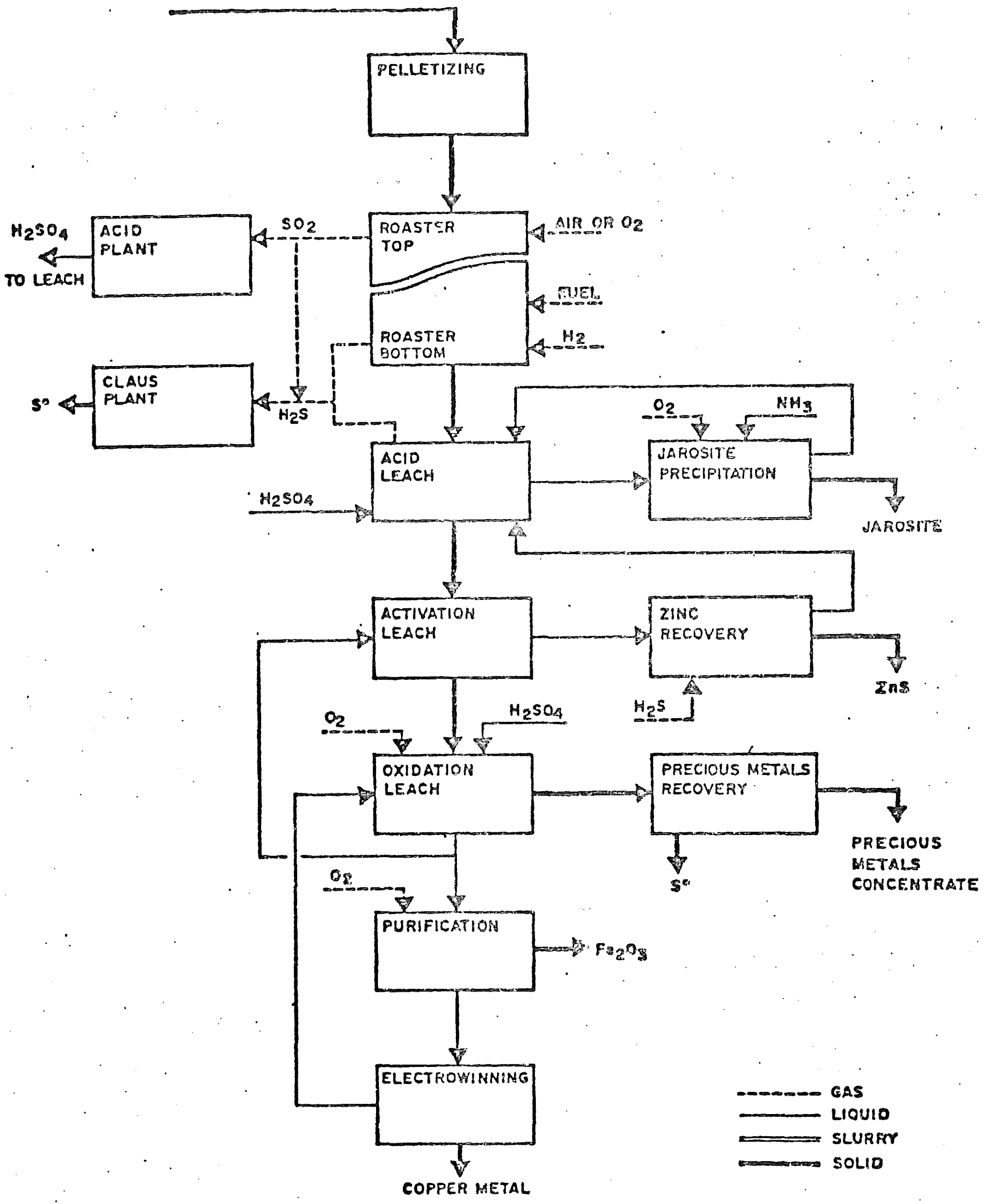


Figure 7

THE SHERRITT-COMINCO COPPER PROCESS[38]
SIMPLIFIED BLOCK FLOW DIAGRAM

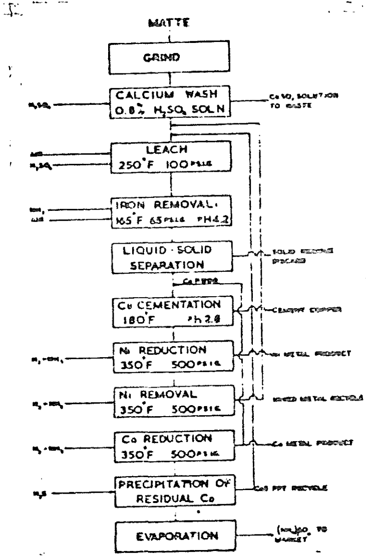


Fig. 8. Acid leach and preferential hydrogen reduction for a nickel-copper- cobalt matte.[41]

extractions of over 90% when leached with 100 grams/liter H_2SO_4 at 180°C and 350 psi air pressure. Table 5 gives relevant data on acid leaching of mattes by different investigators.

Several commercial practices on matte leaching by acid are currently in operation of which special mention should be made of AMAX's Port Nickel refining operations,[42] the Outokumpu refining operations at Harjavalta, Finland,[7] and the process employed at the Rustenburg Platinum Mines in South Africa.[43] At AMAX's Port Nickel Refinery, nickel-copper matte is subjected to an atmospheric leach, where 50-60% of the contained nickel and cobalt dissolves. The partially leached solids are then subjected to a two-stage pressure leach at 205°C and 600 psi using spent electrolyte from the copper tankhouse. Copper is recovered by electrowinning, cobalt is precipitated as cobalt hydroxide and subsequently reduced to cobalt metal by hydrogen gas, and nickel is separated as pure nickel solution and is subjected to hydrogen reduction which yields pure nickel powder. The hydrogen reduction circuit of nickel and cobalt also produces ammonium sulfate as by-product which is purified and sold as crystalline ammonium sulfate. A flowsheet of the above process is shown in Figure 9.

Acid leaching is also employed by the Outokumpu refinery at Harjavalta, Finland for its high-grade nickel-copper matte. The matte is ground and subjected to a two-stage leach in a set of tanks using partially decopperized free acid solution from the electrolytic tank. Copper and nickel are recovered by electrowinning. A flowsheet of the Outokumpu refining operation is given in Figure 10.

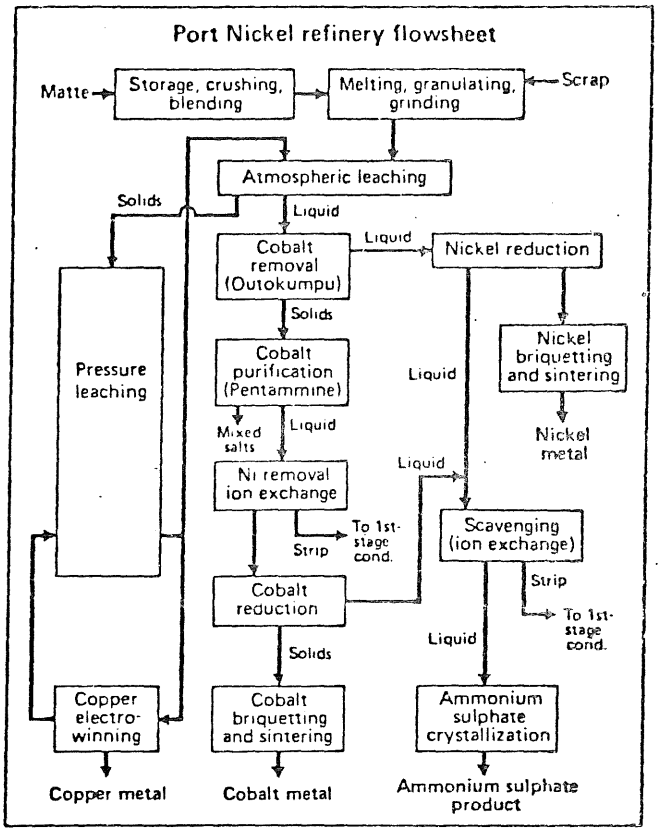

Port Nickel refinery flowsheet
Matte
Storage, crushing, blending
Melting, granulating, grinding
Scrap
Atmospheric leaching
Solids
Liquid
Cobalt removal (Outokumpu)
Liquid
Nickel reduction
Solids
Pressure leaching
Cobalt purification (Pentammine)
Liquid
Nickel briquetting and sintering
Mixed salts
Liquid
Nickel metal
Liquid
Ni removal ion exchange
To 1st-stage cond.
Strip
Scavenging (ion exchange)
Cobalt reduction
Strip
To 1st-stage cond.
Liquid
Solids
Copper electro-winning
Cobalt briquetting and sintering
Ammonium sulphate crystallization
Copper metal
Cobalt metal
Ammonium sulphate product

Figure 9.[42]

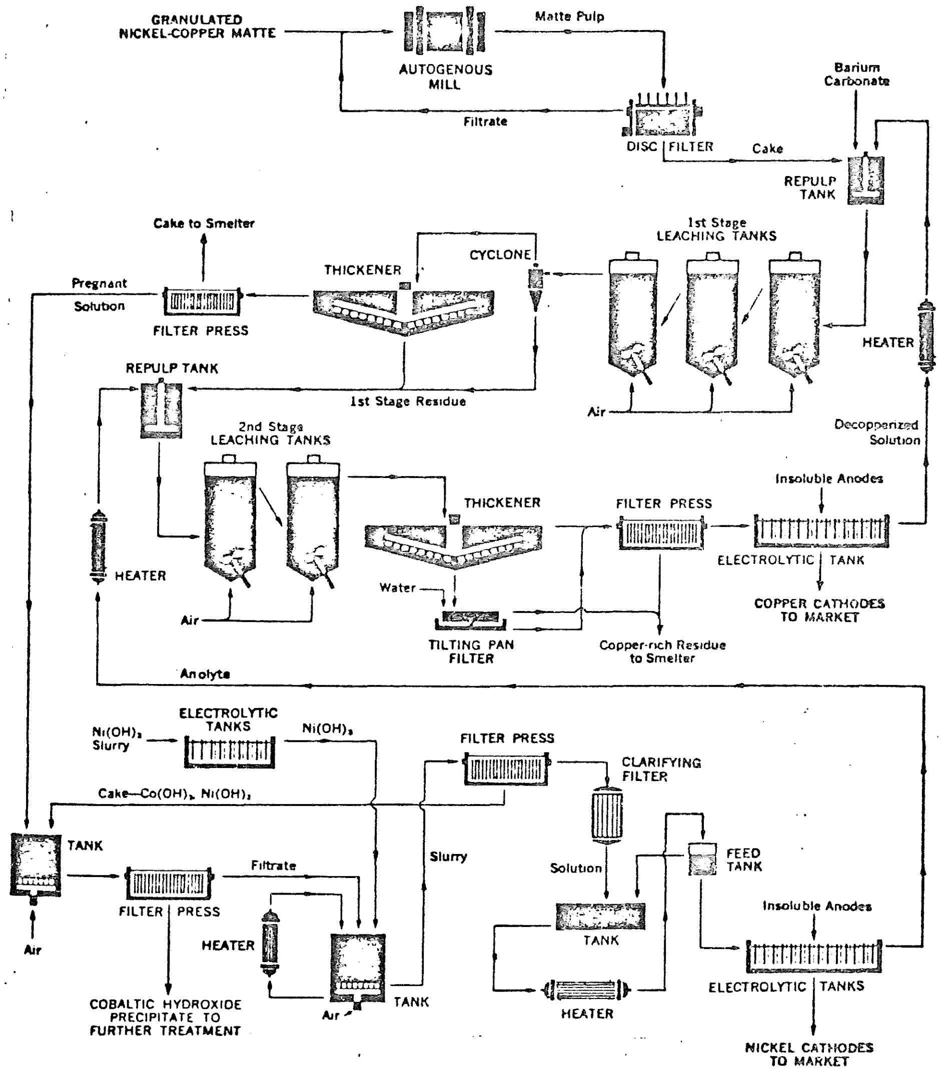


Fig. 10. Flowsheet of Outokumpu refining operations at Harjavalta.[7]

In Rustenburg Platinum Mines, South Africa, copper and nickel are obtained as by-products, the main object of the plant being the extraction of platinum. The flotation concentrate consisting of copper, nickel and iron sulfides with platinum minerals, is smelted in a series of blast furnaces, tapped to converters and blown to high-grade matte. The finely ground matte is then leached with sulfuric acid under pressure to recovery copper and nickel as sulfates which are then subjected to normal electro-refining techniques. The residue, containing the platinum minerals is then subjected to chemical refining to recover the platinum.

Ferric Sulfate Leaching

The earliest investigations on acidic ferric sulfate leaching of copper sulfides were conducted by Sullivan[21-23] and Brown.[44] Several investigations have been carried out on ferric sulfate leaching since the early 60's, including studies by Dutrizac[45-47] and Thomas[48,49] on the effects of various parameters on ferric sulfate leaching of different synthetic minerals.

A brief examination of the behavior of ferric ion in leaching solutions is well worth the effort, especially because published information on this subject is not very extensive. Figure 11 gives the Eh-pH diagram for the $Fe-H_2O-CO_2$ system at 25°C, from which much valuable information can be gleaned. The trivalent species of iron is stable at low pH and high oxidation potentials. In other words, solutions containing trivalent iron are strong oxidizing agents with associated oxidation potentials of about +0.8V. Hence, when a metal

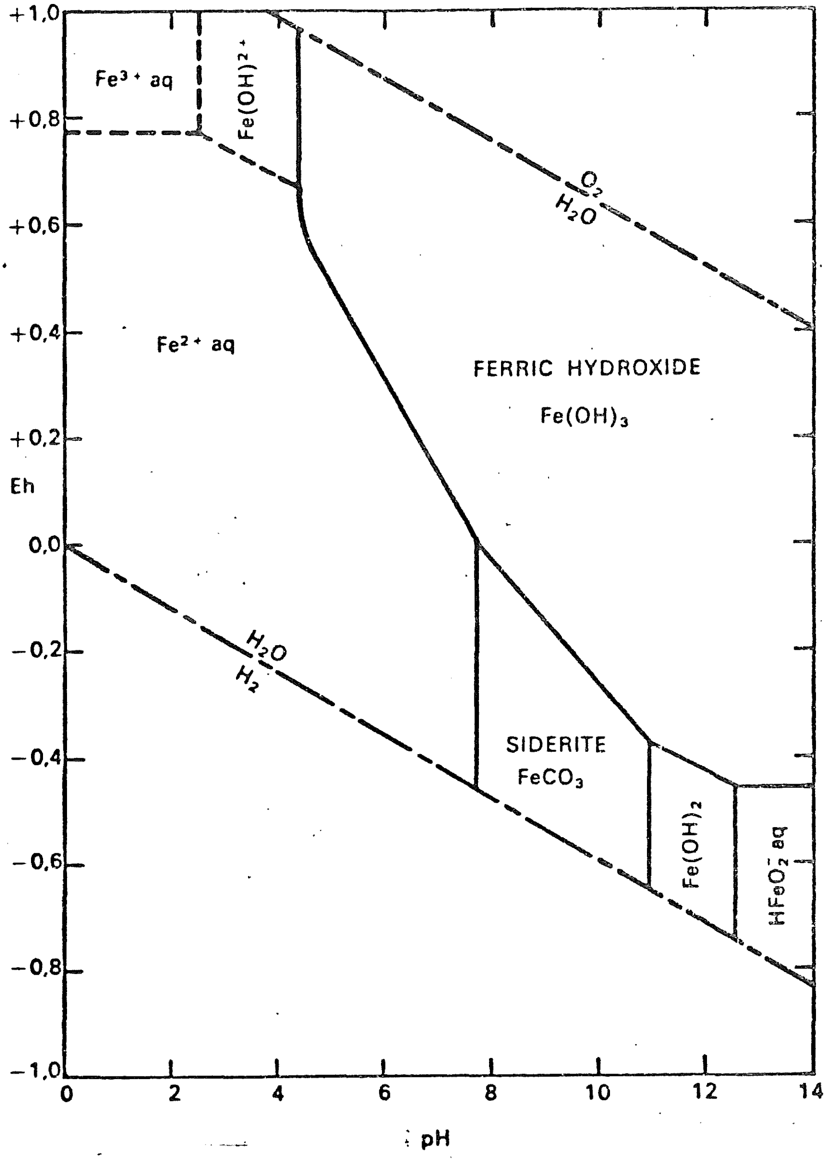


Fig. 11. Eh-pH diagram showing the relationship among metastable iron hydroxide species and siderite at 25°C and 1 atm total pressure.[50] Concentration of dissolved species 10^{-6} M.

sulfide (MS) is immersed in an acidified ferric ion solution, the following reaction is predicted according to thermodynamic data:

$$MS + 8Fe^{3+} + 4H_2O \rightarrow M^{2+} + SO_4 + 8H^{+} + 8Fe^{2+} \qquad ....(20)$$

Although the above relation indicates the formation of sulfate sulfur, in practice it has been found that considerable amount of elemental sulfur is produced. Hence, the leaching reaction can also be represented in the following form:

$$MS + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+} + S^{\circ} \qquad ....(21)$$

The Eh-pH diagram in Figure 11 also brings out some of the difficulties associated with ferric ion leaching. It is seen that the stability range of ferrous ion is much greater than that of ferric ion. The presence of ferrous ions in ferric ion leaching solutions causes problems in two ways. The ferrous ion in the leach liquor proves troublesome in the metal recovery stage because of the difficulty of removing them. Also, the ferrous ion content has been proved to be detrimental to the efficiency of extraction of copper in ferric sulfate solutions.[51] A further limitation of ferric ion leaching solutions is that they are very sensitive to tmeperature and pH changes. Also, an obvious disadvantage as seen from Figure 11 is that at pH above 3 precipitation of ferric hydroxide occurs and becomes more pronounced at increasing temperatures. Precipitation of ferric hydroxide removes the ferric ions from the leaching solution thus reducing its efficacy.

But in spite of these, two ferric ion leaching media have evoked considerable interest. The ferric sulfate leaching and ferric chloride leaching have both been subjects of investigation in the 1930's or earlier. Both ferric sulfate and ferric chloride are readily soluble in cold water, as are their corresponding ferrous salts. Thus concentrated ferric solutions can be used with little danger of salt crystallization occurring. Studies on both ferric sulfate and ferric chloride solutions have revealed certain basic behaviors in each of them, but thorough and fundamental information on them is lacking.

Dutrizac and MacDonald[52] have presented an excellent review of the ferric ion as a leaching medium. Ferric chloride is recognized as a stronger reagent than ferric sulfate, and Jones and Peters[51] have reported that the rate of leaching in ferric chloride solutions was 5-20 times greater than in ferric sulfate solutions. Based on studies of the two leaching reagents on chalcopyrite, these authors report that substantial sulfur oxidation to sulfate occurs only in ferric sulfate solution, while ferric chloride leaching yielded almost quantitative elemental sulfur formation. Above a very low level of ferric ion concentration, the leaching reaction in ferric sulfate solutions was found independent on Fe^{3+}, but in ferric chloride solutions, increasing Fe^{3+} concentration produced beneficial results. Further study into this observation may yield interesting results of both theoretical and practical value. On the other hand, increasing ferrous ion concentrations produced no effect in ferric chloride solutions, but was seriously detrimental to the metal extraction in sulfate solution. Ferric chloride leaching thus outweighs ferric sulfate leaching in its advantages, and this has led to the development of several interesting processes which are briefly reviewed in the next chapter.

Dutrizac et al.[45] have reported the results of leaching discs of synthetic chalcopyrite at temperatures from 50°C to 94°C in acidic ferric sulfate solutions containing ferric ion of 0.001 to 0.6 molar. The reaction has been found to obey the following stoichiometric relation:

$$CuFeS_2 + 2Fe_2(SO_4)_3 = CuSO_4 + 5FeSO_4 + 2S^\circ \qquad \ldots.(22)$$

The critical ferric ion concentration has been reported to be 0.01 molar above which the rate of reaction is independent of the concentration. The rate decreases with time t, and has been found to obey a parabolic law of the form $C = K\sqrt{t}$, where C represents the amount of copper dissolved. This result has been attributed to a constantly thickening layer of elemental sulfur on the surface which retards the progress of the reaction. Dutrizac et al. have further reported that the rate of reaction is controlled by the inward diffusion of ferric sulfate below the Fe^{3+} concentrate of 0.01M and by the outward diffusion of ferrous sulfate above the concentration of 0.01M. The reaction has been found to be independent of pH, disc rotation speed and fine grinding of the concentrates, but is sharply dependent on ferrous ion concentration. Jones and Peters[51] have also reported that ferric sulfate solutions attack the mineral particles in selected areas, especially in fissures and grain boundaries, leaving a large part of the surface unattacked. This places limits on the extent of size reduction on the mineral particles carried out in order to improve the leaching rate and extraction efficiency. Table 8 gives the results of investigators on ferric sulfate leaching.

There is no known commercial practice of direct ferric sulfate leaching of copper or nickel concentrates and hence information on the tailings analysis is not available. Ferric sulfate leaching in practice

TABLE 8. RESULTS OF INVESTIGATIONS ON FERRIC SULFATE LEACHING

Author(s)	Sample		Leaching Conditions				Results, % Extraction			
	Mineralogy	Mesh Size	Conc	Time	Temp °C	O_2 Press. psi	Cu	Ni	S°*	Fe
Sullivan, J. D.[23]	Bornite (Cu_5FeS_4)	100% -100	5% Fe^{3+} 0.5% H_2SO_4	7 days	35	-	77.	-	45.3	35.8
MRRC[36]	Complex chalcopyrite + cubanite + pentlandite + pyrrhotite (Duluth gabbro bulk sulfide concentrate)	100% -150	2.2% Fe^{3+} 2% H_2SO_4	3 hours	150	300	48.2	71.4	-	56.9

*S° represents sulfur in elemental form

may be seen in dump and in situ leaching of copper and uranium ores. Scientific interest in this subject is very active especially due to its close association with bacterial leaching. The advantages in the above leaching techniques are the low cost of operation and their simplicity; the chief disadvantage is the long duration of extraction of the sought-after metals.

Ferric Chloride Leaching

The leaching technique using ferric chloride has been investigated as early as 1916 and has been the basis for several patents.[53-56] Also, Trail and McClelland,[57-59] and Sullivan[21-23] have reported the results of their studies of the effect of various parameters on ferric chloride leaching. More recently, Haver and Wong[60] of the Reno Metallurgy Research Center have developed a leaching process for chalcopyrite concentrates using ferric chloride as the lixiviant. Other recent pro--esses developed along similar lines are the UBC-Cominco process,[56] the Duval CLEAR process,[61] the Cymet process,[62] and the new Cyprus process.[63] Table 9 gives the results of the various investigations on ferric chloride leaching.

Essentially, the technique consists of agitating finely ground concentrates with a strong solution of ferric chloride at a temperature of about 100°C. In the case of chalcopyrite, the following reaction takes place:

$$CuFeS_2 + 3FeCl_3 = CuCl + 4FeCl_2 + 2S^\circ \qquad \ldots.(23)$$

Roman and Benner[34] have proposed the following two-stage mechanism, in which the cupric ions plays a major role as an oxidant.

TABLE 9. RESULTS OF INVESTIGATIONS ON FERRIC CHLORIDE LEACHING

	Sample			Leaching Conditions			Results, % Extraction			
Author(s)	Mineralogy	Mesh Size		Conc g/ℓ	Temp °C	Time, hrs	Cu	Ni	S° ***	Fe
Trail, R. J. and McClelland, W. R.[57]	Amulet ore concentrate (pyrite-pyrrhotite-chalcopyrite concentrate)	-	-	77.1 Fe^{3+} (70.85 Fe^{2+})	90-95	7 5/6	90.2	-	68.1	73.1
Haver, F. P. and Wong, M. M.[60]	Chalcopyrite	98.9%	-325	212 Fe^{3+}	106	2	99.9	-	70.5	73.7
*Milner et al.[56]	Chalcopyrite	95%	-325	128.5 Fe^{3+} (16.0 Fe^{2+})	100	9	99.5	-	79	-
**Kruesi, P. R. et al.[62]	Chalcopyrite	95%	-200	-	75-80	-	99	-	85	-

* UBC-Cominco Process
**Cymet Process
***S° represents sulfur in elemental form

$$CuFeS_2 + 4FeCl_3 \rightarrow CuCl_2 + 5FeCl_2 + 2S^\circ \qquad \ldots.(24)$$

$$CuFeS_2 + 3CuCl_2 \rightarrow 4CuCl + FeCl_2 + 2S^\circ \qquad \ldots.(25)$$

Thus ferric chloride leaching is in fact cupric chloride leaching. This point of view has been substantiated by Jones and Peters[51] on the basis of mixed potential studies.

Ferric chloride proves to be a strong lixiviant for chalcopyrite on account of the high Fe^{3+} concentrations that can be utilized. Further advantage is gained by the fact that the leaching in chloride solutions is unaffected by increasing Fe^{2+} content. Microscopic studies on chalcopyrite by Jones and Peters[51] have revealed that ferric chloride attacks the entire surface of the mineral particle, thus making the extraction dependent on the surface area of the particle. Hence fine grinding was found to be beneficial to improve extractions. Also, higher temperatures contributed to better extraction efficiencies.

In the technique developed by Haver and Wong, copper is recovered from the leach solution by cementation on sponge iron. Excess iron in the leach solution is removed by crystallizing part of the ferrous chloride by roasting in air in a multiple-hearth furnace. The remaining ferrous chloride in the solution is then chlorinated to ferric chloride which is recycled. The residue is treated for the recovery of elemental sulfur, and then subjected to cyanidation to recover gold and silver. Figure 12 gives the schematic flowsheet of the above technique.

The technique claims several advantages. The low energy demand, competitive costs, and the ease of regeneration of the ferric ions are notable merits. The high solubility of the chloride ions and their ability to complex copper readily make this technique more attractive

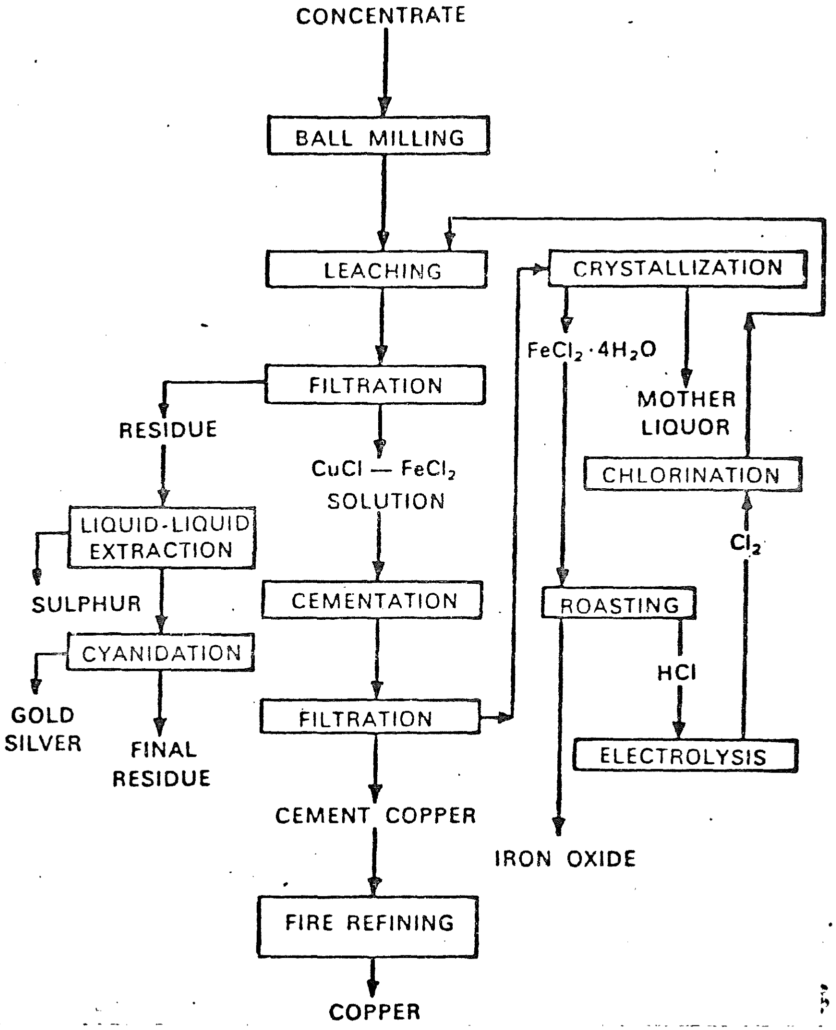


Fig. 12. Schematic flowsheet proposed by Haver and Wong for the treatment of chalcopyrite concentrates.[60]

than the ferric sulfate leaching technique. This method also possesses the advantage of the possibility of completely recovering the precious metals from the residue. But serious limitations envisaged in this technique are corrosion problems arising in material handling and processing, requiring special materials of construction. Also of important consideration is the adverse environmental effects brought about by the chloride fumes and mist.

The UBC-Cominco process was developed and patented jointly by the investigators at the University of British Columbia and Cominco Ltd.[56] The basic difference between this technique and the one proposed by Haver and Wong is the method adopted for winning the copper. In the UBC-Cominco process, metallic copper is added to the leach solution, containing cuprous, cupric and ferrous chloride, in order to reduce the cupric ions to cuprous ions. The cuprous chloride is then crystallized out, and the crystals are treated with hydrogen to form metallic copper and hydrogen chloride, according to the following reaction:

$$CuCl + 1/2\ H_2 \rightarrow Cu + HCl \qquad \ldots.(26)$$

The flowsheet for the UBC-Cominco process is given in Figure 13. The advantages claimed for this process are very high copper extractions (99.95%), high yield of elemental sulfur (>98%), production of iron oxide suitable for sponge iron manufacture, total recoverability of precious metal values and the production of metallic copper that is marketable without refining. However, the same limitations associated with ferric chloride leaching processes apply to this technique, namely corrosion and environmental problems.

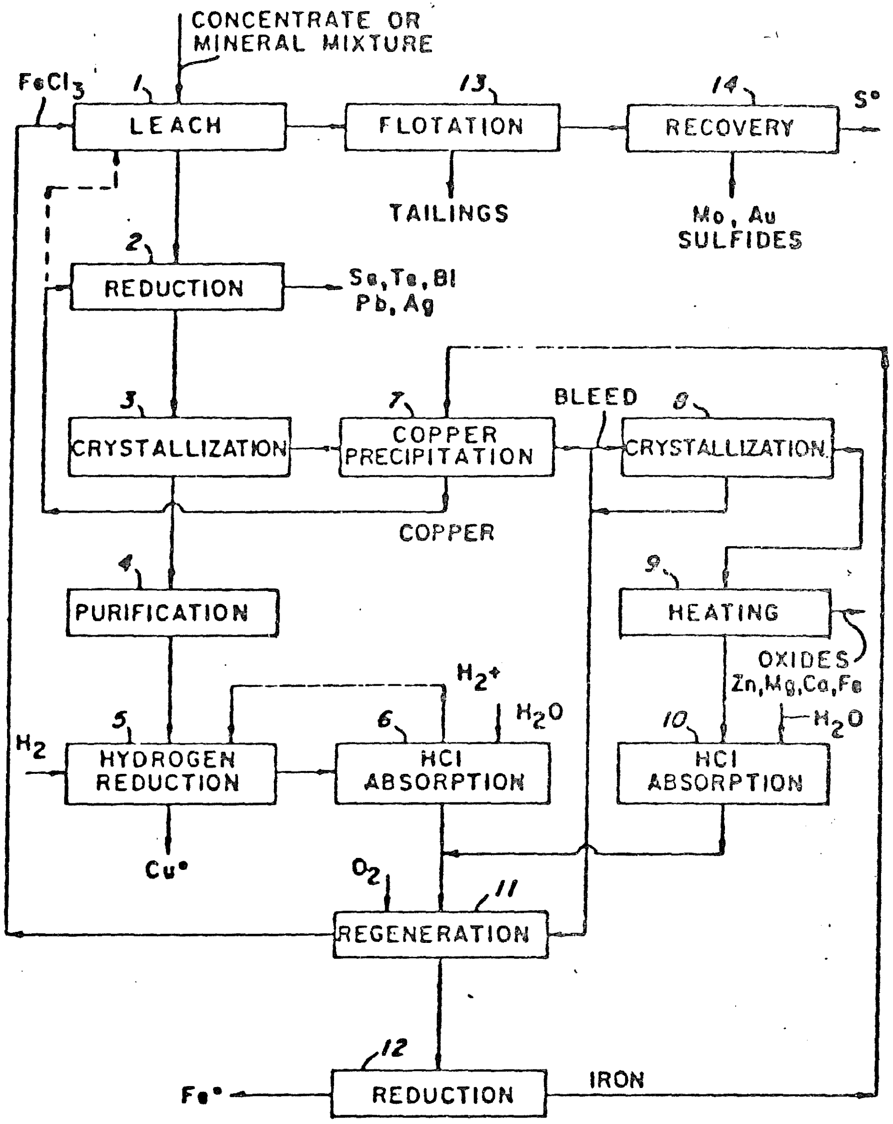


Fig. 13. The UBC-Cominco Process. 56

The Duval CLEAR (Copper Leaching, Extraction And Refining) process developed by the Duval Corporation is based on the general technique of ferric chloride leaching.[61] The notable features are that copper ore is added to reduce cupric ions to cuprous ions and the recovery of metallic copper is accomplished by electrolysis. In addition, this technique provides for the control of the inventory of reactive chloride ions in the process liquor through the addition of a suitable saline metal chloride. The three stages of the process, namely reduction stage, electrolysis stage, and the combined oxidation, regeneration-purge stage for chalcopyrite can be represented by the following partial reactions:

(a) Reduction stage:

$$\mathrm{2CuFeS_2 + 3CuCl_2 \rightarrow \underbrace{4CuCl + FeCl_2}_{(b)} + \underbrace{2S + CuFeS_2}_{(c)}} \qquad \text{....(27)}$$

(b) Electrolysis stage:

$$\mathrm{4CuCl + FeCl_2 \rightarrow 2Cu + \underbrace{2CuCl_2 + FeCl_2}_{(c)}} \qquad \text{....(28)}$$

(c) Combined oxidation, regeneration-purge stage:

$$\mathrm{CuFeS_2 + 2S + 2CuCl_2 + FeCl_2 + 3/2\ O_2 + 3H_2O \rightarrow}$$
$$\mathrm{3CuCl_2 + 3Fe(OH)_3 + 4S} \qquad \text{....(29)}$$

A flow diagram of this process is given in Figure 14. Though the reactions indicate the final iron product as iron oxide, in practice the precipitation of potassium jarosite is implemented, which acts as an effective control mechanism for iron and sulfate ions in the system. The residue consisting of elemental sulfur, jarosite and other insoluble matter is further treated by conventional methods to remove sulfur, jarosite and any insoluble precious metals present. Details regarding

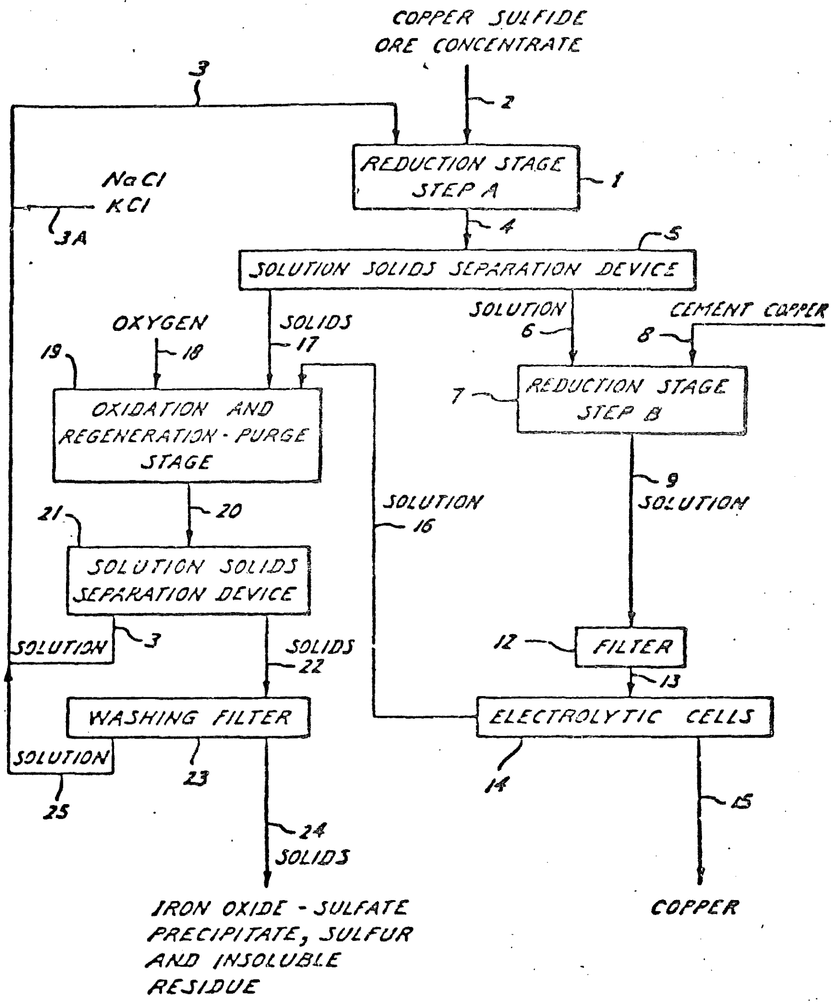


Fig. 14. DUVAL'S "CLEAR" PROCESS.[61]

the feasibility studies and experimental results of this technique are not available. The same limitations applicable to other chloride processes are expected to be present in this technique also.

The Cyprus Metallurgical Processes Corporation has developed the Cymet Process,[62] which is an extension of the ferric chloride leaching. It combines ferric chloride leaching with anodic dissolution of the unreacted sulfides. A 25-tons-of-copper-concentrate per day pilot plant based on this process was reported to be in operation in Tucson.

The basic chemistry of the process is as follows. Chalcopyrite concentrate is finely ground and leached at 70-80°C with ferric chloride in accordance with the following equation:

$$CuFeS_2 + 3FeCl_3 \rightarrow CuCl + 4FeCl_2 + 2S^\circ \qquad \ldots.(30)$$

The leach slurry is sent to the anode compartment of the electrolytic dissolution cells, where more chalcopyrite reacts to form ferrous chloride, cuprous chloride and elemental sulfur.

$$CuFeS_2 + 3HCl - 3e \rightarrow CuCl + FeCl_2 + 2S^\circ + 3H^+ \qquad \ldots.(31)$$

At the cathode, cuprous chloride is reduced to copper

$$3CuCl + 3e \rightarrow 3Cu + 3Cl^- \qquad \ldots.(32)$$

$$3H^+ + 3Cl^- \rightarrow 3HCl \qquad \ldots.(33)$$

The ferrous chloride is purified and sent to electrolytic iron cells, where elemental high purity iron is produced and ferric chloride is regenerated and recycled.

Cathode:

$$3FeCl_2 + 6e \rightarrow 3Fe^\circ + 6Cl^- \qquad \ldots.(34)$$

Anode:

$$6FeCl_2 - 6e + 6Cl^- \rightarrow 6FeCl_3 \qquad \ldots.(35)$$

From pilot plant tests, it is known that about 50 percent of the copper is dissolved in the ferric chloride leaching step and another 30 percent in electrolytic cells and 20 percent is recycled by flotation. The overall extraction of copper is more than 98 percent. About 85 percent of the elemental sulfur is recovered. Figure 15 gives a simplified flow diagram of the Cymet process for chalcopyrite concentrates.

The chemical analysis of the feed and products of the Cymet process is given in Table 10. The tailings arise from the rougher flotation circuit of the leach residue carried out after the removal of the elemental sulfur. It is seen that the tailings contain a considerable amount of iron and sulfur besides insoluble matter. The iron may be chiefly in the form of undissolved pyrite or pyrrhotite and also may arise from unrecovered ferrous chloride. The bulk of the sulfur in the tailings may be in the elemental form and that associated with pyrite or pyrrhotite. Gangue minerals associated with the concentrates may account for the amount of insoluble matter in the tailings.

As can be seen from its chemistry, the unique feature of the Cymet process is the production of high purity, by-product iron. The process holds special advantages of economy, amenability to low grade concentrates, high purity final products and absence of air and water pollution. However, the process is dictated by power costs and market for iron. Additional disadvantages are the production of copper powder which requires further refining, and technological and corrosion problbems involved in the operation of slurry electrolytic cells. Because

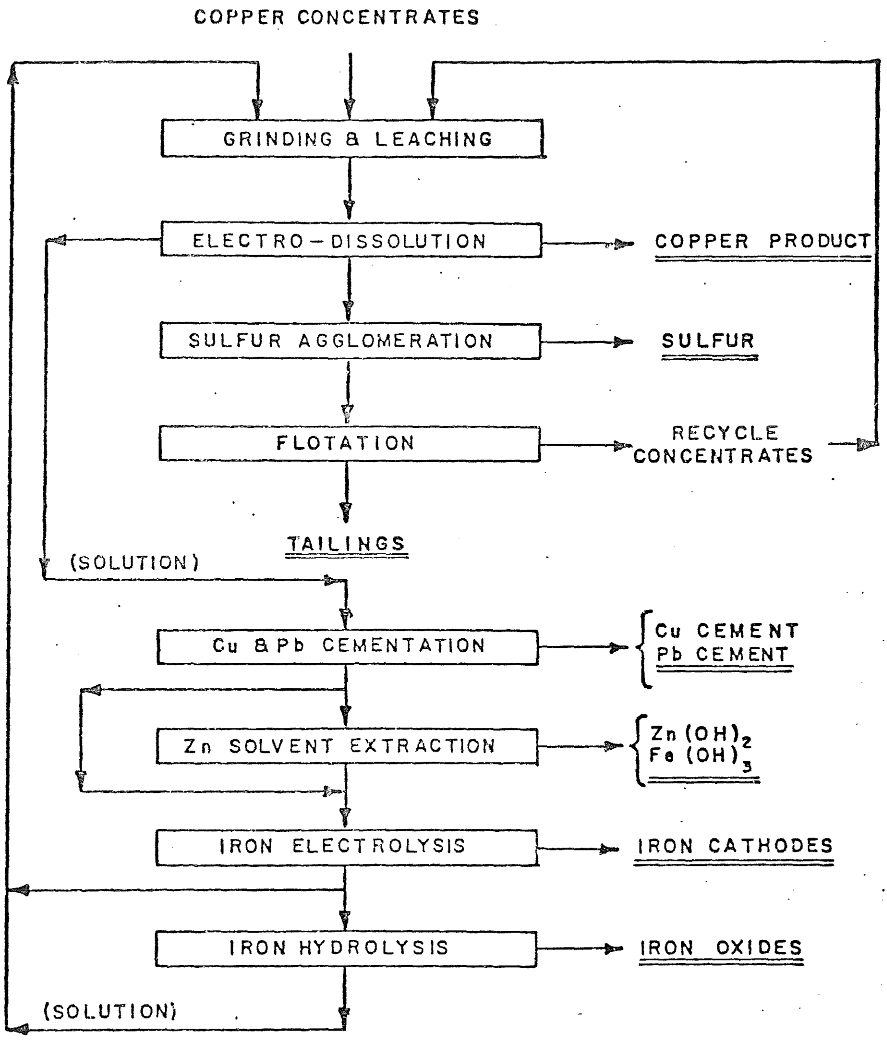


Fig. 15. CYMET PROCESS[62]

Table 10.

Chalcopyrite Flowsheet

Chemical Analysis of Feed and Products [62]

Elements	Chalcopyrite Feed %	Tailings %	Copper Powder %	Refinery Anode Sludge, %	Sulphur Product %
Cu	27.1	0.8	90+	46	
S	32.1	20.0	0.35	0.48	99
Fe	27.5	19.0	1.1	0.75	
Zn	0.26	Trace	0.1	-	
Mo	0.22	0.56	-	-	
Pb	0.07	Trace	0.27	12.0	
Sb	0.04	Trace	0.01		
As	0.03	Trace	<0.005		
Bi	0.02	Trace	0.032		
Se	0.009	Trace	0.0007		0.03
Insoluble	12.24	60.1	-		
Ag	2.4 oz/ton	0.3 oz/ton	0.02	0.48	
Au	0.04 oz/ton	0.0 oz/ton	-		

Electrorefined Copper

Cu 99.95%
Following Trace Elements Detected:

Al	20 ppm
Fe	20 ppm
Mg	50 ppm
Si	25 ppm
Pb	<10 ppm

Electrolytic Iron Product

Fe 99.5%
Following Trace Elements Detected:

Cu	500 ppm	C	80 ppm
S	3 ppm	H_2	50 ppm
Mo	30 ppm	N_2	30 ppm
Pb	100 ppm	Al	50 ppm
O_2	350 ppm	Ni	150 ppm
P	20 ppm		

Cu Recovery	99%
Ag Recovery	97%
Au Recovery	60%

of its shortcomings, the Cymet process has been shelved in favor of a newer and much improved process developed by the Cyprus Mines Corporation and named the Cyprus Copper Process.

Although the Cyprus Copper Process was developed for the extraction of copper from concentrates produced from porphyry ores, it is adaptable to other copper-bearing concentrates.[65] Figure 16 shows the flowsheet for the process as applied to chalcopyrite concentrates.

The concentrate is subjected to a cupric ion leach in a chloride medium, which generates cuprous ions (Cu^{+}). The pregnant liquor after filtration is subjected to a crystallization step whereby cuprous chloride crystals are obtained. After separating the cuprous chloride crystals, the liquor is subjected to an exothermic oxidation which converts the cuprous ion to cupric (Cu^{++}) and ferrous ion to ferric (Fe^{+++}). This is sent to the second-stage leach where a ferric ion leach of the unreacted concentrate of the first-stage leach takes place, extracting the remaining copper and converting it into cupric ion. The liquor is sent to the first-stage leach and the underflow is sent to tails washing to remove trace copper and to a flotation circuit to recover molybdenite and elemental sulfur.

The cuprous chloride crystals are reduced to metal by injecting the crystals into a fluidized bed of sand in a medium of hot circulating hydrogen. The following reaction takes place:

$$CuCl + 1/2\ H_2 \rightarrow Cu + HCl\uparrow \qquad \ldots.(36)$$

Copper is deposited around the sand particles forming nodules which are withdrawn when they are approximately 92 percent copper and 8 percent sand. The hydrochloric acid vapor generated is scrubbed and re-

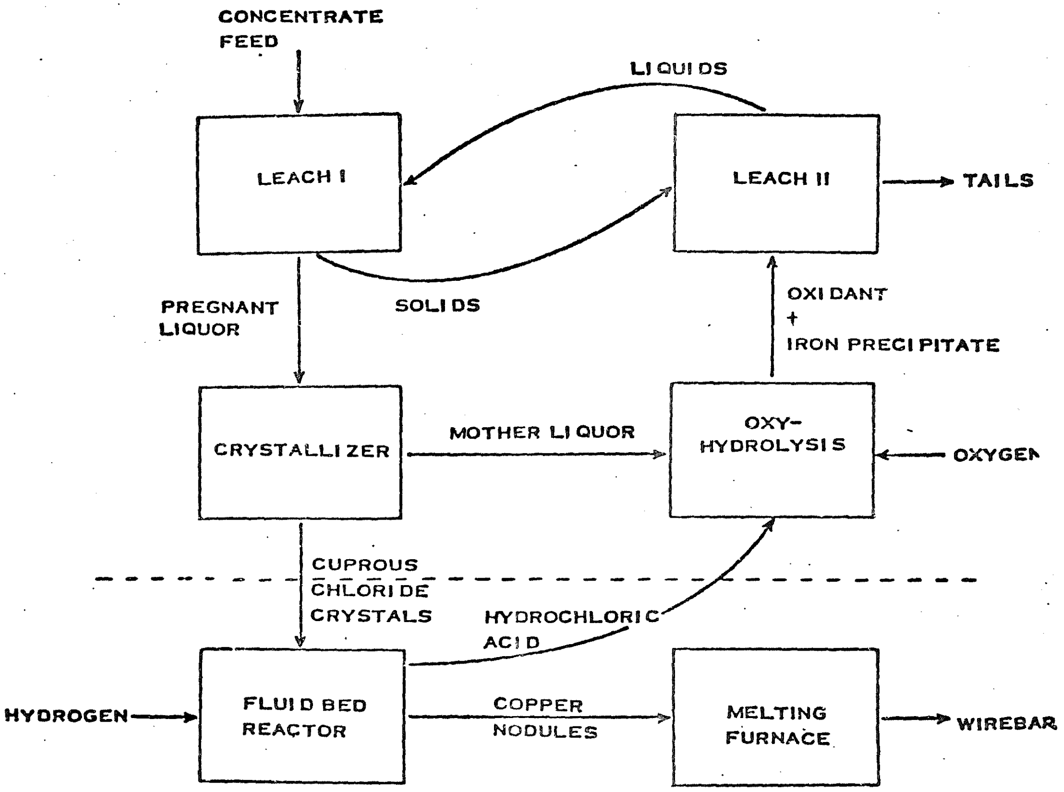


Fig. 16. THE CYPRUS COPPER PROCESS[65]

turned to the hydrometallurgical circuit. The copper nodules are fed to a melting furnace and minor contaminants are removed by slagging, after which the pure copper is poured into wirebars.

The Cyprus Copper Process is hailed as a "technological breakthrough" because of its low consumption of reagents, power and labor, amenability to a high degree of automation, pollution-free operation, and applicability to all known sulfide copper concentrates. The process claims a significantly lower capital cost per ton of copper than that for conventional smelting and refining facilities. It also permits economic construction of relatively small plants which can be tailored to the size of mine output. The operating costs per pound of copper for the Cyprus Copper Process have been estimated at 16.7 cents per pound of wirebar, including twenty-year depreciation and excluding by-product metal credits.

Nitric Acid Leaching

Application of nitric acid as a leaching agent for metal sulfides has been reported as early as 1909.[66] Several processes based on nitric acid leaching of copper sulfides were patented[67,68] and even reached the pilot plant stage.[69-71] But none of these emerged as a commercial operation because of the excessive costs of nitric acid, the absence of proper technology to regenerate the acid from the nitrogen oxides produced as a reaction product, and difficulties in recovering the copper from solution.[34] Then, after a period of more than thirty years, interest in nitric acid leaching revived when Schaufelberger[72] patented a process for leaching copper and other metal values from arsenide ores, employing a mixture of nitric and sulfuric acids as lixiviant. Several investigators have since then studied the effect of nitric acid on metal sulfides, both per se[73,74] and as a catalyst in sulfuric acid leaching.[75,76]

The basic chemistry of the nitric acid leaching on chalcopyrites has been given by Prater et al.[73] as follows. Initially, the oxidation of sulfide sulfur to elemental sulfur takes place with the formation of soluble copper and iron salts. Subsequently, the elemental sulfur is oxidized to sulfate depending on conditions. The continued formation of copper and iron salts leads to the neutralization of sulfuric acid. When the free acid has been consumed the ferric sulfate hydrolyzes and precipitates from solution as hydrogen jarosite. An idealized equation for the above-mentioned reactions may be given as follows:

$$6CuFeS_2 + 10NHO_3 + 10H_2SO_4 \rightarrow 6CuSO_4 + 10NO\uparrow + 12S^\circ\downarrow$$
$$3Fe_2O_5 \cdot 4SO_3 \cdot 9H_2O\downarrow + 6H_2O \qquad \text{....(37)}$$

However, in practice the idealized situation mentioned above may not exist exclusively. Some copper nitrate is formed and remains in solution as small quantities of ferric salts and acid. Also, depending on conditions, part of the elemental sulfur may be oxidized to sulfate and NO_2 may be evolved instead of NO. Figure 17 shows the flowsheet for nitric acid leaching of copper concentrates proposed by Prater et al.[73]

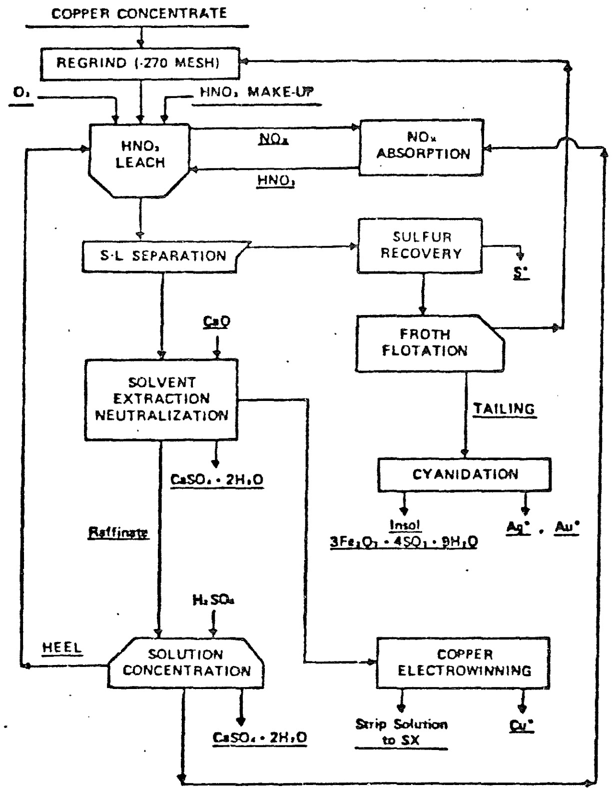


Fig. 17. Flowsheet for processing copper concentrates with nitric acid.[73]

The reactions taking place in nitric acid leaching of sulfides is not yet clearly understood, and further study is needed in this area. Depending on the acid concentration, either NO or NO_2 or a definite ratio of both gases are produced. This can be seen from the following equations and Figure 18.

$$6CuFeS_2 + 10HNO_3 + 15H_2SO_4 \rightarrow 6CuSO_4 + 3Fe_2(SO_4)_3 + 10NO + 12S^\circ + 20H_2O \quad \text{....(38)}$$

$$2CuFeS_2 + 10HNO_3 + 5H_2SO_4 \rightarrow 2CuSO_4 + Fe_2(SO_4)_3 + 10NO_2 + 4S^\circ + 10H_2O \quad \text{....(39)}$$

From Equations 2 and 3 it can be noted that for the same amount of nitric acid, three times as much copper can be extracted when NO is the reaction product. Hence reaction (38) is favored. However, the whole situation is further complicated by the fact that NO and NO_2 react with water and oxygen in the following manner:

$$NO + 1/2\ O_2 \rightarrow NO_2 \quad \text{....(40)}$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \quad \text{....(41)}$$

$$2NO + 3/2\ O_2 + H_2O \rightarrow 2HNO_3 \quad \text{....(42)}$$

Thus nitric acid concentration is an important consideration. By controlling the nitric acid concentration, almost exclusive evolution of NO may be possible. Studies show that below 25 percent HNO_3 nearly pure NO was produced. In the flowsheet proposed by Prater et al.[73] the NO_x gas mixture evolved from the leach was taken to an absorption tower where it was contacted with cold water in the presence of O_2 to regenerate HNO_3.

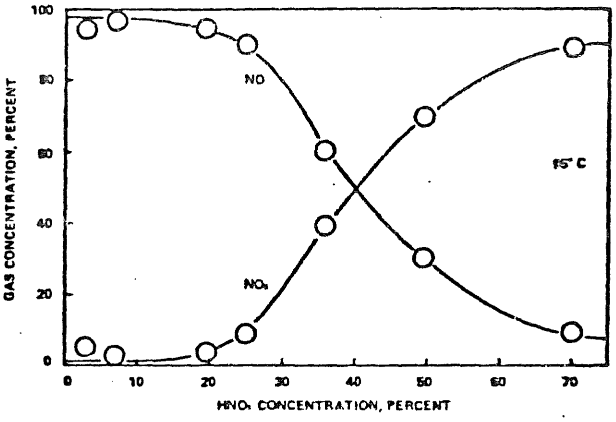


Fig. 18. The distibution of NO and NO_2 as a function of HNO_3 concentration while leaching copper concentrates.[73]

Table 11 gives the data on different investigations of nitric acid leaching of sulfides. The metal extractions in nitric acid leaching were found to be dependent on acid concentration, mineral type, particle size, temperature and time.[73] Studies on chalcopyrite have indicated that copper recovery increases with increasing time, acid concentration and temperature.[74] Dissolution of iron follows the same trend as that of copper.[74] Studies on nitric acid leaching of a low-grade nickel-copper sulfide concentrate indicated that nickel recovery increases with increasing time up to about one hour, and increases with increasing acid concentration up to 30 percent HNO_3 at which concentration almost total recovery was achieved.[77] Prater et al.[73] have reported that among the copper sulfides tested, tetrahedrite was the most easily oxidized mineral and chalcopyrite the least. Table 12 gives the relative reactivity of different copper sulfides tested, as reported by these authors.

The most desirable sulfur product in nitric acid leaching is elemental sulfur, and hence conditions are chosen to increase the net yield of elemental sulfur by maximizing the formation reaction of elemental sulfur and minimizing the oxidation of elemental sulfur to sulfate. It has been reported that the formation of elemental sulfur rather than sulfate is promoted by increasing either the leach temperature or the HNO_3 concentration when a deficiency of HNO_3 is present.[73] On the other hand, overall $S°$ yield is decreased with increased H_2SO_4 concentration. But, increasing leach temperature and HNO_3 concentration also accelerates the oxidation of $S°$ to sulfate.

TABLE 11. RESULTS OF INVESTIGATIONS ON NITRIC ACID LEACHING

	Feed			Leaching Conditions			Results % Extraction		
Author(s)	Mineralogy	Mesh Size		Conc of HNO_3 %	Temp (°C)	Time	Cu	Ni	S°
Prater, J.D., et al.[73]	Chalcopyrite + bornite + pyrite concentrates	-	-	50	95	40 min	99.8	-	-
Habashi, Fathi[77]	Pyrrhotite + pentlandite + chalcopyrite concentrates	100%	-400	30	100	8 hrs	86.5	98.5	65.5
Habashi, Fathi[74]	Chalcopyrite concentrates	-	-	2.5	100	8 hrs	82	-	47.2

Table 12. Relative reactivity and elemental sulfur yield of pure minerals leached with nitric acid.[73]

Mineral	**Relative Reactivity**	**Elemental Sulfur Yield, % of Reacted Sulfur**
Cu_3SbS_3	10	40
Cu_2S	8	75
FeS	7	60
FeS_2	7	3
Cu_9S_5	6	55
CuS	6	50
Cu_5FeS_4	5	60
$CuFeS_2$	2	45

Hence, it appears that an optimum value of temperature and HNO_3 concentration exists for maximum net yield of S°. Habashi[74] reports that for chalcopyrite elemental sulfur recovery increases with increasing time and temperature up to 100°C when leached by dilute acid (7.5 percent HNO_3). When concentrated acid (60 percent HNO_3) is used, the S° increase initially formed decreases with time and temperature. The yield of elemental sulfur was also found to be dependent on the mineralogy of the feed. The best S° yields are given by chalcocite (Cu_2S), bornite (Cu_5FeS_4) and pyrrhotite (FeS), pyrite giving a low elemental sulfur yield. Chalcopyrite gives a yield of intermediate value.[73] Sulfur recovery as elemental sulfur under most favorable conditions for nitric acid leaching of chalcopyrite was found to be 40 to 50 percent.[74]

The behavior of iron in nitric acid leach circuit is of particular interest. By proper adjustment of leaching conditions, iron is precipitated as hydrogen jarosite ($3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$), which is crystalline, readily filterable and does not entrain copper.[73] The formation of hydrogen jarosite is favored by high pH, high temperature, high percent solids and a reasonably high sulfate concentration. The pH increase is caused by the gradual consumption of HNO_3 and H_2SO_4 as seen from the following reaction:

$$6CuFeS_2 + 22HNO_3 + 9H_2SO_4 \rightarrow 6CuSO_4 + 3Fe_2(SO_4)_3 + 22NO + 6S° + 20H_2O \quad ....(43)$$

This rise in pH precipitates iron as hydrogen jarosite according to the following reaction provided favorable temperature and percent solids prevail:

$$6Fe^{+++} + 4SO_4^{=} + 14H_2O \rightarrow 3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O + 10H^{+} \quad \ldots.(44)$$

The formation of hydrogen jarosite is dependent on the sulfate concentration. If adequate sulfate is not available in the leach solution, then formation of $2Fe_2O_3 \cdot 5H_2O$ takes place instead of hydrogen jarosite. Severe deficiency of sulfate results in the precipitation of $FeO \cdot (OH)$.[73]

Nitric acid leaching claims several advantages.[73] It achieves high extraction of copper, solubilization at moderate temperature, moderate pH and atmospheric pressure, and recovers a portion of the sulfur in the elemental form. Another notable feature is the efficient rejection of iron into the leach residue as easily filterable hydrogen jarosite. The disadvantages of this leach system chiefly lie in the absence of previous experience of commercial operation, and handling of nitric acid and nitrogen oxides which are dangerous materials. Winning of copper from the liquor and recovery of precious metals also prove to be difficult in the nitric acid leach system.

A process claiming the above advantages of nitric acid leaching, and in addition reporting effective copper electrowinning from leach liquor, recovery of precious metals and environmentally acceptable disposal practice, has been developed by the E.I. Dupont de Nemours Company.[76] Named "The Nitric-Sulfuric Leach Process" (Figure 19), it has demonstrated 99 percent copper leaching from chalcopyrite and production of cathode grade copper. Process evaluation, carried out

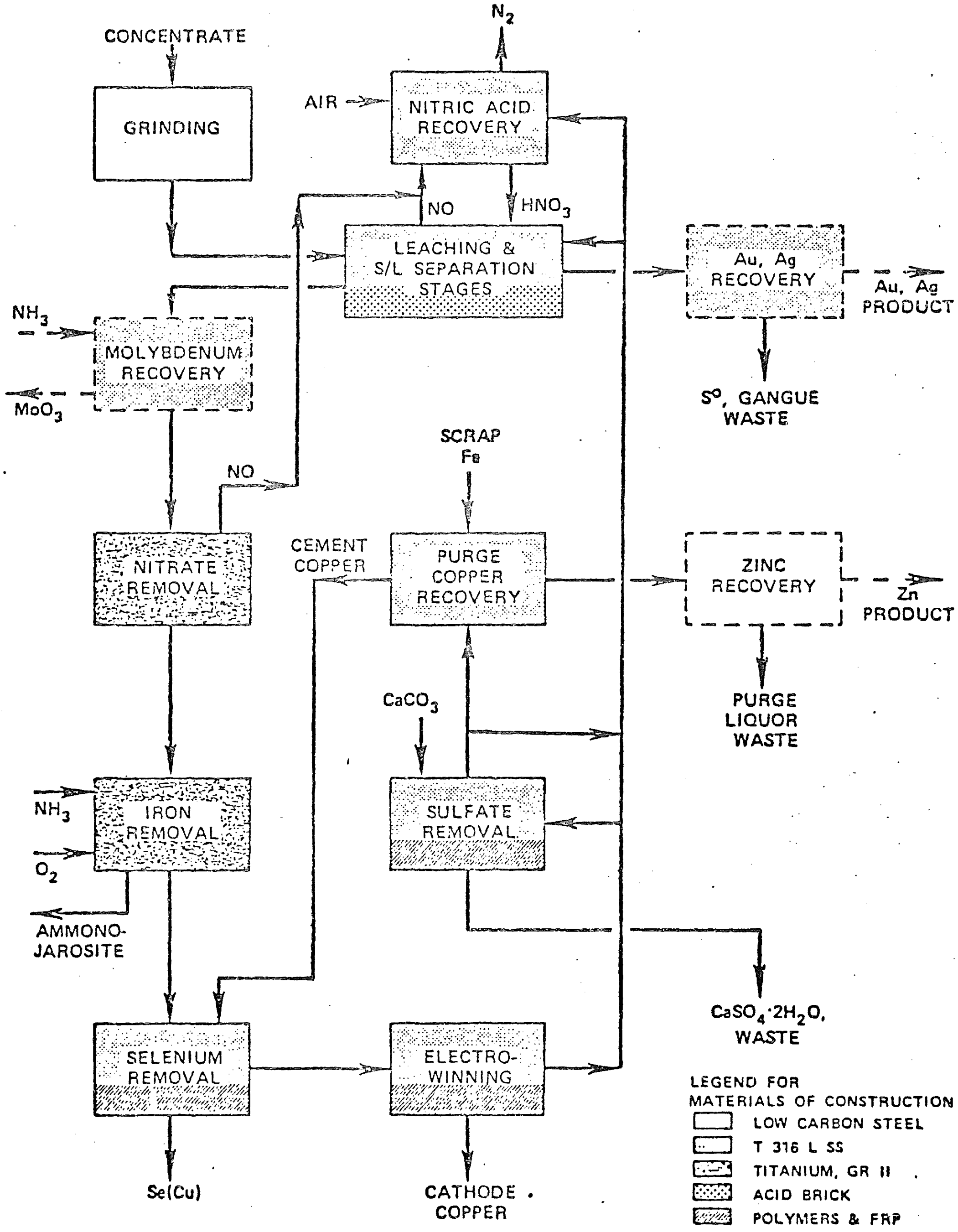


Figure 19. NITRIC SULFURIC LEACH FLOWSHEET[76]

by the Kennecott Copper Corporation, has shown that the process is competitive with pyrometallurgical and other hydrometallurgical processes. Process improvements of the NSL process is underway to further reduce costs and make the process commercially more attractive.

6. Bacterial Leaching

Bacterial leaching of sulfide minerals has been a much studied subject ever since Colmer and Hinkle in 1947 first demonstrated the role of bacteria in leaching.[78] In 1949, Temple and Colmer successfully isolated the bacteria, Thiobacillus ferrooxidans, from the drainage waters of a West Virginia coal mine,[79] and this led to greater interest in this field. Since then, many investigators have studied the mechanism and progress of bacterial leaching on various sulfide minerals such as chalcopyrite, covellite, bornite, chalcocite, pyrite, millerite, pentlandite, etc.[80-84]

Essentially bacterial leaching involves the oxidation of a mineral into a soluble and easily extractable form, the bacteria themselves functioning as a catalyst to the process or as a generating agent of ferric ions which in turn oxidize the mineral. Several strains of bacteria are recognized to be contributing to the leaching of sulfide minerals, the important ones of these being Thiobacillus thiooxidans and Thiobacillus ferrooxidans. These organisms have the shape of a bacillus of dimensions of about 0.5 by 1.0-2.0 microns with a single pole flagellum.[85] Thiobacillus thiooxidans has the ability to oxidize elemental sulfur, sulfur dioxide and thiosulfate, and draws it energy from the oxidation reactions. Thiobacillus ferrooxidans is capable of oxidizing not only thiosulfates, tetrathionates and sulfides, but also oxidizes ferrous ions to ferric ions in an acid medium. These two microorganisms are autotrophic and use carbon dioxide as the sole source of carbon necessary for the generation of cellular tissue and obtain energy by the oxidation of the aforementioned substances. They thus live and grow even in strongly acidic environments (pH 1.5-3.0) and in the presence of many heavy metals which are highly toxic to most other forms of life.

Two mechanisms of bacterial oxidation have been postulated. The direct bacterial attack of the mineral in the presence of dissolved oxygen has been supported by Razzell,[80] Bryner et al.,[81] Duncan et al.,[82] Beck and Brown,[86] etc., and has been demonstrated for some sulfides such as ZnS and CuS.[52] The other mechanism is the indirect leaching action of ferric ion brought about by the bacterial oxidation of dissolved iron in the presence of oxygen. Sutton and Corrick,[87] Malouf and Prater,[88] etc. have postulated this mechanism to be taking place in chalcopyrite dissolution, the chief role of bacteria being only to provide an active ferric sulfate lixivant. It is probable that both the mechanisms are operative during the actual leaching, with one predominating the other depending upon the conditions of leaching, the minerals involved, and the bacteria in use.

The mechanism of dissolution of chalcopyrite concentrates as proposed by Sutton and Corrick[87] follows the scheme given below:

Chalcopyrite initially undergoes air oxidation:

$$CuFeS_2 + 4O_2 \rightarrow CuSO_4 + FeSO_4 \qquad ....(45)$$

The ferrous sulfate produced is oxidized to ferric sulfate by oxygen in the presence of bacteria:

$$4FeSO_4 + 2H_2SO_4 + O_2 \xrightarrow{bacteria} 2Fe_2(SO_4)_3 + 2H_2O \qquad ....(46)$$

The ferric sulfate attacks the chalcopyrite forming more ferrous sulfate which repeats the oxidation cycle:

$$CuFeS_2 + 4Fe^{+3} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S° \qquad ....(47)$$

The elemental sulfur generated during the leach is converted to acid by the bacteria, and keeps the iron in solution:

$$S° + 1\ 1/2\ O_2 + H_2O \xrightarrow{bacteria} H_2SO_4 \qquad ....(48)$$

Reaction (45) proceeds slowly and hence initial leaching rate is relatively slow, but accelerates with time to some limiting value.

Razzall and Trussell,[83] and Duncan and Trussell[84] studied the bacterial leaching of millerite (NiS) and pentlandite [$(Fe,Ni)_9S_8$], and reported that the dissolution of nickel from pentlandite was more rapid. They have also proposed that the dissolution is effected by direct bacterial action. This mechanism is further confirmed by Torma[89] who obtained high dissolution rates from pure NiS using iron-free bacterial solutions. However, when iron is present in the system, as in the leaching of pentlandite, it is quite likely that ferric ion attack would be an additional significant factor contributing to the dissolution. The bacterial oxidation of pentlandite has been stated as follows:

$$(Ni,Fe)_9S_8 + 17\ 5/8\ O_2 + 3\ 1/4\ H_2SO_4 \xrightarrow{bacteria}$$
$$4\ 1/2\ NiSO_4 + 2\ 1/4\ Fe_2(SO_4)_3 + 3\ 1/4\ H_2O \qquad ....(49)$$

Table 13 shows the results of several investigations on bacterial leaching of sulfide minerals. It is to be noted that the investigations vary

TABLE 13. RESULTS OF INVESTIGATIONS ON BACTERIAL LEACHING USING THIOBACILLUS FERROOXIDANS

Author(s)	Feed		Temp (°C)	Time	Yield, %	
	Mineralogy	Particle Size			Cu	Ni
Pinches, A., et al.	Chalcopyrite + bornite + pyrite + covellite concentrates	2.1 μm	35	-	79.5	-
Duncan, D.W., et al.	Chalcopyrite concentrates	100% -400 mesh	-	120 hrs	59	-
Duncan, D.W. and Trussel, P.C.	Chalcopyrite (museum grade mineral)	100% -325 mesh	35	33 days	100	-
Duncan, D.W. and Trussel, P.C.	Millerite (museum grade mineral)	100% -325 mesh	35	23 days	-	58
Sakaguchi, H., et al.	Chalcopyrite concentrates	-37 μ	35	400 hrs	60	-

on such details as experimental conditions, leaching medium, procedure adopted, etc., and hence for additional specific information on the investigations, the reader is referred to the references cited.

A review of published information on bacterial leaching points out the following as among the chief factors in leaching:[91]

(a) An available source of substrate.

(b) Supply of carbon dioxide which is the sole carbon source for the thiobacilli

(c) Supply of oxygen.

(d) Supply of essential nutrients like nitrogen.

(e) Water as a carrier of the nutrients including phosphorous, as a source of trace elements, and as a solvent for the solvated metal

(f) An acidic environment

(g) Particle size

(h) Temperature

(i) Additives.

The availability of a substrate is one of the primary requirements for the oxidation of metal sulfides by the bacteria. It is most desired that the substrate be soluble, like with ferrous sulfate; but for insoluble substrates, adequate exposure of the sulfide minerals must be made. This makes particle size of the mineral a very important factor in metal extractions with bacteria. Razzell et al.[83,92] reported that copper dissolution was faster with fine particles of chalcopyrite than coarser ones, and the maximum extraction was obtained with 42 μm size fraction. Further, studies on synthetic copper sulfides have shown that the rate of bacterial oxidation is almost doubled when particle size is reduced from 104 to 64 μm size.[93] Hence, fine particles increase the surface area exposed to the bacterial attack and enhance the dissolution rates. However, it has been reported that the rate of copper release from chalcopyrite increases with decreasing particle size down to sizes below 400 mesh, at which point some other factor becomes rate-controlling.[94] Further limits on the size reduction of the particles are imposed by the operational problems caused by the poor permeability of finely ground slimes and the economy of grinding costs.

For effective functioning, bacteria need oxygen, nitrogen, phosphate and carbon. In addition, calcium, magnesium and potassium are beneficial. The supply of adequate oxygen is one of the major considerations in bacterial leaching, and this is illustrated by the fact that in the case of chalcopyrite, 2.13 pounds of oxygen are necessary to release one pound of copper from the mineral. The oxygen is provided by adequate ventilation and application of water. The aeration also provides the system with carbon dioxide which is the sole source of carbon essential for bacterial growth. Glucose has also been investigated as a possible source of carbon.[80] Ammonium salts are the major suppliers of nitrogen to the bacteria, although urea has been found to be equally effective.[95] The other nutrients are supplied by suitable additives. Each of these additives appears to have an optimum concentration. Table 14 gives the concentrations of typical nurients.[34]

pH plays an important role in bacterial oxidation, and its effect has been well investigated and reported.[81,83] Bacteria are active between a pH value of 1.5 and 3.5, and the optimum pH range varies with the mineral leached. For example, the optimum pH values for chalco-

TABLE 14.

CHEMICAL COMPOSITION OF A TYPICAL NUTRIENT[34]

Component	*Concentration (g/l)*
$(NH_4)_2SO_4$	0,1–5
K_2HPO_4	0,5–5
KCl	0,05–0,1
$Al_2(SO_4)_3 \cdot 18H_2O$	1,0–8,0
$MgSO_4 \cdot 7H_2O$	0,01–3,0
$MnSO_4 \cdot H_2O$	0,05
$Ca(NO_3)_2 \cdot 4H_2O$	0,01
Na_2SO_4	0,05

pyrite, chalcocite and covellite lie between 2.3 and 2.5.[96] Above a pH of 2.5 ferric iron percipitates, and the rate decreases. The decrease in rate could be due to the coating of the precipitate on the sulfide particles or due to the removal of the ferric ion oxidant from the system. Lower limit to acidity may be due to the tolerance of the bacteria to the H^+ ions.[34]

Bacterial activity has been found to closely depend on the temperature. The optimum temperature range for leaching with Thiobacillus Ferrooxidans has been reported to be between 25 and 45°C[96] (Figure 20). Dissolution rates fall sharply above 40°C and all biological activity ceases above 50°C.[97] However, recent studies have indicated that bacterial leaching in the temperature range 50°C to 80°C can be achieved by Thermophilic acidophilic thiobacteria.[96] This presents the possibility of higher extraction rates on account of the increased temperatures. Further investigation is necessary to fully understand this phenomenon.

The effect of solubilization of iron from the metal sulfides in bacterial leaching systems has been reported by Torma.[90,98] Iron hydrolyses to a basic ferric hydroxide which deposits on the surface and inhibits further bacterial action. Thus the reaction rate decreases from a maximum value at the start of the reaction to a value dependent on the diffusion rate through the hydroxide deposit and the reacted shell. According to the next hydrolysis reactions, the iron precipitate has the following composition.[90]

$$Fe_2(SO_4)_3 + 2H_2O \rightleftarrows 2Fe(OH)SO_4 + H_2SO_4 \qquad \text{....(50)}$$

$$1\ 1/2\ Fe_2(SO_4)_3 + 6H_2O \rightleftarrows H[Fe(SO_4)_2 \cdot 2Fe(OH)_3] + 2\ 1/2\ H_2SO_4 \qquad \text{....(51)}$$

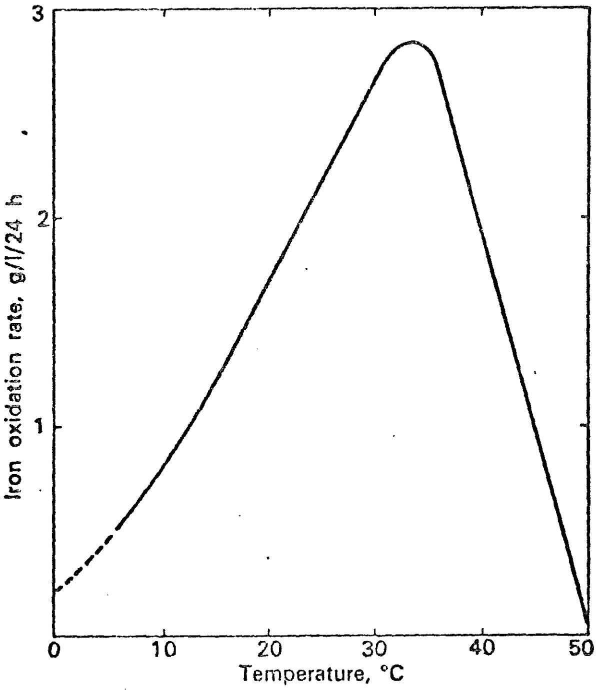


Fig. 20. Effect of temperature on rate of iron oxidation by bacteria.[34]

$$Fe_s(SO_4)_3 + 6H_2O \rightleftharpoons 2Fe(OH)_3 + 3H_2SO_4 \qquad ....(52)$$

The above reactions remove iron from the solution by yielding sulfuric acid. Thus the removal of Fe^{+3} ions could also lead to the decrease of the dissolution rate. These difficulties can be overcome and excellent extraction of metals can be achieved by regrinding the residue, in single or multi stages, to expose fresh surfaces for releaching.

A schematical representation of a microbial batch leaching process for chalcopyrite concentrates is given in Figure 21[99] and a simplified flow diagram of bacteria leaching of ores and minerals is given in Figure 22.[85] In the process, at the solvent extraction stage, the leached metal values are transferred from the aqueous phase into the organic phase. The aqueous phase is then recycled to the leaching step. The metal values from the organic phase is stripped and sent to the recovery step. The recycling aqueous solution will contain variable amounts of organic constituents depending upon the solubility of the solvents used and the mechanical losses due to entrainment. Studies have shown that these contaminants adversely affect bacterial leaching of chalcopyrite by reducing the oxidizing ability of Thiobacillus ferrooxidans.[100,101] Thus the dissolved organics contribute to a reduction in the solubilisation of metals from the ore or minerals in such a flowscheme and also represent an economic loss. Further, they also pose hazards if these solutions containing the organic compounds are released into the environment. It is recommended therefore that the aqueous recycling liquor be treated with activated charcoal or other inert absorbent to remove all organic matter before recycling or release into the environment.[85]

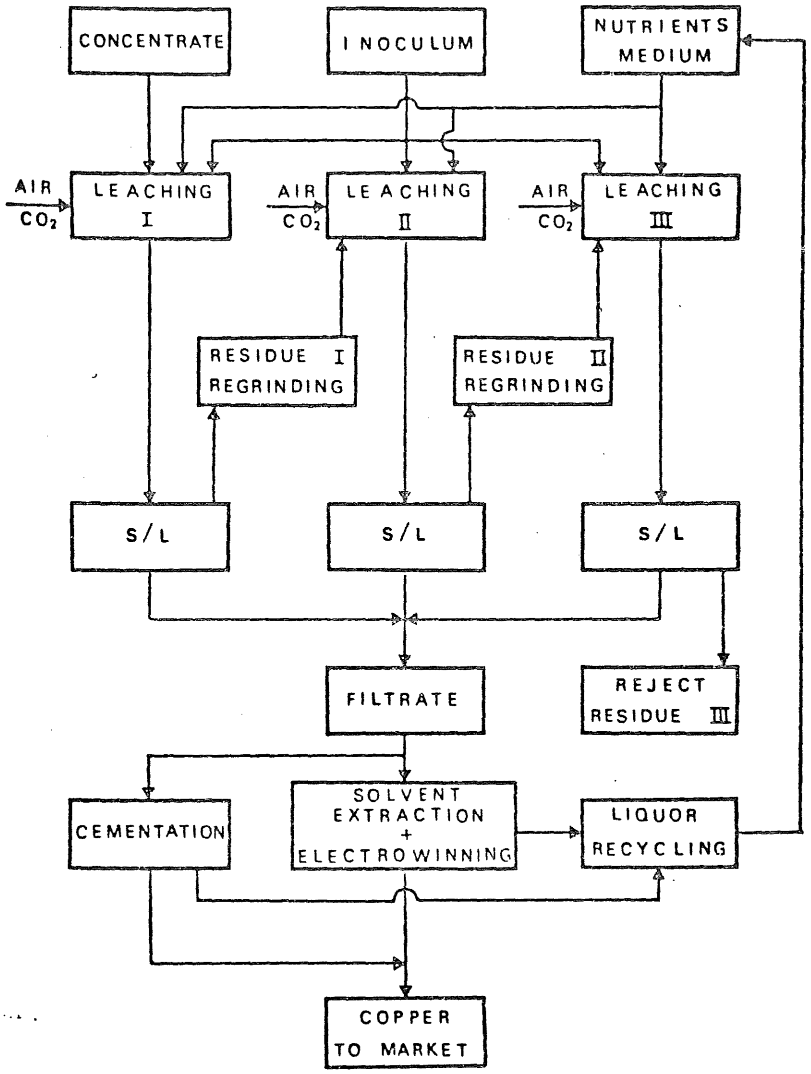


Fig. 21 Schematical representation of a microbiological batch leaching process for chalcopyrite concentrate treatment. 99

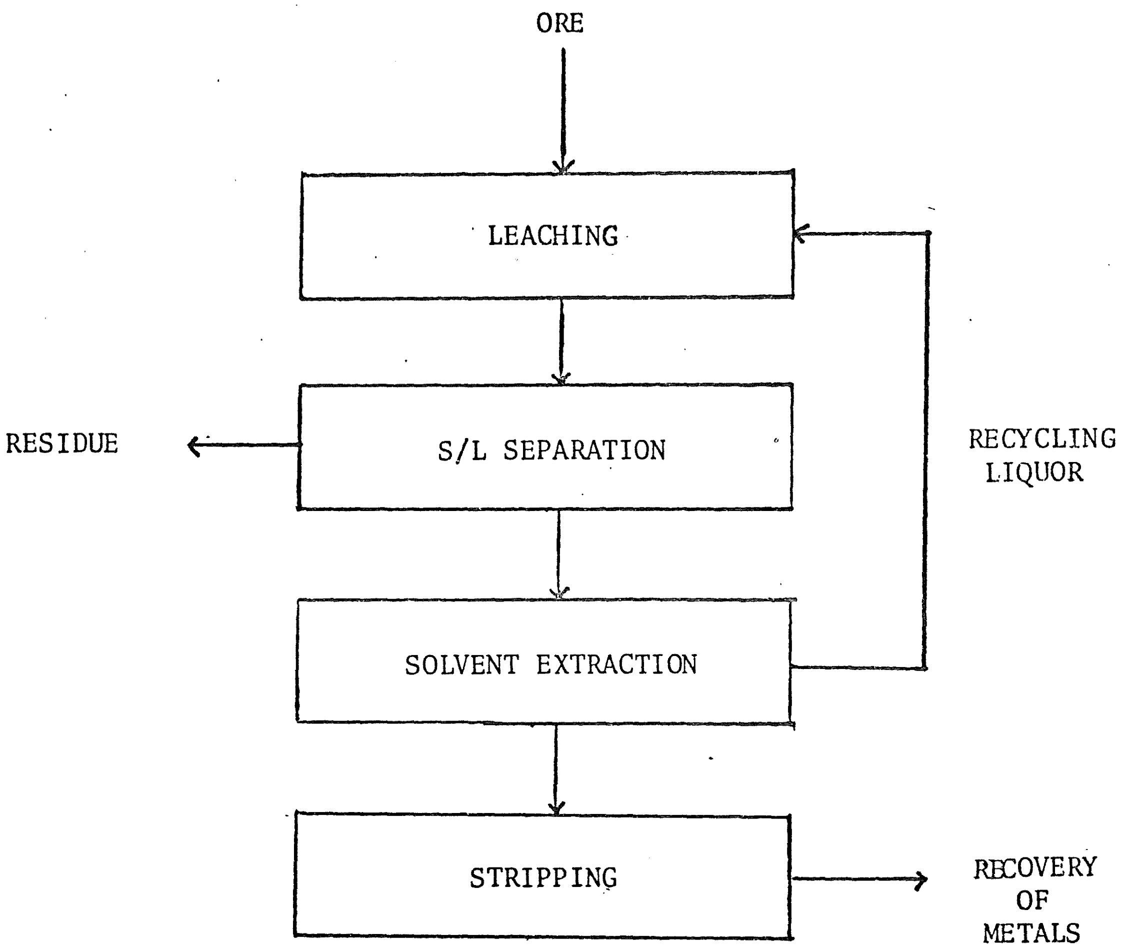


Fig. 22. Simplified flowdiagram for bacterial leaching of ores and minerals.

Bacterial leaching is associated with the conventional *in situ* heap and dump leaching methods employed for low-grade ores. Several of these are in operation in the U.S.A. The *in situ* leaching operation of the Rancher's Explorations and Development Company at Arizona handles 4 million tons of about 0.8% copper ore leaching 20 tons of copper per day.[102] Another plant in Arizona, Asarco's Silver Bell Unit, dump leaches 5 million tons of mine waste containing 0.2-1% copper. Bacterial leaching technique has the advantages of low capital cost and of providing an effective way to treat low grade deposits and wastes from conventional mining methods. The chief demerit lies in the long durations of leaching encountered. Though bacterial leaching of copper and nickel sulfide concentrates has been well investigated in the laboratory, there appears to be no commercial operation of the same. However, the investigations suggest that the technique is well suited for the treatment of sulfide concentrates, and hence warrants further studies towards commercializing the technique with respect to the concentrates.

B. STUDY OF HYDROLYSIS OF IRON

The study of hydrolysis of iron has not been as widely investigated as warranted by its importance especially in metallurgical processes. In metallurgical systems, such as the extraction processes of zinc and copper for example, the leach solutions contain considerable amounts of iron besides the metal values extracted. In zinc and copper leach solutions the iron content can be as high as 30 g/ℓ and 60 to 90 g/ℓ respectively. The iron content of these solutions has to be reduced to very low levels before the solution can be sent to the electrowinning or hydrogen reduction circuit. This can be effectively accomplished by the precipitation of iron from the leach solutions. Iron can be precipitated in various forms such as jarosite, basic compounds, ferric oxide and goethite. The form iron is precipitated must be weighed against considerations such as handling properties of the precipitates, environmental hazards, economic factors, ~~loss~~ due to coprecipitation or entrainment of precious metals, etc. Also, in those leaching processes where iron is directly rejected into the residue it is essential to understand the nature of the iron compound present in the residue. In view of these, it becomes very important to know precisely the conditions of formation and behavior of the hydrolysis products both in laboratory and real-life situations. A good portion of research in this area has been in connection with the zinc plant residues and this has led to the Jarosite process, developed independently by the Electrolytic Zinc Co. of Australiasia Ltd., in Australia, Det Norske Zinkkompani A/S in Norway, and Asturiana de Zinc S.A., of Spain.[107] Details of the process have been given elsewhere.

Precipitation of iron takes various forms in different systems. In the ammoniacal leach systems, the iron present in the concentrates is almost completely oxidized to an insoluble hydrated ferric oxide, $Fe_2O_3 \cdot xH_2O$, which is reported to form a coating on the sulfide particles. In the nitrate systems, iron precipitates from the solution as ferric hydroxide $Fe(OH)_3$, goethite FeOOH, or ferric oxide Fe_2O_3, depending on the temperature and acid concentration. Chloride systems yield ferrous chloride as the initial iron product which is oxidized to ferric chloride and recycled to the leaching circuit, or roasted to ferric oxide to be used in the production of iron. In the sulfate or bi-sulfate systems, iron precipitates as jarosites $AFe_3(SO_4)_2(OH)_6$ (where A can be H_3O, Na, K, Rb, Ag, NH_4, Tl, Pb/2 or Hg/2), basic ferric sulfate $Fe(OH)SO_4$, or ferric oxide Fe_2O_3, depending chiefly on the acid levels, temperature and the type and amount of cations present in the solution. It is to be noted that while hydrothermal precipitation of iron from ammoniacal, nitrate and chloride solutions yield relatively simple products such as oxides and hydroxides of iron, the precipitates from sulfate solutions are more complex due to the formation of a number of basic salts in addition to oxides and hydroxides. Since our interest lies in the treatment of sulfides, this discussion is restricted to the hydrolysis of iron in the sulfate system.

Studies on hydrolysis of iron have been carried out using ferric sulfate solutions with or without other cations, and plant leach solutions, and the hydrolysis was investigated under various experimental conditions. Significant information on the Fe_2O_3 - SO_3 - H_2O system has been presented as early as 1922 by Posnjak and Merwin.[103] It can be seen from their solid model (Figure 23) that hydronium jarosite ($3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$), basic sulfates and ferric oxide are formed at various temperatures between 50 and 200°C. Also, as the temperature increases the relative amounts of the hydrolysis products in the system changes. This is more evident by observing the isothermal reactions of the solid model at three different temperatures[18] (Figures 24-26). At 75°C, hydronium jarosite and ferric oxide monohydrate $Fe_2O_3 \cdot H_2O$ have been precipitated out of the solution. As the temperature increases the amount of $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ increases and that of $Fe_2O_3 \cdot H_2O$ decreases, as can be observed on the isotherm at 110°C. At 200°C, however, $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ has completely disappeared from the system, while ferric oxide monohydrate has given way to anhydrous ferric oxide which is present in large amounts. Also, a small amount of basic sulfate, $Fe_2O_3 \cdot 2SO_3 \cdot H_2O$ is present in the system. This study thus suggests a sequence of precipitation products as the temperature is increased. This sequence has been further investigated by Umetsu et al.[105] who have demonstrated by means of X-ray diffraction analysis the hydrolysis of iron at 185°C and 200°C yield the following precipates as a function of time:

Ferric sulfate (aq) → Hydronium jarosite → Basic sulfate →
$Fe_2(SO_4)_3$ $(H_3O)Fe_3(SO_4)_2(OH)_6$ $Fe(OH)SO_4$

Ferric oxide
Fe_2O_3

The ferric oxide is thus precipated from ferric sulfate solutions at 185°C and 200°C with hydronium jarosite and basic sulfate as the intermediate products.

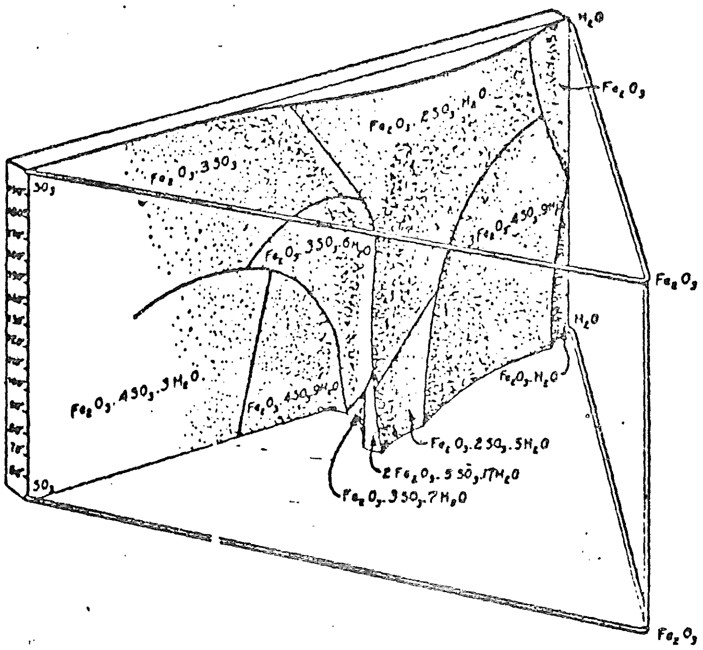


Fig. 23. Solid model of the system, Fe_2O_3–SO_3–H_2O, from 50° to 200°. 103

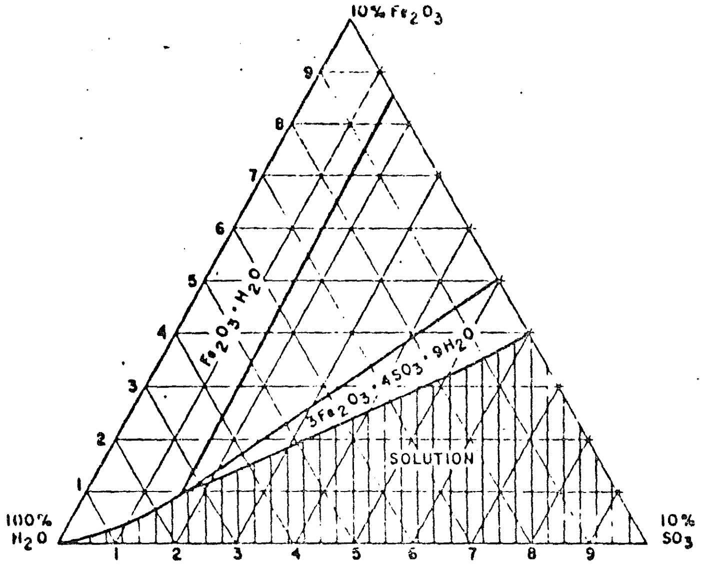


Fig. 24 System Fe_2O_3–SO_3–H_2O. Equilibrium at 75°C 104

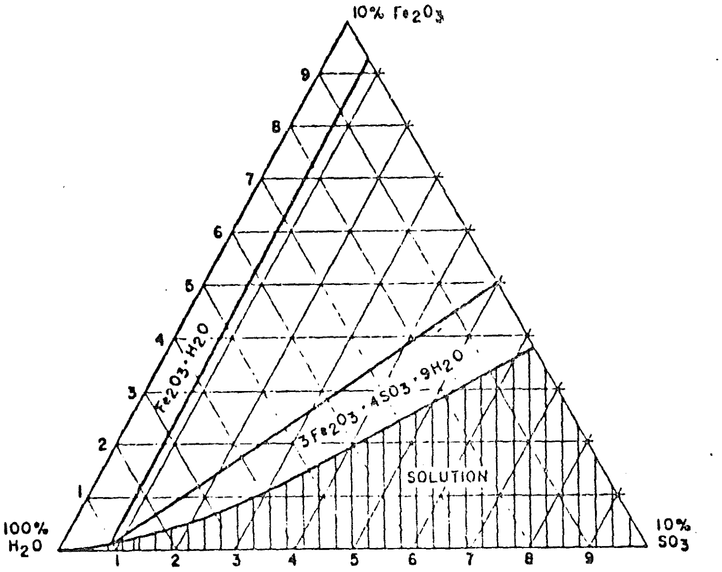


Fig. 25 System Fe_2O_3–SO_3–H_2O. Equilibrium at 110°C [104]

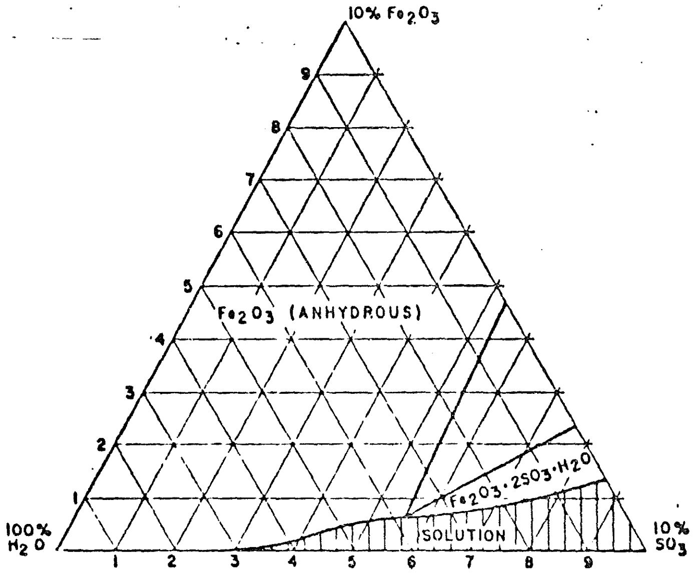


Fig 26 System Fe_2O_3–SO_3–H_2O. Equilibrium at 200°C [104]

The parameters involved in the precipitation of the iron compounds have been studied by several investigators.[106-108] The chief controlling parameters were found to be pH, concentration of ferrous or ferric ions and the concentration of sulfate or bisulfate. Further studies along these lines by Umetsu et al.[101,109] have revealed the cation concentration to be an additional significant parameter. This is evident from Figure 27 where ferric oxide Fe_2O_3 changed to basic sulfate $Fe(OH)SO_4$ at 60 g/ℓ H_2SO_4 in absence of $ZnSO_4$, but in presence of 50 g/ℓ $ZnSO_4$, the transition to $Fe(OH)SO_4$ increased to 80 g/ℓ H_2SO_4. When 80 g/ℓ $ZnSO_4$ was added, the product remained as Fe_2O_3 even at 120 g/ℓ H_2SO_4. Similar trend was observed when $CuSO_4$ was added in place of $ZnSO_4$. In addition, where the temperature of hydrolysis was increased from 185°C to 200°C, the transition of Fe_2O_3 to $Fe(OH)SO_4$ also took place at higher concentrations of H_2SO_4 with increasing $ZnSO_4$ content (Figures 28-31). This behavior demonstrates the strong influence of cationic concentration on the precipitation of Fe_2O_3 and $Fe(OH)SO_4$ from ferric sulfate solutions, and suggests that a similar behavior could be taking place in the case of jarosites also.

Jarosite compounds, the earliest hydrolysis products according to the sequence suggested by Posnjak and Merwin and Umetsu et al, have been found to precipitate at temperatures between 90-95°C and pH 1.3-1.7 (corresponding to 3-8 g/ℓ free acid) from ferric sulfate solutions containing Na^+, K^+, or NH_4^+ ions. Jarosites are a group of compounds having the general formula $AFe_3(SO_4)_2(OH)_6$ where A can be H_3O, Na, K, Rb, Ag, NH_4, Tl, Pb/2 or Hg/2. Dutrizac and Kaiman[110] have characterized all known jarosite compounds, and Table 15 lists their chemical

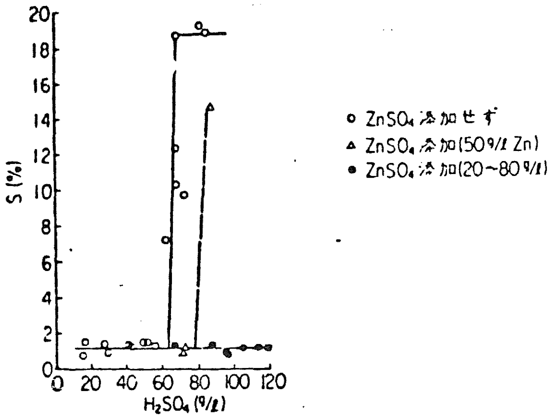


Fig. 27. Sulfur content in hydrolysis product as a function of free H_2SO_4 (200°C) 117

Formula	Chemical Name	Mineral Name
$(H_3O)Fe_3(SO_4)_2(OH)_6$	hydronium jarosite	hydronium jarosite (carphosiderite in early literature)
$NaFe_3(SO_4)_2(OH)_6$	sodium jarosite	natrojarosite
$KFe_3(SO_4)_2(OH)_6$	potassium jarosite	jarosite
$RbFe_3(SO_4)_2(OH)_6$	rubidium jarosite	no mineral equivalent
$AgFe_3(SO_4)_2(OH)_6$	silver jarosite	argentojarosite
$(NH_4)Fe_3(SO_4)_2(OH)_6$	ammonium jarosite	ammoniojarosite
$TlFe_3(SO_4)_2(OH)_6$	thallium jarosite	no mineral equivalent
$Pb_{0.5}Fe_3(SO_4)_2(OH)_6$	lead jarosite	plumbojarosite
$Hg_{0.5}Fe_3(SO_4)_2(OH)_6$	mercury jarosite	no mineral equivalent

Table 15. Chemical and mineral names of jarosites. 110

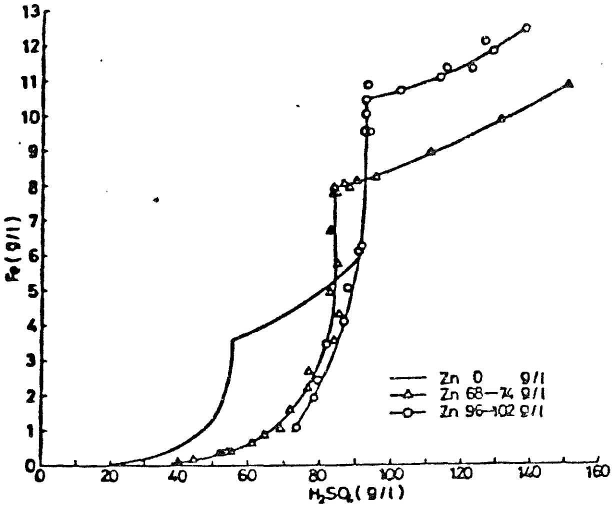


Fig. 28. Iron content versus free H_2SO_4 (185°C) 109

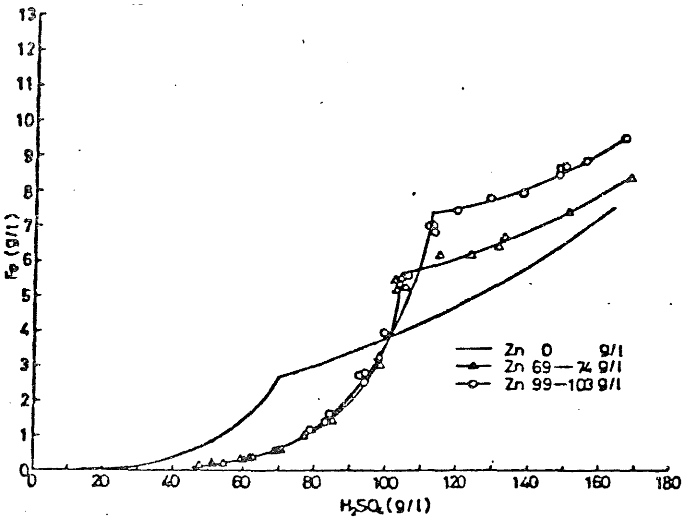


Fig. 30. Iron content versus free H_2SO_4 (200°C) 109

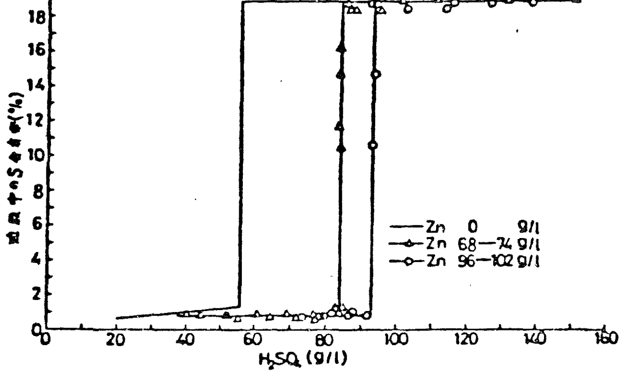


Fig. 29. Sulfur content versus free H_2SO_4 (185°C) 109

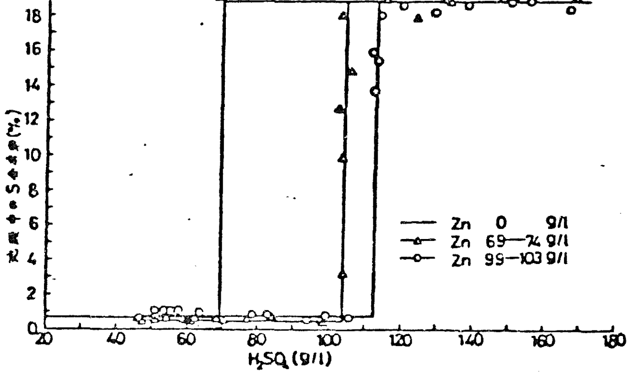


Fig. 31. Sulfur content versus free H_2SO_4 (200°C) 109

and mineral names as reported by the above authors. The precipitation of jarosites depends on the temperature, acid concentration and the presence of cations like K^+, Na^+ and NH_4^+, an increase in temperature and a decrease in free acid concentration leading to an increase in jarosite formation.[107] In the absence of alkali, hydronium jarosite has been synthesized in the temperature range 25-170°C.[111] From laboratory investigations carried out on leach solutions derived from zinc plant spent electrolyte, Haigh[106] has reported the formation of hydronium jarosite in the temperature range 170-200°C. Also, it can be seen from Figure 32 that formation of natrojarosite is indicated from temperatures of about 25°C to 200°C. Hence, these facts point to the possibility that hydronium jarosite and natrojarosite may precipitate out at all temperatures between 25°C and 200°C, the extent of precipitation and the type of precipitates depending on the temperature and the solution conditions respectively.

Jarosite seldom precipitates in the pure form; it often exists as a solid solution of sodium, potassium, or ammonium jarosite and hydronium jarosite. Precipitation of jarosite greatly depends on the type and amount of ions present in the solution, and the effects of these should be clearly understood to enable suitable additions of jarosite-precipitants when necessary. Addition of stoichiometric amounts of various jarosite-precipitants to the leach solution showed that above 180°C all precipitants produced approximately the same effects on hydrolysis, while at temperature of 160°C and below potassium jarosite was the least soluble among the jarosites studied (Figure 33). From economic considerations, assuming loss of the precipitant on hydrolysis, Haigh[106] reports

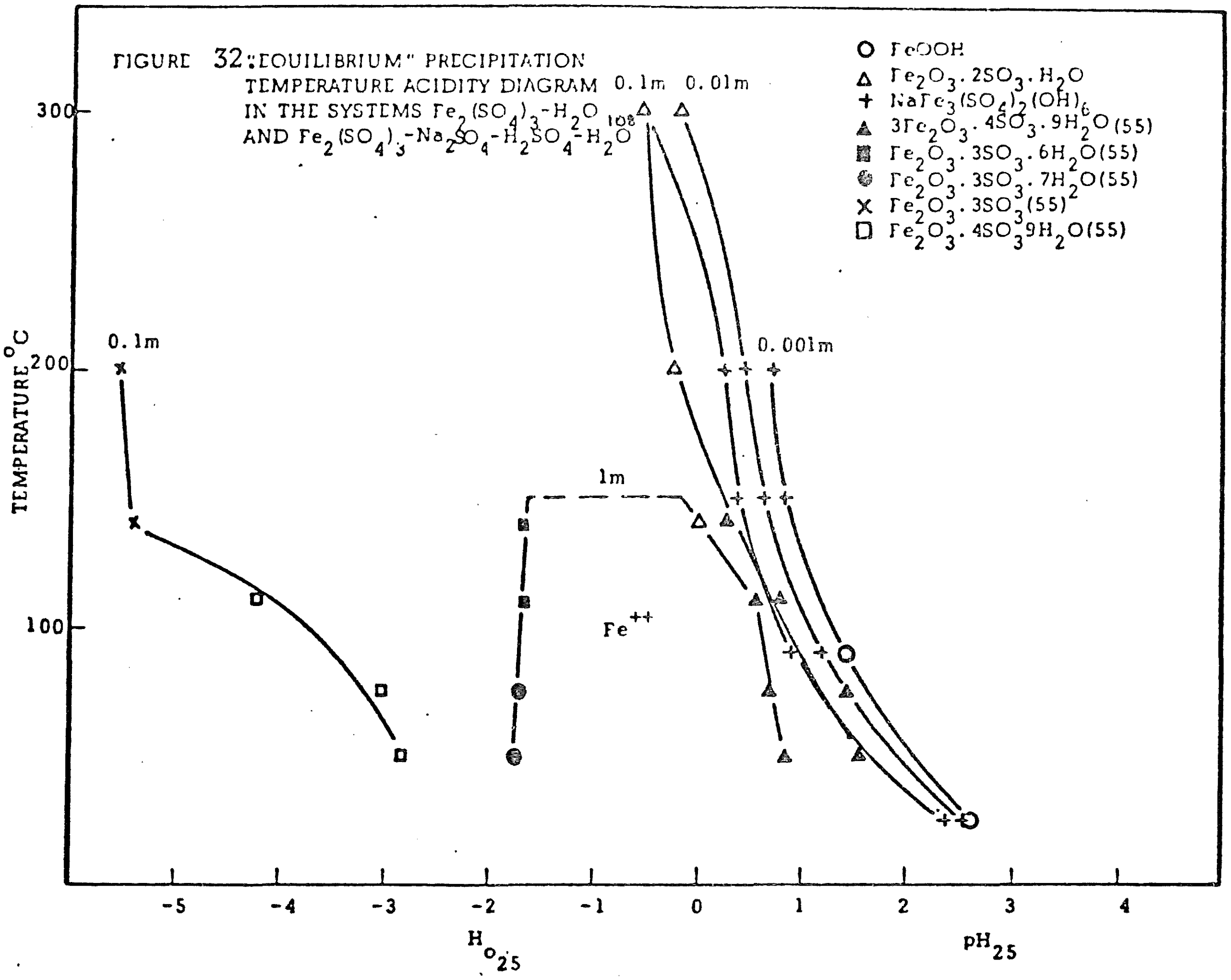


FIGURE 32: "EQUILIBRIUM" PRECIPITATION TEMPERATURE ACIDITY DIAGRAM IN THE SYSTEMS $Fe_2(SO_4)_3-H_2O$ AND $Fe_2(SO_4)_3-Na_2SO_4-H_2SO_4-H_2O$

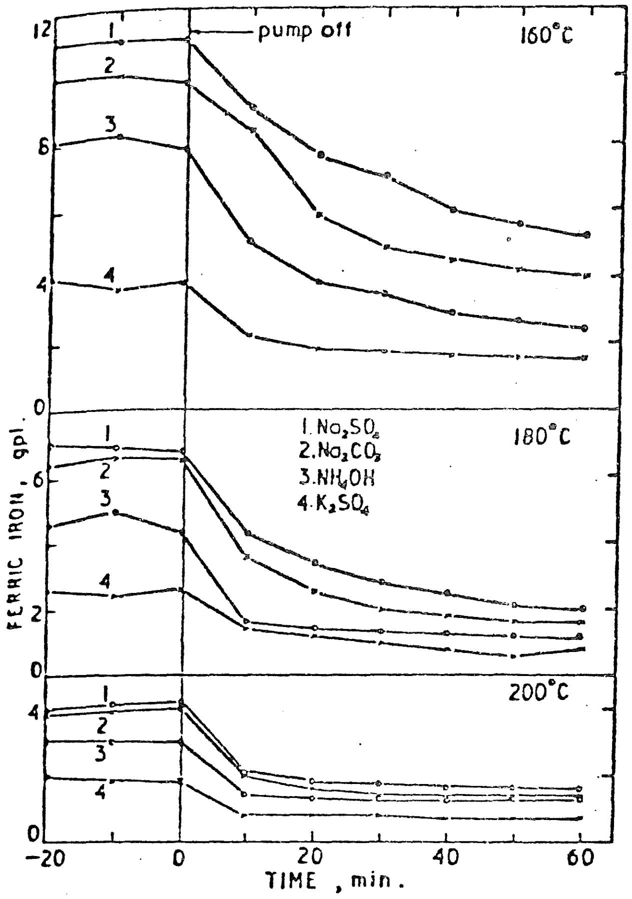


Fig. 33 Effect of stoichiometric additions of reagents on iron concentration.

that ammonia is preferable to sodium or potassium. Studies on the effect of ammonia additions to the solution showed that above the stoichiometric level even quite large increases in ammonia additions produced little effect on the hydrolysis, whereas below stoichiometric levels, even small changes in ammonia concentrations produced a large effect (Figure 34). It is thus seen that both the quantity and type of cations already present in the solution, or to be added in controlled amounts, can affect precipitation of jarosite.

The reactions of jarosite formation are complex but are summarized by Steinveit[112] (Table 16). A typical jarosite formation reaction is as follows:

$$3Fe_2(SO_4)_3 + 2NH_4OH + 10H_2O \rightarrow 2NH_4Fe_3(SO_4)_2(OH)_6 + 5H_2SO_4 \quad ....(53)$$

It is seen from above that the process generates acid. This can be also noted from Figure 35 which indicates the effect of acidity on the extent of hydrolysis at 200°C. The initial acidity in the Tests 1-5 in Figure 35 before the addition of either acid or calcine was 12.4 g/ℓ H_2SO_4. The increase in acidity of the solution leaving the autoclave is contributed chiefly by the hydrolysis and the regeneration of acid. Since the precipitation of jarosite greatly depends on the acidity level of the solution, it is necessary to maintain a low acid concentration in the solution before hydrolysis. Tozawa[113] has derived the Eh-pH relationships involved in jarosite formation and has plotted the Eh-pH diagram (Figure 36) and the log[Fe^{+3}] - pH relationship (Figure 37). These indicate that jarosites are stable below pH 2.4 and are quite oxidizing. Also higher temperatures favor jarosite formation (Figure

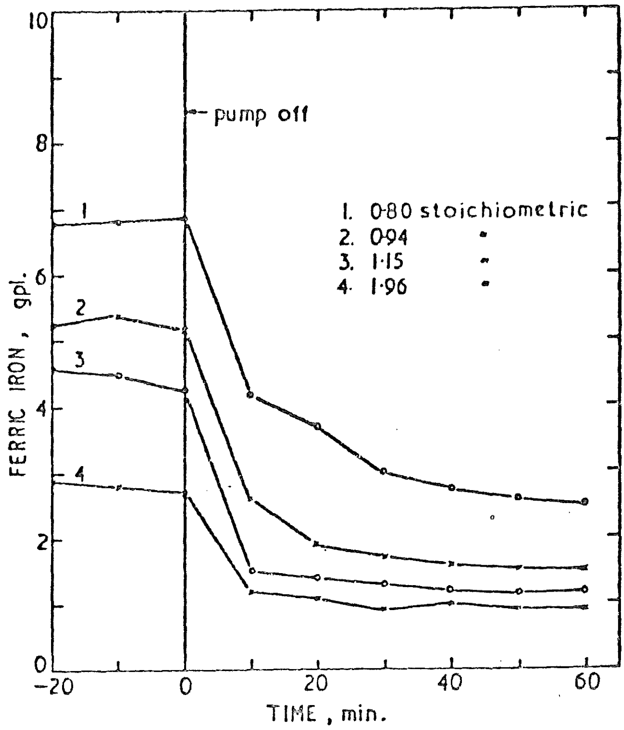


Fig 34 Effect of ammonia additions on iron concentration at 180°C. 106

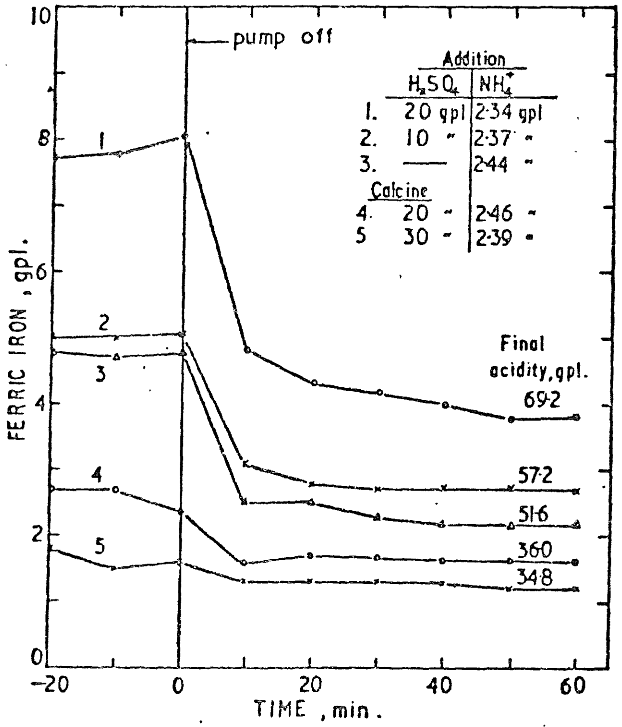


Fig 35 Effect of acidity on iron concentration at 200°C. 106

(1): $3Fe_2(SO_4) + 6H_2O = 6Fe(OH)SO_4 + 3H_2SO_4$

(2): $4Fe(OH)SO_4 + 4H_2O = 2Fe_2(OH)_4SO_4 + 2H_2SO_4$

(3): $2Fe(OH)SO_4 + 2Fe_2(OH)_4SO_4 + 2NH_4OH = (NH_4)_2Fe_6(SO_4)_4(OH_{12}) + 5H_2SO_4$

(4): $2Fe(OH)SO_4 + 2Fe_2(OH)_4 \cdot SO_4 + Na_2SO_4 + 2H_2O = Na_2Fe_6(SO_4)_4(OH)_{12} + 6H_2SO_4$

(5): $2Fe(OH)SO_4 + 2Fe_2(OH)_4 \cdot SO_4 + 4H_2O = (H_3O)_2Fe_6(SO_4)_4(OH)_{12} + 5H_2SO_4$

(6): (1)+(2)+(3):
$3Fe_2(SO_4)_3 + 10H_2O + 2NH_4OH = (NH_4)_2Fe_6(SO_4)_4(OH)_{12} + 5H_2SO_4$
ammonium jarosite

(7): (1)+(2)+(4):
$3Fe_2(SO_4)_3 + 12H_2O + Na_2SO_4 = Na_2Fe_6(SO_4)_4(OH)_{12} + 6H_2SO_4$
carphosiderite

(8): (1)+(2)+(5):
$3Fe_2(SO_4)_3 + 14H_2O = (H_3O)_2Fe_6(SO_4)_4(OH)_{12} + 5H_2SO_4$
carphosiderite

Table 16. Hydrolysis reactions of ferric sulfate.[114]

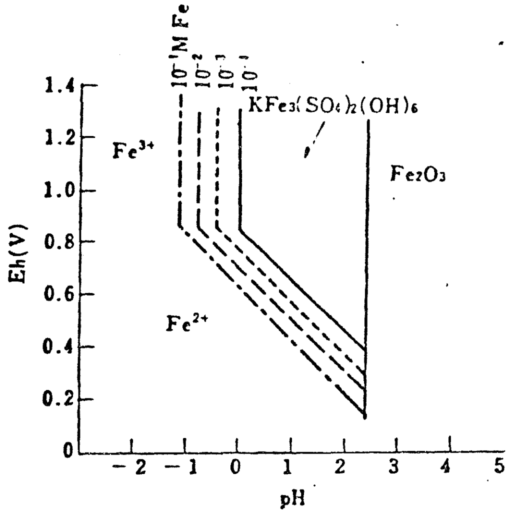


Fig. 36. Stability region of jarosite.[113]

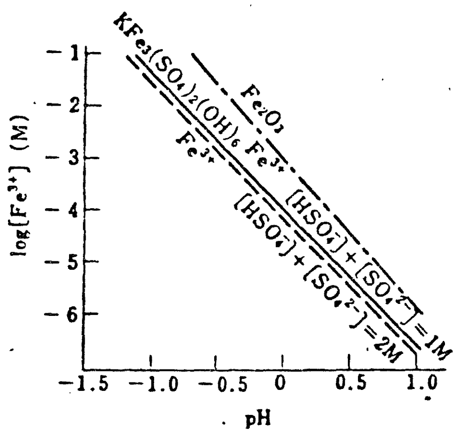


Fig. 37. Log$[Fe^{+3}]$ - pH relation in iron hydrolysis.[113]

38) and the rate of precipitation decreases as temperature decreases, but the results published by Haigh indicate that above 180°C, increases in temperature have little effect on the hydrolysis, but below 180°C changes in temperature produce quite a large effect (Figure 39). Jarosite precipitates quite rapidly after 1 hour at the temperature employed (Figure 40) but the precipitation slows down considerably after 2 hours.

Precipitation of iron as jarosite is a convenient way of removing excess quantities of iron from hydrometallurgical processing solutions. Jarosites can be precipitated from strongly acidic media, which thus obviates the necessity of neutralization. They also have the added advantage of easy filtering characteristics. Jarosite precipitation also serves as an effective method for sulfate control in the process. However, trace metals such as silver, if present in the residue, tend to precipitate as jarosite, thus making their recovery or elimination more difficult.[110] This disadvantage can be avoided by careful study and control of jarosite formation.

The jarosite process in operation at the Electrolytic Zinc Company of Australiasia, Limited in Australia treats the zinc plant residue containing chiefly of zinc ferrite ($ZnO \cdot Fe_2O_3$).[115] The residue is leached with spent electrolyte at 70-95°C. Both zinc and iron go into solution. The iron is removed by precipitating it as jarosite brought about by controlling the pH and adding required amounts of aqueous ammonia to the solution at 90-95°C. The jarosite is filtered out and washed, and after further purification the iron free solution is sent to the electrolytic tank for zinc recovery. The jarosite process as applied to zinc plant residue treatment claims several advantages some

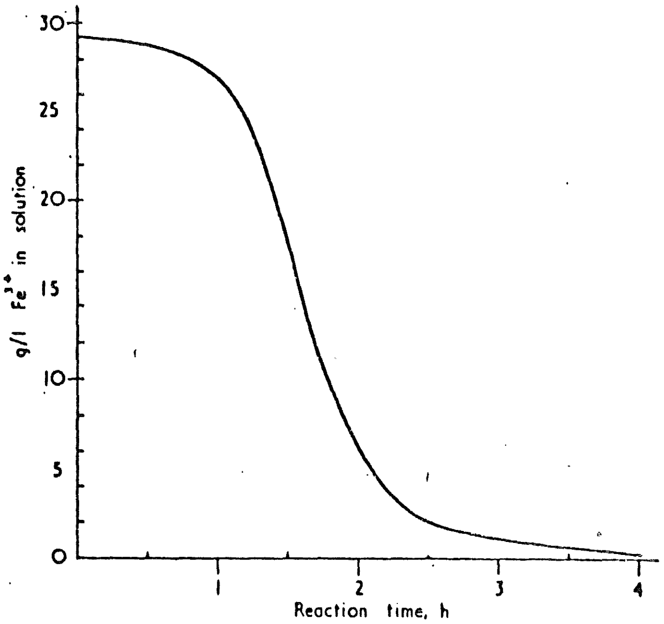


Fig 40 Progress of precipitation of iron as jarosite. Solution: 29·1 g/l Fe^{3+}, 45 g/l H_2SO_4 112

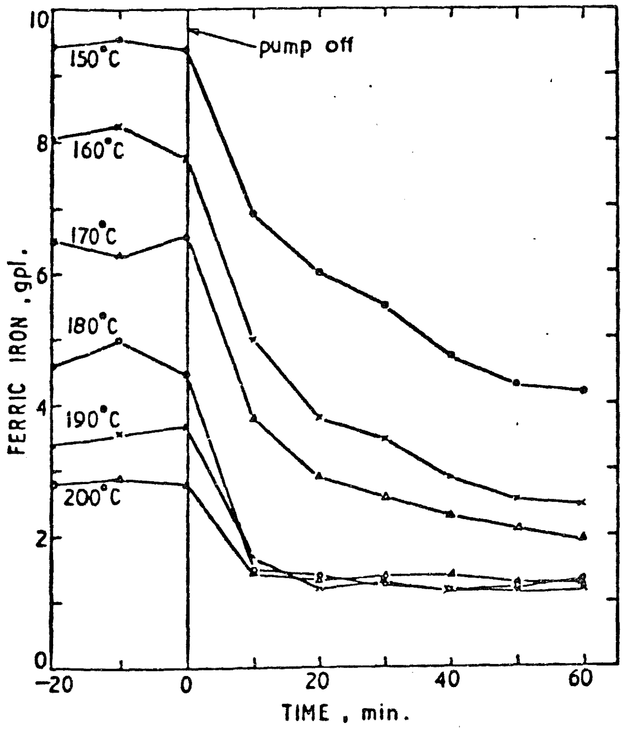


Fig 39 Effect of temperature on iron concentration with stoichiometric addition of ammonia. 106

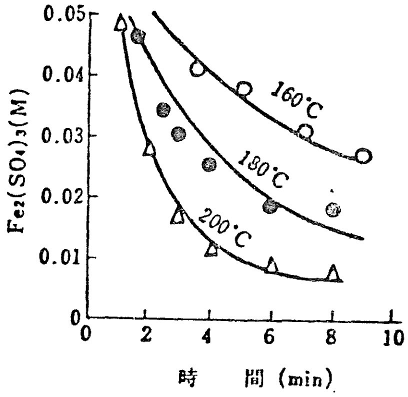


Fig. 38. Rate of Fe^{+3} hydrolysis 113

of which are simplicity of operation, use of conventional equipment, easily available reagents, good yield of metal values from the residue, etc.

Formation and behavior of basic ferric sulfates have not been studied as much as those of other hydrolysis products of iron, Kwok and Robins[108] have shown that natrojarosite [$NaFe_3(SO_4)_2(OH)_6$] and hydronium jarosite [$3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$] convert to basic sulfate [$Fe_2O_3 \cdot 2SO_3 \cdot H_2O$] at 300°C and pH below 0 (Figure 32). Also, it can be noted from the figure that natrojarosite and hydronium jarosite have very close stability regions. Kunda et al.[116] have reported that the conditions for hydrolysis of ferrous sulfate to basic ferric sulfate were 204°C, 20 psi O_2 100 to 150 g/ℓ Fe in the feed solution and 1 hour retention time. Also, according to Umetsu and Sasaki,[117] basic ferric sulfate precipitated from acidic ferric sulfate solutions above a free acid level of 69.3 g/ℓ H_2SO_4 at 200°C and above 55.8 g/ℓ H_2SO_4 at 185°C. More study is essential to understand the formation reactions and nature of basic ferric sulfate.

The precipitation of ferric oxide Fe_2O_3 is generally favored by higher temperatures and low acid concentrations. Haigh[106] reports that above 180°C, Fe_2O_3 is the main phase precipitated from the leach solutions. Based on hydrolysis studied carried out on pure ferric sulfate solutions, he has shown that at 200°C, Fe_2O_3 is precipitated at low acid concentrations and a basic compound $Fe_2O_3 \cdot 2SO_3 \cdot H_2O$ is precipitated at higher acid concentration. At 180°C, however, the solution yields Fe_2O_3 at low acid concentrations and hydronium jarosite $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, at higher concentrations. There is no mention of the exact acid levels involved in the precipitation of these compounds. However, Haigh reports that below 180°C, ferric oxide precipitates at total acid levels below 20 g/ℓ H_2SO_4. Umetsu and coworkers[109,117] have investigated the hydrolysis of acidic ferric sulfate solutions at 185°C and 200°C and have reported the results (Figures 28-31). Their studies indicate that at 200°C the hydrolysis and precipitation of ferric oxide occurred up to the free acid concentration of 69.3 g/ℓ H_2SO_4, above which ferric basic sulfate was precipitated. At 185°C, the free H_2SO_4 limit was 55.8 g/ℓ below which Fe_2O_3 precipitated. There is thus an obvious disparity in results regarding levels of acidity between the Australian and the Japanese investigators. However, Umetsu et al.[105] have reported that in presence of $ZnSO_4$, the hydrolysis of iron in the form of Fe_2O_3, at 200°C, was possible up to a free acid level of about 120 g/ℓ H_2SO_4 (Figure 27). This result brings out the possibility that the Fe_2O_3 precipitation could be further affected by the presence of other cations in the solution such as Cu, Ni, Co, etc. and consequently defining the exact conditions of precipitation of Fe_2O_3 becomes individualistic and difficult.

Davey and Scott[118] have reported their studies on the Goethite process, by which iron is precipitated out of solution in the form of geothite (FeOOH). Goethite was precipitated from sulfate solutions containing 30 g/ℓ Fe at 70-90°C at a pH of 2-3.5. Kwok and Robins[108] have also reported the formation of goethite in 0.001 M Fe^{+3} solutions containing Na^+, at temperatures below 90°C (Figure 32). Studying the effect of MgO and NaOH additions to ferric sulfate solutions at 80°C, Umetsu et al.[119] have reported that goethite precipitates at pH 1.0-1.8

when MgO was added. Addition of NaOH to ferric sulfate solutions precipitated natrojarosite [$NaFe_3(SO_4)_2(OH)_6$] above 10.7 g/ℓ H_2SO_4 and geothite below 10.7 g/ℓ H_2SO_4. At 10.7 g/ℓ H_2SO_4, a mixture of goethite and natrojarosite was formed. The geothite precipitated has excellent filtering characteristics, and the process affords iron removal to very small amounts in the solutions. However, goethite tends to be heavily contaminated with anionic and cationic impurities and as a result requires considerable washing and desorption treatment.

It is worthwhile at this point to briefly review the salient features of precipitation of the three main iron compounds, namely jarosite, ferric oxide and goethite. Jarosite is precipitated at low pH and at temperatures generally between 90-100°C in the sulfate medium. Natrojarosite, ammoniojarosite, or any other jarosite can be precipitated selectively by adding controlled amounts of the required cation. Ferric oxide is precipitated at temperatures around 200°C and does not require cationic additions. Goethite can be formed at temperatures between 70 and 90°C at pH 2-3.5. It has the advantage that it can be precipitated from any anionic medium, and does not require the addition of cation. However, it has the disadvantage of heavy contamination by the cations and anions of the system. All the three forms of precipitates have excellent filtering characteristics. A tabular comparison of these three precipitation processes in shown in Table 17.

It is to be expected that the precipitated compounds are not pure, but contain other foreign substances as contaminants. For instance, precipitated ferric oxide contains about 1-2% sulfur (Figures 29 and 31) which can be reduced to as low as 0.01% by roasting at 1000°C.[117] In

Table 17.
Comparison of iron precipitation processes[118]

	Process		
	Goethite	Jarosite	Hematite
Operating conditions			
pH	2—3.5	<1.5	Up to 2% H_2SO_4
Temperature	70—90° C	90—100° C	≃ 200° C
Anion	Any	SO_4^{2-} only	SO_4^{2-} only (?)
Added cations required	Nil	Na^+, K^+, NH_4^+ (= R)	Nil
Product			
Compound formed	α- and β-FeOOH (α-Fe_2O_3)	$RFe_3(SO_4)_2(OH)_6$	α-Fe_2O_3
Cationic impurities	Medium	Low (apart from "R")	Low
Anionic impurities	Medium[a]	High	Medium
Filterability	V. good	V. good	V. good
Fe in filtrate	<1 g/l (often <0.05 g/l)	1—5 g/l	≃3 g/l

[a] Good scavenger for fluoride in electrolytic zinc plants.

acid solutions, hydrolysis is confined to tri- and quadrivalent elements, thus enabling separations from lower-valent elements which may contaminate the hydrolysis product. But contamination is still possible by coprecipitation. Coprecipitation of other ions in the solutions can take place either by absorption at the surface of the particles exposed to the solution or by occlusion of the foreign ions during the formation of the precipitates. Absorption of the salts containing the lattice cation or the lattice anion normally occurs at the surface of the precipitates and the absorbability increases with decreasing solubility and decreasing electrolytic dissociation of the absorbed compound.[120] Figure 41 shows the solubility curves for some compounds commonly encountered in leach solutions. It should be noted that solubility decreases at higher temperatures and except $CuSO_4$, all the other compounds cited have decreasing solubilities above 100°C. Thus it is quite reasonable to expect absorption of foreign ions onto the compounds precipitated at temperatures above 100°C.

Kolthoff and Sandell[120] report that when hydrous oxide of ferric iron is formed with an excess of ammonia in the presence of copper, zinc, magnesium, etc. hydroxyl ions are primarily absorbed on the precipitates, with the simultaneous absorption of one of the other ions mentioned. They further state that the precipitate gets badly contaminated irrespective of whether the foreign ions are originally present in the solution or are added immediately after precipitation. Dissolving the precipitate and reprecipitating it one or more times has been suggested as a method to decrease the amount of the absorbed ions. The precipitation of jarosites also may be accompanied by the precipitation of toxic

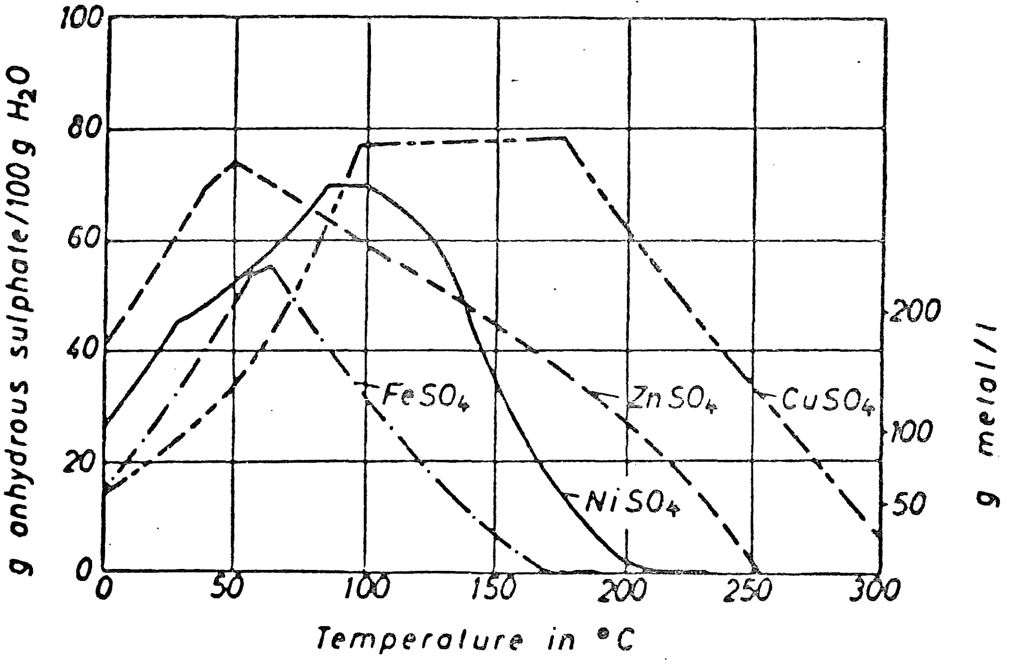


Fig. 41. Solubility of some metal- sulfates as a function of temperature.

impurities in the solution. The removal of these impurities from the solution is variable and depends on several factors such as the pH of precipitation, level of impurities in the solution, completeness of iron precipitation, crystallinity and particle size of the precipitate, etc.

Table 18 shows the common hydrometallurgical processes generating a discard iron residue, and the form of iron in the residue.[121] The discard iron generally runs to quite a large volume. For nickel sulfide concentrates, the discard iron residue equals at least four times the weight of nickel processed, and for chalcopyrite it is 1 to 1.2 times the copper processed. Due to these large amounts of iron in the tailings, studies have been made for recovering the iron. In ammoniacal leach processes, the iron present in the tailings is associated with unreacted metal sulfides, gangue, absorbed metal ions and ammonium sulfate, and hence treatment of the iron product to recover the iron becomes difficult. Iron from geothite has been reported to be easily recoverable in spite of contaminated zinc or lead. Kunda and Veltman[122] have studied the decomposition of jarosites, both thermal decomposition and decomposition in an aqueous slurry, and have reported conditions for recovery of iron from jarosites as hematite or magnetite. Iron residues from the pressure sulfuric acid, or from nitric-sulfuric acid leach processes, are usually contaminated with unreacted sulfide and gangue, because precipitation of iron is carried out during the leaching process. Hence, recovery of iron in a marketable form is more difficult than even in the case of alkaline leach processes. However, the process itself can be modified to yield iron in the form of jarosite

Process	Process Description	Iron Residue
Ammoniacal pressure leach for copper or nickel concentrates	Pressure oxidation with air or oxygen in ammoniacal solution; separation of residue, pressure hydrogen reduction or electrowinning for metals recovery. Ammonium sulphate by-product	— mixed hydrated iron oxides — pyrite — other unreacted sulphides — gangue
Roast - leach - electrowin for zinc or copper concentrates	Oxidation roast; hot sulphuric acid leach, iron removal by controlled precipitation, electrowinning for metals recovery; SO_2 by-product	— sodium or ammonium jarosites $\left.\begin{matrix}— N_a \\ — NH_4\end{matrix}\right\rangle Fe(SO_4)_2 2Fe(OH)_3.$ — Goethite [FeO.OH]
Pressure sulphuric acid leach for copper or zinc concentrates	Pressure oxidation with oxygen in sulphuric acid solution; iron removal by controlled pH adjustment; electrowinning for metals recovery; S by-product	— Iron hydroxides and hydroxy-sulphates $Fe(SO)_4$ OH $Fe(OH)_3$ — pyrite — gangue — other unreacted sulphides
Nitric-sulphuric acid leach for copper concentrates	Atmospheric leach; iron removal by controlled precipitation; electrowinning for metals recovery; S by-product.	— Hydronium jarosite [$3Fe_2O_3$. $4SO_3$ $9H_2O$] — pyrite — other unreacted sulphides — gangue

Table 18. Hydrometallurgical Processes Generating a Discard Iron Residue.[121]

or basic ferric sulfates which could be processed to hematite or magnetite

The form and behavior of iron in the residue becomes highly significant especially in view of its environmental implications. Hydrated iron oxides, basic sulfates or jarosites, though relatively stable under atmospheric conditions, have low bulk densities and high absorption and water retention properties, making complete removal of soluble metallics difficult.[121] In time, these materials may under suitable conditions leach out heavy metals to the ground water and cause serious environmental problems. It is also quite possible that some of these compounds may undergo decomposition under appropriate conditions and prove hazardous to the environment either in the intermediate stages of decomposition, or as the final product. Ammonium jarosite, for instance, has been shown to decompose under certain conditions to hematite or magnetite at as low a temperature as 25°C.[122] Data on the solubility of jarosites and the effect of solution pH in contact with the iron-containing residues have not been reported in detail. Also, the release of cations from the hydrolysis products of iron to the ground water and their effect both on the environment as well as the source material have not been investigated.

In spite of considerable published information available on the hydrolysis of iron, the overall picture is still hazy. Control of the precipitation reactions during hydrolysis is only possible when the stability regions of each of the products are known. It may be worthwhile to summarize here the data available on the hydrolysis products and their expected stability regions. Jarosite is expected to be present in the precipitation at all hydrolysis temperatures between 25°C and 200°C. Ferric oxide Fe_2O_3 is the major component of the precipitate when hydrolyzed at temperatures above 180°C. The precipitation temperature range of ferric basic sulfate has not been clearly defined but the basic sulfate is expected to be present in the precipitate when hydrolyzed at temperatures above 140°C. Below 90°C, goethite has been known to precipitate out of the solution. Thus, the hydrolysis of iron at any temperature yields a precipitate that contains goethite, jarosite, ferric basic sulfate, ferric oxide, the proportion of each in the precipitate being determined chiefly by the temperature and the free acid concentration in the solution. It should also be recognized that the stability regions of the hydrolysis product is greatly dependent on the composition of the solution and the content and type of ionic species present in it. Therefore, charting the stability regions of the hydrolysis products becomes impracticable due to the distinct nature of each hydrolysis process. The study of formation, behavior and characterization of the hydrolysis products has a great impact from the point of view of environmental pollution. Information regarding the environmental aspects of the hydrolysis is scarce. Hence, further research is strongly suggested in this area.

C. CHEMISTRY OF OXIDATION AND DISPOSAL OF SULFUR

The production and utilization of sulfur plays a major role in the selection of any leaching method for sulfides. The process economy is also very much dependent on the sulfur product obtained. For example, the Sherritt-Gordon process produces ammonium sulfate as the sulfur end product and on its marketability depends the economic viability of the process. The utilization and disposal of the sulfur product is dependent on the leaching method employed, energy demands and environmental considerations. The amount of sulfur obtained from a mine producing 22 million tons of sulfide ore per year is about 121,470 metric tons.[123] In 1976, the total production of sulfur in the United States was 10.8 million metric tons while the demand was 10.5 million metric tons. The projected production and demand of sulfur in 1980 is 12.8 and 11.8 million metric tons respectively.[124] Hence, it is apparent that effective utilization and storage of sulfur assumes much importance in view of the increasing production. Therefore, the extraction method chosen has to take into consideration the sulfur product yielded during the process and its disposal. Jansen and Milligan[125] have briefly discussed the chemistry of sulfur and its disposal techniques.

In the direct leaching of sulfide minerals, it is known that sulfide sulfur does not readily oxidize to sulfate in spite of providing a highly oxidizing environment. The sulfur product obtained after leaching and the degree of conversion of one sulfur species to another are dependent upon the conditions of leaching such as pH, temperature and the mineral studied. Acid leaching of sulfide minerals, for example, generally leads to the formation of elemental sulfur. For minerals like galena, sphalerite and pyrrhotite, the conversion of sulfide sulfur to elemental sulfur below about 100°C is almost quantitative according to the equation:

$$MS + 1/2O_2 + 2H^+ \rightarrow M^{II} + S^\circ + H_2O \qquad \ldots.(54)$$

But for copper minerals and pyrite, the yield of elemental sulfur is not quantitative. About 10 to 15 percent of the sulfide sulfur in chalcopyrite and more than 50 percent of the sulfur in pyrite is converted to sulfate.[11,126] Based on literature survey, Hisamatsu[127] reports the following conditions regarding elemental sulfur and sulfate formation:

(1) S° formation is favored at pH below 2 and temperature below 160°C.

(2) Sulfate tends to form when pH is above 2, and polythionate formation becomes possible at pH above 5-6.

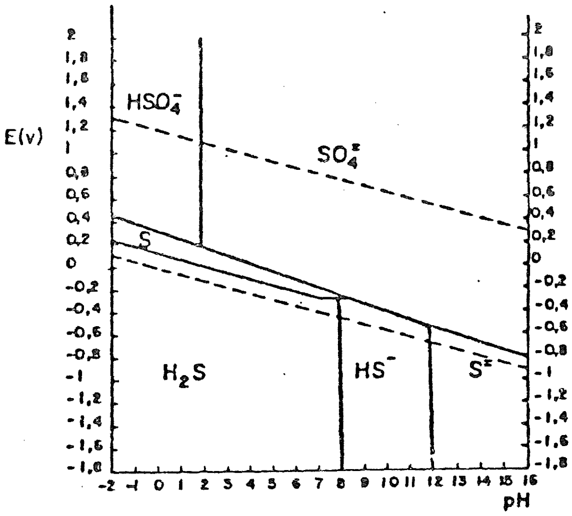
(3) Sulfate is formed above 160°C even in strongly acidic solutions.

Apart from these, other sulfate species are formed in the intermediate stages of oxidation from sulfide to elemental sulfur or sulfate. The extent of formation and type of species formed depend chiefly on the pH of the solution. Hence it is worthwhile to examine in detail the stability data and oxidation reactions of sulfur in acidic and alkaline media.

An examination of the potential-pH diagram of the S-H_2O system (Figure 42) indicates the stable regions of various sulfur species. The narrow region of elemental sulfur below pH 9 lies completely in the

Fig. 42 Potential-pH diagram for the sulfur-water at 25°C[125]

(Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions)



stability domain of water. Hence, sulfur is stable in the presence of water and acid solutions free from oxidizing agents. In alkaline solutions, elemental sulfur is unstable and tends to disproportionate at high pH giving thiosulfate and sulfate ions. Sulfates, on the other hand, are stable in the presence of water and aqueous solutions of all pH's both in the presence and absence of oxidizing agents. Sulfates can be formed by the oxidation of H_2S, HS^-, $S^=$, S° or other sulfur compounds. Below the regions of elemental sulfur and sulfates are the regions of stability of H_2S, HS^-, and $S^=$ which signify stability of these ions in the presence of water and aqueous solutions of all pH's free from oxidizing agents. Hence it is seen that acid leaching of sulfides, which is generally carried out at pH less than 3, yields elemental sulfur as the primary stable product. Further oxidation can lead to sulfate formation. In alkaline systems, elemental sulfur is not formed as a stable product by virtue of its behavior in the potential-pH diagram. Instead, leaching in alkaline media favors sulfate as the stable product and this fact is substantiated by experience.

Other sulfur species that can accompany the formation of elemental sulfur or sulfate include sulfides, thiosulfates, polythionates, sulfites and sulfamaates. It is significant that the intermediate forms of sulfur, such as thiosulfate ($S_2O_3^=$) and polythionates ($S_xO_6^=$ x = 2 to 6) are absent from the potential -pH diagram of the S-H_2O system, though they have been observed to occur in neutral and basic solutions. This can be attributed to the fact that, at least in basic solutions, the kinetic factors play a more important role in the oxidation of sulfur than the thermodynamic factors predicted from the diagram.[10] The mechanism and sequence of oxidation of sulfides in aqueous environment is not yet clearly understood. However, investigations on this subject conducted by Okabe and coworkers,[128-131] Mackiw,[132] Forward,[5,10,14] and others, throw some light on the oxidation reactions of sulfur species in acidic and alkaline medium.

In alkaline solutions, oxidation of sulfur compounds has been more extensively studied, especially in connection with the Sherritt-Gordon process. Jaura et al.[133] have suggested that the oxidation of sulfide to sulfate in alkaline medium takes the following path:

Sulfide → polysulfide → elemental sulfur → sulfite → thiosulfate → tetrathionate → dithionate → sulfate.

A similar oxidation path has been proposed also by Vallance et al.[134]

According to Jaura et al.[133] sulfides oxidize to form polysulfides which undergo further oxidation to form elemental sulfur

$$[H_2S + O = H_2O + S] \times X \qquad \ldots.(55)$$

$$XS + H_2S = H_2S_{X+1} \qquad \ldots.(56)$$

$$H_2S_{X+1} + O = H_2O + (X+1)S \qquad \ldots.(57)$$

The occurence of elemental sulfur in alkaline medium has been reported by Reilly.[135-136] He has shown that in the ammoniacal leaching system, as much as 60 percent of the sulfur can be recovered in the elemental form by dissolving it in a non-miscible organic solvent as soon as it is formed.[136] With elemental sulfur and oxygen being available in an alkaline medium, further oxidation leads to the formation of sulfite. The potential-pH diagram for sulfite and thiosulfate (Figure 43) shows that sulfite is a metastable ion in aqueous alkaline solutions.

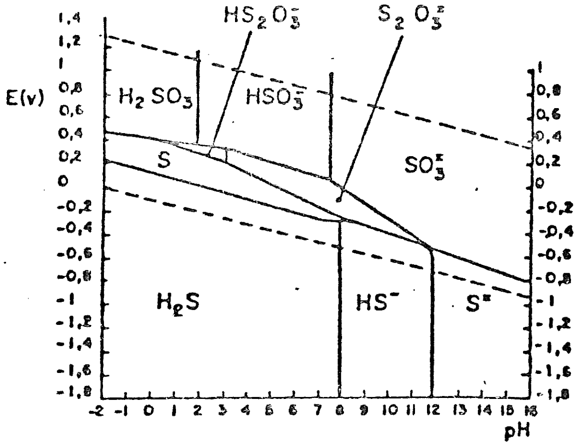


Fig. 43. Potential-pH diagram for sulfites and thiosulfates[125].

(Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions)

In strong alkaline medium, elemental sulfur dissolves in sulfite solution to give thiosulfate.

$$S^{\circ} + SO_3^{=} = S_2O_3^{=} \qquad \text{....(58)}$$

Thiosulfate is also formed when elemental sulfur dissolves in weak alkaline solutions

$$12S^{\circ} + 6OH^{-} = S_2O_3^{=} + 2S_5^{=} + 3H_2O \qquad \text{....(59)}$$

Thiosulfate is a stable ion in aqueous solutions up to a pH of 12. On oxidation, tetrathionate is produced as the primary product.[129,133]

$$2S_2O_3^{=} + O + H_2O = S_4O_6^{=} + 2OH^{-} \qquad \text{....(60)}$$

Tetrathionate is also produced when thiosulfate undergoes instant oxidation in the presence of copper salts in the solution, reducing cupric ion to cuprous ion.[137] Small quantities of trithionate are also produced as a result of the oxidation of thiosulfate.

$$3S_2O_3^{=} + 4O + H_2O = 2S_3O_6^{=} + 2OH^{-} \qquad \text{....(61)}$$

Tetrathionate readily reacts with sulfite in alkaline solutions to give trithionate and thiosulfate.[129]

$$S_4O_6^{=} + SO_3^{=} = S_3O_6^{=} + S_2O_3^{=} \qquad \text{....(62)}$$

When heated, tetrathionate decomposes into trithionate and elemental sulfur.

$$S_4O_6^{=} = S_3O_6^{=} + S^{\circ} \qquad \text{....(63)}$$

Tetrathionate also decomposes to pentathionate and trithionate when catalyzed by thiosulfate ion.

$$2S_4O_6^{=} = S_5O_6^{=} + S_3O_6^{=} \qquad \text{....(64)}$$

The pentathionate thus formed is unstable in alkaline medium and decompc to tetrathionate and thiosulfate.

$$S_5O_6^{=} + SO_3^{=} = S_4O_6^{=} + S_2O_3^{=} \qquad \text{....(65)}$$

Similar reactions take place in the case of hexathionate also. In general, reactions (64) and (65) can be represented as:

$$2S_nO_6^{=} = S_{n+1}O_6 + S_{n-1}O_6^{=} \qquad \text{....(66)}$$

$$S_{n+1}O_6^{=} + SO_3^{=} = S_nO_6^{=} + S_2O_3^{=} \qquad \text{....(67)}$$

The formation of polythionates thus takes place in a complex manner, but generally, as seen from Figure 44, as the polythionate contents increase the thiosulfate content reaches an upper limit and then decreases.

Tetrathionate oxidizes further to dithionate and sulfate with small quantities of thiosulfate.

$$S_4O_6^{=} + 2OH^- + 6O = S_2O_6^{=} + 2SO_4^{=} + 2H^+ \qquad \text{....(68)}$$

$$2S_4O_6^{=} + 6OH^- = 3S_2O_3^{=} + 2SO_3^{=} + 3H_2O \qquad \text{....(69)}$$

The amount of sulfite formed is extremely small and is probably oxidized to sulfate in absence of free sulfur.

$$SO_3^{=} + O = SO_4^{=} \qquad \text{....(70)}$$

Dithionate formed by the oxidation of tetrathionate finally oxidizes to sulfate.[133]

$$S_2O_6^{=} + 2OH^- + O = 2SO_4^{=} + H_2O \qquad \text{....(71)}$$

Tetrathionate may also get oxidized completely to sulfate.[129]

$$S_4O_6^{=} + 14OH^- = 4SO_4^{=} + 6H^+ + 4H_2O \qquad \text{....(72)}$$

Yukosuka et al.[129] have reported that the amount of sulfate produced as a result of oxidation of thiosulfate accounted for 72 percent of the

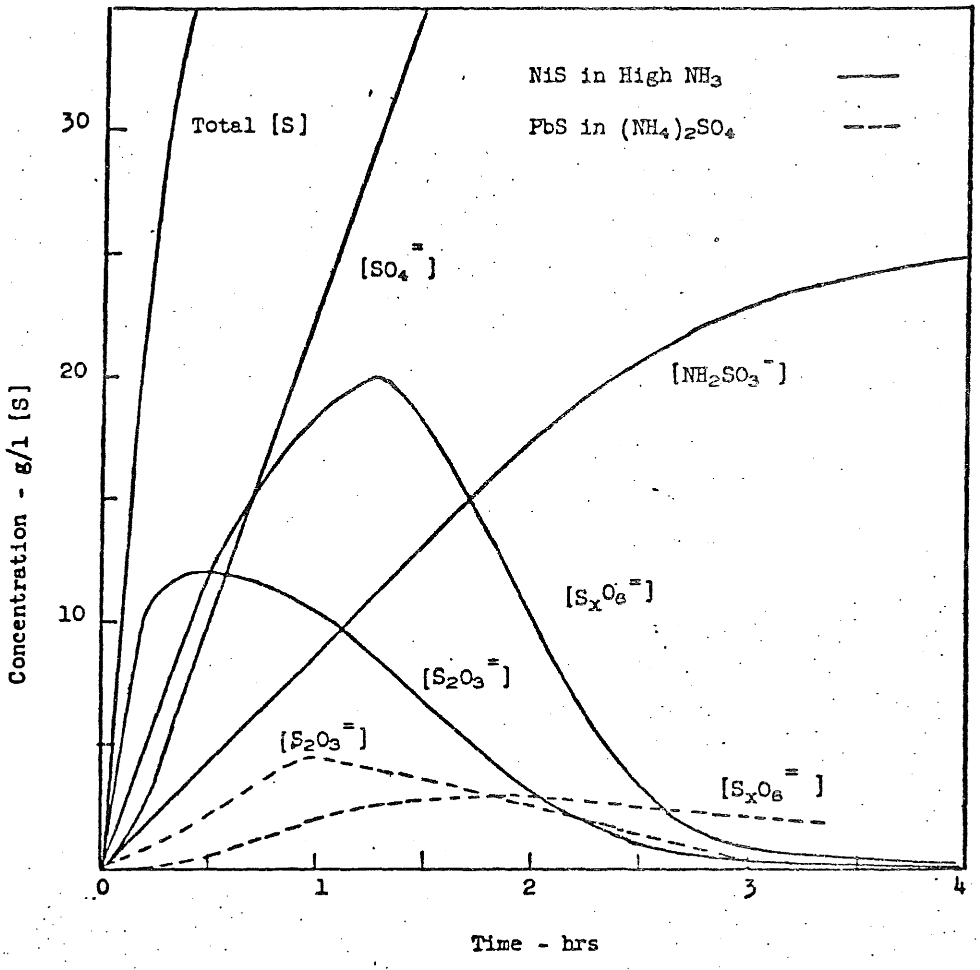


Figure 44. Sulphur Oxidation During An Oxidizing Pressure Leach [10]

sulfur oxidized. It is reasonable to assume that the remaining sulfur may be in the form of dithionate, thiosulfate and sulfite.

Thus from known data it seems probable that the oxidation of sulfides in alkaline medium takes place by the path suggested by Jaura et al. The stability diagram (Figure 45), drawn on the basis of data reported by Plante and Sutherland, and Kurtnacker et al.,[141] shows the presence of dithionate at alkaline pH and lends support to the possibility that dithionate may be the species that precedes, or co-exists with, sulfate. Further investigation is required to elucidate the mechanism of oxidation.

In ammoniacal systems, essentially the same oxidation reactions discussed above are expected to be taking place, with the exception that, in addition to sulfate, sulfamate is also formed as a final product. Investigations carried out to determine the type and amount of sulfur species in ammoniacal solutions indicate that the final products of leaching sulfide minerals are only sulfate and sulfamate, the sulfate accounting for 70 percent of the total sulfur in the system.[132] Analysis of the leach solution indicated that no sulfite was present. Trithionate has been found to be the predominant thionate species in the solution, and this fact can also be noted from Figure 45. Thus in ammonia leaching, the sum of sulfate, thiosulfate, trithionate and sulfamate accounts for all sulfur present in the leach solution.

Studies by Okabe and coworkers[130,131] on effects of various parameters on sulfur oxidation in ammoniacal solutions show interesting results. It is found that the yield of sulfamate by the oxidation of ammonium thiosulfate increased with increases in the ammonia concentra-

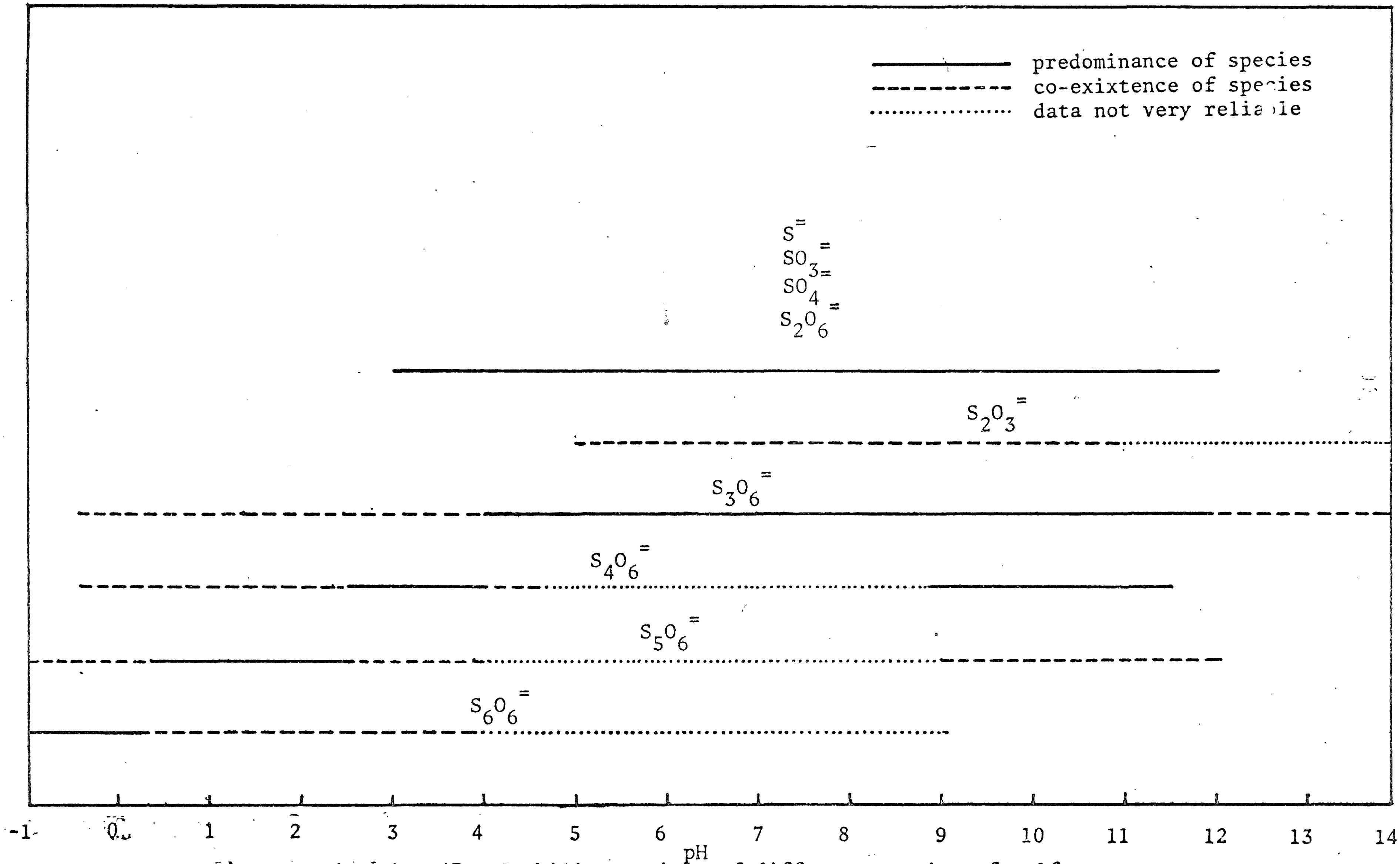


Fig. 45. Stability regions of different species of sulfur.

tion. The yield is maximum at an oxygen pressure of 50 kg/cm^2 and reaction temperature of 100°C. Cupric ion is the most suitable catalyst to increase the reaction rate and the yield of sulfamate, giving maximum yield at 0.1-0.2 mol/liter of cupric ion.[131]

The oxidation path from sulfide to elemental sulfur in acidic solutions is less defined than that in basic solutions. Several investigations have shown the presence of thiosulfate and polythionates in acidic solutions, but the mechanism of oxidation of sulfides to thiosulfates is not quite established. As mentioned earlier, Jaura et al.[133] suggest that in alkaline medium the sulfides oxidize to polysulfides which further oxidize to sulfur through a complicated course of reactions. Perhaps a similar mechanism exists in acidic medium also. Thiosulfate may be the intermediate product leading finally to elemental sulfur. The behavior of thiosulfate and polythionates in acidic solutions has been sufficiently investigated to suggest an oxidation path.

Mizoguchi et al.[129] have reported that in acidic solutions thiosulfate decomposes to form elemental sulfur as a lower oxidation state species, and tetrathionate, sulfite and sulfate as higher oxidation state species, as represented by the following equations:

$$5S_2O_3^= + 6H^+ = 2S + 2S_4O_6^= + 3H_2O \qquad ....(73)$$

$$S_2O_3^= + H^+ = S + HSO_3^- \qquad ....(74)$$

$$3S_2O_3^= + 2H^+ = 4S + 2SO_4^= + H_2O \qquad ....(75)$$

Studies on oxidation of thiosulfate with H_2O_2 by the same co-author (Okabe and coworkers[129]) has shown that at pH 4, the reaction products of the oxidation were only tri- and tetrathionates formed according to the following equations:

$$2S_2O_3^{=} + H_2O_2 = S_4O_6^{=} + 2OH^{-} \qquad \ldots.(76)$$

$$3S_2O_3^{=} + 4H_2O_2 = 2S_3O_6^{=} + 2OH^{-} + 3H_2O \qquad \ldots.(77)$$

These authors have further shown that tetrathionate is the primary and predominant product of oxidation of thiosulfate in acidic media, trithionate being formed in small quantities, as shown in Figure 46. The tetrathionate produced decomposes to pentathionate and trithionate under the catalytic action of thiosulfate. This can be explained by the two-stage reaction mechanism:[138,139]

$$S_4O_6^{=} + S_2O_3^{=} = S_5O_6^{=} + SO_3^{=} \qquad \ldots.(78)$$

$$S_4O_6^{=} + SO_3^{=} = S_3O_6^{=} + S_2O_3^{=} \qquad \ldots.(79)$$

Trithionate may also be formed according to the following equation.

$$4HSO_3^{-} + S_2O_3^{=} + 2H^{+} = 2S_3O_6^{=} + 3H_2O \qquad \ldots.(80)$$

Several investigators have reported the following general reaction to be important in the formation of polythionates from thiosulfate in acidic solutions:[139-142]

$$S_nO_6^{=} + S_2O_3^{=} + H^{+} = S_{n+1}O_6^{=} + HSO_3^{-} \ (n>3) \qquad \ldots.(81)$$

The polythionates formed react with other sulfur species in the solutions, or decompose, depending upon the conditions. In weakly acidic solutions, trithionate decomposes according to the following reaction:[128]

$$S_3O_6^{=} + H_2O = S_2O_3^{=} + SO_4^{=} + 2H^{+} \qquad \ldots.(82)$$

Tetrathionate decomposes to give sulfate and sulfur:

$$3S_4O_6^{=} + 2H_2O = 7S + 5SO_4^{=} + 4H+ \qquad \ldots.(83)$$

Acidic sulfite solution also decomposes to elemental sulfur and sulfate with the intermediate formation of thiosulfate.[128] Higher thionates

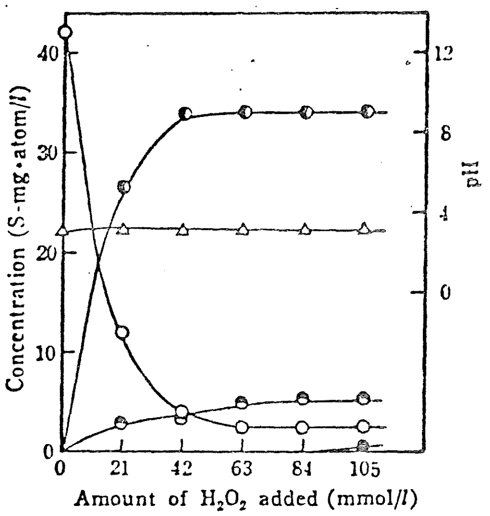


Fig. 46. Oxidation of sodium thiosulfate with hydrogen peroxide in an acidic solution 129

Temperature : 25°C

○ : $S_2O_3^{2-}$, ◐ : $S_4O_6^{2-}$, ◓ : $S_3O_6^{2-}$,
● : SO_4^{2-}, △ : pH

are formed by the following general reaction illustrated earlier by Equations 64 and 65.

$$2S_nO_6^= = S_{n+1}O_6^= + S_{n-1}O_6^= \qquad \ldots.(84)$$

Finally, higher acidities often produced sulfate as the only oxidation product of thiosulfate, tetrathionate and trithionate, as illustrated below with hydrogen peroxide acting as the oxidizing agent.

$$S_2O_3^= + 4H_2O_2 = 2SO_4^= + 2H^+ + 3H_2O \qquad \ldots.(85)$$

$$S_4O_6^= + 7H_2O_2 = 4SO_4^= + 6H^+ + 4H_2O \qquad \ldots.(86)$$

$$S_3O_6^= + 4H_2O_2 = 3SO_4^= + 4H^+ + 2H_2O \qquad \ldots.(87)$$

The oxidation of thiosulfate completely to sulfate is also greatly favored by the presence of iron (Figure 47).

The pH of the solution plays a key role in the stability of different sulfur species. Pollard et al.[143] have reported that as the number of sulfur atoms in the polythionates increases, the region of stability is formed at high acidities. This is further substantiated by the stability regions diagram of Figure 45. The figure shows that both pentathionate and hexathionates are stable only low pH's. Trithionate is quite stable down to pH 3 (Figure 45)[141] decomposing to precipitate sulfur as the pH decreases, and forming tetrathionate and hexathionate in strong acid solutions. Tetrathionate is stable at higher acidities than those at which trithionates decompose, and at strong acid media decomposes to give sulfur. Pentathionate is unstable at low acidities, being stable at strong acid media, and disproportionating to tetrathionate and hexathionate at high acidities.

$$2S_5O_6^= \rightarrow S_4O_6^= + S_6O_6^= \qquad \ldots.(88)$$

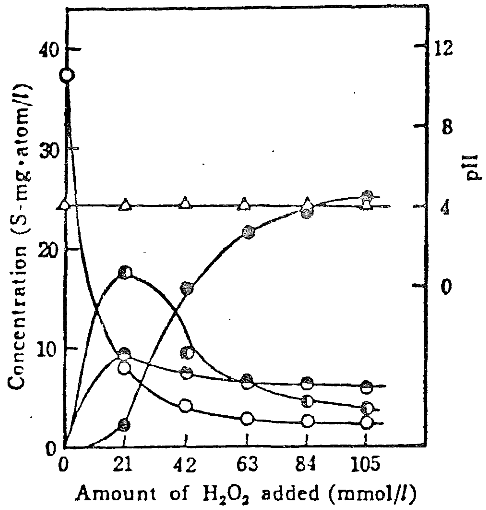


Fig. 47 Oxidation of sodium thiosulfate with hydrogen peroxide in the presence of iron 129

Temperature : 25℃, Fe : 50 ppm
○ : $S_2O_3^{2-}$, ◐ : $S_4O_6^{2-}$, ◓ : $S_3O_6^{2-}$,
● : SO_4^{2-}, △ : pH

The tetrathionate, as mentioned earlier, further decomposes to deposit sulfur. Hexathionate is stable at high acidities, and decomposes at lower acidities. Thus it is seen that the pH of the solution determines the formation, decomposition and coexistence of different sulfur species in the solution.

Schmidt[146] has proposed an alternative oxidation path to thiosulfate. He has shown that in nonaqueous solutions anhydrous thiosulfuric acid decomposes into sulfur trioxide and hydrogen sulfide.

$$H_2S_2O_3 \rightarrow H_2S + SO_3 \qquad \ldots.(89)$$

This leads to the formation of trithionate

$$H_2S + 2SO_3 = H_2S_3O_6 \qquad \ldots.(90)$$

Thus, he has suggested that trithionate is the primary oxide product of thiosulfate in acid solution, which then builds up higher thionates. This mechanism has been supported also by Blausius and Burmeister,[142] and Pollard et al.[143] At first sight it would seem that this viewpoint is in contrast to that of Okabe, but the apparent discrepancy may be explained by the fact that the pH of the solution plays a much more important role than is realized, and hence may alter the earliest formation of the products according to the solution conditions. However, though further investigation is essential in this area, from what has been reviewed a general path of oxidation in the acid medium can be surmised to be as follows:

sulfide → (polysulfides) → thiosulfate → tetrathionate → elemental sulfur → sulfate.

Thus from theoretical considerations as well as experimental observations, it is known that elemental sulfur and sulfate are the two major forms of sulfur produced on leaching the minerals. The choice between them as the final sulfur product is governed by various factors such as the type of leaching system, time and temperature considerations, environmental impact, capital costs and technological risks. Production of elemental sulfur has the preponderant advantage that it can be conveniently stored and transported. Sulfate is only attractive when immediate market is available for its disposal. Hence, elemental sulfur is preferred to sulfate production. In order to minimize the formation of intermediate sulfur compounds discussed earlier, and to obtain the desired sulfur end product, the leaching conditions are selected carefully, with the help of the potential-pH diagram of the S-H_2O system. For example, elemental sulfur formation is normally favored by a minimum amount of oxidizing agent, a high acidic or ferric concentration which maintains the pH at about 2.5, and a temperature between 100 and 120°C as evidenced by Figure 5. Likewise, sulfate formation is favored by a maximum of oxidizing agent and a pH higher than 2.5.

Chemical treatments are often carried out to convert one form of sulfur to a more desirable form. In ammonia leaching of sulfides, for example, the thiosulfates and sulfamates present in the leach liquor are converted to sulfate by oxidation and hydrolysis. The sulfamate concentration in the effluent is also controlled by keeping the ammonium ion concentration in the leach to the minimum. An attractive method to convert sulfate to elemental sulfur is by bacterial reduction. British scientists have reported as early as the '50's the production of elemental sulfur from calcium sulfate (gypsum) using sulfate-reducing and photosynthetic sulfur bacteria.[145] Bacterial reduction has a promising future on account of its low capital and operating costs. The process requires a temperate climate, a cheap and adequate supply of nutrients, facilities for handling the nutrients and reaction products, facility for the separation of sulfur from the reaction products and unreacted nutrients, and an appropriate treatment method for the reaction product for recycle, disposal or sale.

The disposal of the sulfur end product is, as mentioned before, an important consideration in the selection of the leaching method. The sulfur product in ammonia leaching is disposed of as either ammonium sulfate or gypsum. Ammonium sulfate is sold as a fertilizer. Production of gypsum enables regeneration of ammonia, but the gypsum has to be disposed of either in the manufacture of products like gypsum board, cement, etc. or by dumping in the ground. Gypsum dissolves up to 0.241 grams in 100 cc of cold water and hence disposal of gypsum in the ground poses environmental problems. Elemental sulfur when obtained as the end product, can be marketed in the same form, stored conveniently, or converted to any useful sulfur compound. Another obvious form of sulfur as an end product is sulfuric acid which is only attractive if there are immediate facilities for its consumption.

Thus the study of the chemistry of sulfur, its oxidation reactions, its behavior during leaching, and methods of disposal are important from environmental, economic and energy considerations. Leaching sulfide minerals in basic solutions yields sulfate as the end product of sulfur while acid solutions could yield elemental sulfur. The oxidation path from sulfide to sulfate in basic solutions involves thiosulfate, polythionates and dithionate as the intermediate products.

Less is known about the oxidation path in acid solutions, but it seems probable that thiosulfate and polythionates are formed as unstable intermediate products. The stability region diagram of different species of sulfur (Figure 45) indicates that among polythionates, higher polythionates such as hexathionate and pentathionate are the predominant species in acid solutions while trithionate and tetrathionate occur predominantly in neutral and basic solutions. A general reaction path cannot be confidently stated from the literature review on account of the complex nature of the reactions involved, and their dependence on pH and temperature, the influence of these on the reactions having not been sufficiently investigated and reported. Hence further investigation is essential in this field in order to fully understand the mechanism and sequences of oxidation reactions of sulfur species in various systems of sulfide leaching.

D. STUDY OF SOLUBILITY CHARACTERISTICS OF SILICATE MINERALS

Bulk sulfide flotation concentrates of Duluth gabbro samples have been reported to contain mainly plagioclase, olivine and pyroxene as the gangue which constitutes as high as a third of the concentrates. Minor amounts of serpentine, talc, amphibole and chlorite are also present.[147] The dissolution characteristics, structure alterations, release of cations, etc. of these silicates might play a role in the environmental make-up of the region. A study, therefore, of the nature and behavior of silicate minerals during leaching and weathering is warranted.

The nature and structure of minerals undergo various alterations due to geological and weathering processes. It is known that several mineralogical modifications can be formed at different temperatures and pressures by cooling a melt of one or more constituent minerals. In nature this takes place over geological periods resulting in a complete change in the nature of the original mineral constituents. Subsequently, weathering processes subject the minerals to further transformations. Many factors contribute to the transmutation of the minerals. These include the structure and composition of the minerals, character of liquid (salt solution, acid, water, etc.), particle size, temperature, pressure, humidity, history of the minerals, etc. For example, mafic minerals such as olivine, pyroxene, amphibole, biotite, etc., undergo weathering more rapidly than felsic minerals like plagioclase, K-feldspar, muscovite, quartz, etc. Also minerals formed at highest temperature (olivine and calcic plagioclase) tend to decay more rapidly than others.[148] The pH of the solution also plays a significant role in dictating the amount of different ions released from the minerals. The above are only generalized statements and are by no means without exceptions on account of the several physical and environmental factors simultaneously in force on the mineral species. A literature search was therefore undertaken to obtain a clearer idea of the alteration of minerals, especially silicates, under different conditions commonly encountered in hydrometallurgical leaching. It was found that information is available on hydrothermal reactions and mineral transformations at high temperatures and pressures pertaining to the natural geological process. But this is not relevant to the present purpose of study because of the different temperature and pressure conditions and the long periods of time involved in the geological processes. Information is also available on the weathering processes on minerals, and results of laboratory experiments with simulated weathering conditions have been recorded. But the investigations have been carried out using distilled water or carbonic acid in a narrow pH range. The pH's of interest to the present discussion fall outside the pH range that has been examined and hence this information also is not especially useful. However, the literature search has revealed certain interesting facts pertaining to some aspects of silicate dissolution.

The effect of pH on the dissolution of silica from minerals is of importance in leaching. Figure 48 shows the quantity of silica dissolved from olivine, biotite, albite and quartz at different pH's. It is seen that except for quartz, silica dissolution below pH 5 increases

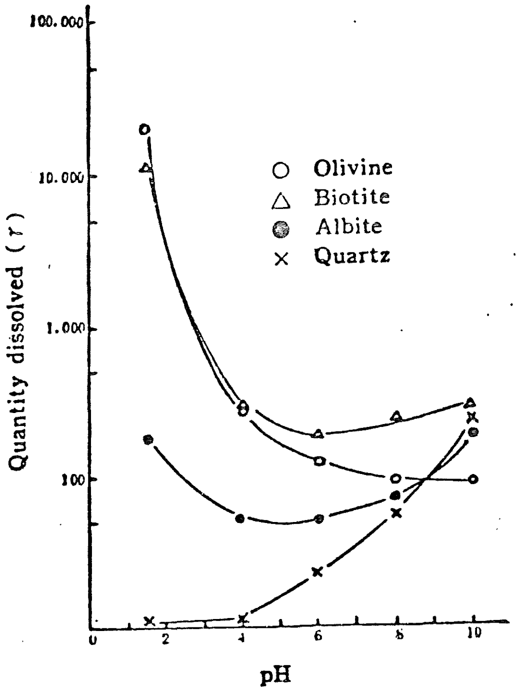


Fig 48. The relation between the minerals and the quantity of silica dissolved.

with increasing acidity. Silica dissolution is also dependent on the mineral dissolved and its silica content. Olivine and biotite, having low silica content, are more easily dissolved in acid solution than in alkaline solution, but albite and quartz, having higher silica content, exhibit the reverse characteristics.[149] The presence of complexing agents such as organic acids in the solution has a significant effect on silica dissolution. It has been reported that at pH = 1.5 the amounts of silica and other elements dissolved from the mineral are not affected by the presence and nature of organic acids. But at pH's between 4 and 10, the quantities of elements, including silica, dissolved vary and are dependent on the complexing power of the organic acid.[149]

The weathering of silicates is chiefly a process of hydrolysis.[148] The hydrolysis of the mineral forsterite (magnesium-rich olivine) illustrates the process.

$$Mg_2SiO_4 + 4H_2O \rightarrow 2Mg^{++} + 4OH^- + H_4SiO_4 \qquad \text{....(91)}$$

Water is generally a little acidic due to dissolved carbon dioxide, and the extra hydrogen ions present favor hydrolysis. Dissolution studies on pyroxenes, olivine and other silicate minerals have indicated that the quantity dissolved was much more in CO_2-containing water than in distilled water.[150] When stronger acids than carbonic acid such as sulfuric acid are present locally, the dissolution becomes more pronounced and complete. Because the hydrogen ions are consumed during the hydrolysis, the solution in contact with the silicate mineral becomes less acidic and may eventually become alkaline. Besides acidity, the presence of other ions in the solvent also tends to affect dissolution. For example, studies have shown that Si dissolution decreases with increasing dissolved Al, and, under certain circumstances, with increasing Ca and Mg. The amounts of various cations released from different minerals are shown in Table 19.[151]

In the case where a silicate contains several cations, the dissolution rate of each cation is different from that of each of the other cations in the same mineral. But the dissolution of elements may or may not correspond to the stoichiometry of the mineral. For example, in Figure 49 the ratio of dissolved elements from olivine is close to the ratio of elements in the mineral, i.e., the dissolution is stoichiometric. This also indicates that there is no selectivity of cations during the dissolution. In the process of weathering, release of silica and some cations takes place at the surface of the mineral, the cations being replaced by hydrogen ions. Thus there is a preferential removal of cations at the surface which leads to the formation of a coating. This coating has characteristics different from that of the original mineral and therefore alters the mode of dissolution. Also, the coating tends to screen the underlying mineral grains and hence dissolution of most silicates proceeds very slowly.

The form in which silica is released from the mineral is worthy of note. A major portion of silica is set free in the form of silicic acid, as represented in Equation (91). In local conditions where the concentration of the weathering solutions is higher, silica may be released as colloidal or amorphous silica. The silica released may undergo natural conversion brought about by certain plants to form amorphous particles of SiO_2. Interaction of silica with Al or Mg leads to the

Table 19.
Concentration of cations in the pulp at various pH values (Parts per million) [151]

Mineral	pH	Na	K	Ca	Mg	Fe	Al
Quartz	3.9	X	X	X	X	0	0
	7.2	X	X	X	X	0	0
	10.3	X	X	X	X	0	0
Albite	0.7	2.1	0	X	X	0.4	10.6
	4.0	0.2	0	X	X	0	1.6
	11.6	X	0	X	X	0	2.3
Microcline	0.7	1.4	0	X	X	0	4.0
	5.0	0.5	0	X	X	0	1.5
	11.4	X	0	X	X	0	1.8
Augite	1.0	1.6	0	8.7	6.1	1.0	6.5
	3.5	0.4	0	4.6	1.6	0	0.5
	6.15	0.6	0	1.2	0.5	0	0.05
	9.25	X	0	0	0.02	0	0
	12.3	X	0	19.0	0.02	0	0.6
Spodumene	0.9	1.4	X	X	X	0	3.6
	2.4	1.4	X	X	X	0	1.2
	5.8	0.3	X	X	X	0	0.6
	6.5	1.4	X	X	X	0	0
	7.6	X	X	X	X	0	0
	9.0	X	X	X	X	0	1.6
Olivine	1.4	0.2	0	X	131.0	17.5	X
	3.7	0	0	X	16.5	1.6	X
	6.2	0	0	X	1.6	0	X
	7.4	0	0	X	0.7	0	X

X No determination made

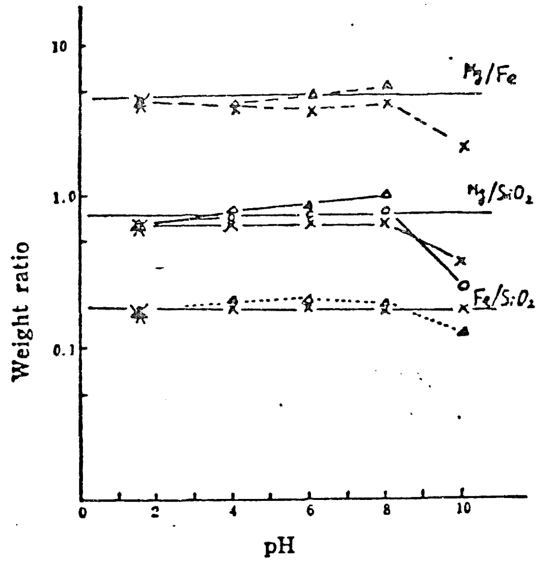


Fig 49. Weight ratios among silica, iron and magnesium dissolved from olivine

× EDTA △ Citric acid ○ Without organic acid
······ Fe/SiO$_2$ —— Mg/SiO$_2$ --- Mg/Fe

formation of clayey minerals such as chlorite and serpentinite. Conditions permitting, recrystallization of silica into minute grains of quartz also takes place. In some types of minerals, such as amphiboles and pyroxenes, silica may not be released at all but remain in the mineral as amorphous residues.

It is likely that the silicate minerals would undergo some changes when subjected to the severe conditions of temperature, pressure and chemical treatment during leaching. Knowledge of the nature of the alteration in the minerals would be of great value in predicting the environmental implications of the hydrometallurgical leaching process. The altered coating, if any, on the silicate surface may behave in an entirely different manner from that of the mineral itself, thus changing the metallurgical leaching characteristics of the mineral. The change in morphology of the silicate particle and of its surface characteristics is of interest, especially on account of its significance to the environment. Also, the chemical and mineralological change brought about by hydrometallurgical leaching the original silicate warrants investigation. Knowledge on the above mentioned aspects is at present nonexistent and further investigation is strongly suggested.

III. MATERIALS AND METHODS

A. METALLURGICAL LEACHING OF CU-NI CONCENTRATE AND ENVIRONMENTAL LEACHING OF ITS LEACH RESIDUES

1. Materials

a. Concentrates

The sample used was a bulk sulfide flotation concentrate of a copper-nickel bearing Duluth gabbro from the INCO test pit southeast of Ely, Minnesota. The chief copper-bearing minerals in the concentrate were chalcopyrite ($CuFeS_2$) and cubanite ($CuFe_2S_3$). Nickel was present as pentlandite [(Ni,Fe)S]. In addition, pyrrhotite (FeS) was also present. A partial chemical analysis of the concentrates is given in Table 20. An elemental analysis of the concentrate by Barringer Research Ltd. is given in Appendix 1. Size fractions of -325 mesh and -400 mesh were used in the studies.

b. Leaching Reagents

Sulfuric acid. BAKER analytical-reagent grade sulfuric acid was used. The required amount of acid was diluted with distilled water in all experiments.

Ammonium hydroxide. Chemically pure grade DUPONT reagent was used, diluted with distilled water as required.

Ammonium sulfate. Analytical-reagent grade granular crystals were

TABLE 20. PARTIAL CHEMICAL ANALYSIS OF THE CU-NI CONCENTRATES OF DULUTH GABBRO

	%
Copper	13.58
Nickel	2.68
Cobalt	0.15
Iron	28.39
Sulfur	22.56

used.

Sodium chloride. Granular crystals of chemically-pure grade FISHER reagents were used.

2. Apparatus and Methods

a. Metallurgical Leaching

Autoclave. The apparatus used in all pressure leaching experiments was a 1 liter Autoclave Engineer, magnedrive, packless autoclave made of 316 stainless steel. The agitator shaft was driven by a 186.5 watts D.C. motor. A Pyrex glass stirrer was used. A Forma Heat jacket-type heater rated for 1.7 KW at 110 Volts AC, equipped with iron-constantan thermocouple, was used to heat the reaction chamber. The temperature was controlled by a standard control unit carrying temperature indicators, temperature controller, tachometer and agitator speed controller. Oxygen or nitrogen gas was supplied to the reaction vessel from pressurized cylinders by means of copper tubing and standard valves with gauge.

Experimental Procedure. The same experimental procedure was used in all metallurgical leaching tests. The leaching solution was prepared according to the selected conditions and was mixed with 10g of the concentrates in a Pyrex glass reaction vessel. This was placed in the reaction chamber of the autoclave, and the autoclave was sealed. The air inside was driven out by a stream of nitrogen and the vent was closed. The nitrogen gas pressure was adjusted to a selected value. The agitator was started and its speed was adjusted. The reaction vessel was then heated to the required temperature in an atmosphere of nitrogen. When the reaction temperature was attained, passage of nitrogen was stopped and oxygen was sent in at a specified pressure. The pressure recorded included the vapor pressure of the solution. The temperature controller maintained the reaction temperature within ±2°C. The reaction was allowed to proceed for the retention time selected. At the end of the experiment, the pressure was relieved, the heater and the agitator switched off, and the passage of oxygen stopped. The reaction vessel was taken out and cooled rapidly by plunging it in cold water. The solution when cooled was filtered with the help of a Buchner funnel. The filtrate was collected, was made up to a definite volume and a sample was sent for chemical analysis. The residue was then washed well with distilled water, and the wash water collected and analyzed. The residue was dried, weighed and a portion was chemically analyzed. The remaining residue was stored for further studies.

Sulfuric acid leach. Several leaching experiments were carried out in order to achieve maximum extraction of metal values. Leaching parameters, chiefly the acid concentration and retention time, were varied in order to arrive at an optimum combination resulting in maximum extraction. The conditions which finally led to satisfactory results included 90 g/ℓ H_2SO_4 and 12 hours of retention time. Besides, 4 grams of sodium chloride per liter of solution was added in order to facilitate and expedite the extraction. This was done on the basis of a report by Subramaniam and Ferrajuolo.[152] The experimental conditions and results of the sulfuric acid leach are given in Table 21.

Ammonia leach. A series of experiments with varying conditions such as concentrations of ammonia and ammonium sulfate, retention time, agitation speed, size fraction of concentrates, oxygen pressure, and temperature were carried out in order to arrive at the optimum condi-

TABLE 21. EXPERIMENTAL CONDITIONS AND RESULTS OF SULFURIC ACID LEACHING AND AMMONIA LEACHING.

Leach System	Concentration of Leach Solution g/ℓ	Temperature °C	O_2 Pressure psi	Retention Time Hours	Weight of Residue g	Leachate ...g					Extraction %				
						Cu	Ni	Co	Fe	S	Cu	Ni	Co	Fe	S
Acid Leach	90 H_2SO_4 + 3 NaCl	110	400	12	3.0	1.295	0.322	0.018	2,625	9,8	97,8	99,2	98	95.3	49,3
Ammonia Leach	157.5 NH_3 + 171$(NH_4)_2SO_4$	100	150	12	7.0	1.367	0.222	0.014	-	17.465	95.7	94,6	81,3	4,9	97,3

Concentrate 10g; mesh size 100% -400; solution volume 400 ml; agitation 700 rpm.

tions resulting in maximum extraction. The experiment which yielded the best results had a solution composition of 9.3 M NH_3 + 1.3 M $(NH_4)_2SO_4$. The experimental conditions and results of the ammonia leach are given in Table 21.

b. Environmental Leaching

This consisted of a series of equilibration tests performed on the leach residues of the sulfuric acid leaching and ammonia leaching of the copper-nickel concentrates. The experimental scheme was adapted from the environmental leaching tests developed by Eisenreich.[153] 1g of the residue was suspended in 100 ml of distilled water in an acid-cleaned 250 ml beaker. Initial pH of the suspended solids in distilled water was recorded, and the contents of the beaker was stirred for 100 hours by a glass stirrer by means of a cone drive stirring motor. The temperature of the laboratory was maintained at 20°C. The pH of the sample was recorded periodically. The pH meter used was IONALYZER model 401 of Orion Research. Corning standard combination electrode was used in all experiments. Distilled water was added as and when necessary to maintain the volume in the beaker to 100 ml.

After 100 hours of agitating the suspended solids, the stirring was stopped, the final pH recorded, and the sample was centrifuged for 30 minutes at 12000 rpm in an INTERNATIONAL Model HT centrifuge. The supernatant liquid obtained after centrifuging was transferred carefully to a clean bottle and sent in for detection of released ions. The solid was suspended in 100 ml of fresh distilled water in an acid-cleaned 250 ml beaker. The initial pH was recorded, and the contents of the beaker was subjected to another cycle of 100 hours of stirring as before. The agitation, centrifuging and resuspension of the solids in distilled water were repeated until the final pH after 100 hours of each cycle showed consecutively the same value for a minimum of four cycles. At the end of each cycle, the distilled water was analyzed for released ions. After the equilibration tests, the solids was air-dried and stored carefully for further examination.

c. X-ray Diffraction Analysis

Specimens for the x-ray diffraction tests were prepared using a small amount of the sample by smearing a thick solution of the sample in water on a glass slide. This was air-dried and placed on the specimen holder of the x-ray equipment. A PHILLIPS NORELCO apparatus was used with a scanning time of 1° per minute, and CuKα radiation. The diffraction patterns were thus obtained for each of the leach residues.

d. Scanning Electron Microscope Analysis

The acid and ammonia leach residues were examined by means of a JEOL JEM-100CX scanning transmission electron microscope or a CAMBRIDGE MkIIA scanning electron microscope, both before and after the environmental leaching tests. Several micrographs of each residue were taken. The original copper-nickel concentrate was also examined using the electron microscopes and photographed.

e. Trace Element Analysis

At the end of the environmental test of the residues, samples containing 50 milliliters of the centrifuged water were placed in 125 ml polypropylene bottles. To each bottle was added 0.95 milliliter of 10 to 1 diultion of concentrated ultrex grade nitric acid as preservative. The water samples were then delivered to the Regional Copper-Nickel Study for shipment to Barringer Research Ltd. of Toronto, Ontario, Canada for analysis of elemental composition of the samples.

B. PREPARATION OF AND EQUILIBRATION STUDIES ON THE HYDROLYSIS PRODUCTS OF IRON

1. Materials

a. Reagents

Ferric sulfate. Chemically-pure BAKER analyzed reagent was used in all experiments.

Sulfuric acid. Chemically pure BAKER analyzed reagent was used in all experiments. The required concentrations were made by diluting with distilled water.

2. Apparatus and Methods

a. Preparation of Hydrolysis Products of Iron

The same autoclave that was described earlier for the metallurgical leaching studies of the Cu-Ni concentrate, was used for the preparation of the products of iron hydrolysis. Calculated amounts of ferric sulfate were mixed with selected concentrations of sulfuric acid for each of the hydrolysis products required. The solution was then subjected to the required temperature and pressure in the autoclave for a determined period of time. At the end of the experiment, the contents of the reaction vessel were cooled and filtered. The filtrate was made up to a definite volume and stored. The solid product of iron hydrolysis was dried and weighed. A portion of this product was then analyzed by means of x-ray diffraction technique and its diffraction pattern was obtained. This was compared with the standard ASTM cards. The experiments were repeated several times for each of the hydrolysis product for different experimental conditions until samples whose x-ray diffraction patterns matched very well with those of the standard ASTM cards of the required hydrolysis products were obtained. This ensured a pure product. The samples were then chemically analyzed and stored for further studies. The filtrate of these selected experiments were also sent for chemical analysis.

b. Equilibration Studies

The method used was essentially the same as that for the copper-nickel leach residues. 1g of the hydrolysis product was suspended in 100 ml of distilled water in a clean 250 ml beaker and agitated for 100 hours. The pH of the sample was recorded periodically. At the end of 100 hours, the pH of the sample was recorded and the sample was centrifuged. The supernatant liquid was sent in for detection of released ions, and the solids subjected to another cycle of 100 hours of agitation. This was repeated for each of the hydrolysis products until the pH of the sample at the end of 100 hours remained the same for at least four consecutive tests. After this final equilibration, the hydrolysis product was air-dried and stored for further studies.

Initially, the equilibration tests were conducted with and without aeration. To one beaker, air was supplied from a compressed air cylinder by means of tubing, and a capillary tube extending almost to the bottom of the beaker. The beaker was kept open to the atmosphere during the course of the experiment. Another similar experiment was performed with no air supplied by artificial means. The mouth of this beaker was covered with aluminum foil with provision for the entry only of the glass stirrer. In all other respects, the experiments corresponded to the standard method described earlier.

c. X-ray Diffraction Analysis

The x-ray diffraction technique was the chief method of identification and test of purity of the hydrolysis products. The x-ray diffraction patterns of the samples after equilibration were also taken to compare with those of the original samples. The specimen preparation for the x-ray diffraction analysis was the same as that described for the Cu-Ni concentrates and the leach residues--namely, smearing and air-drying a solution of the sample on a glass residue. As before, a PHILLIPS NORELCO x-ray equipment was used with CuKα radiation and 1° per minute scan time.

d. Scanning Electron Microscope Analysis

Electron photo micrographs of the hydrolysis products were taken both before and after equilibration tests. As before, a JEOL JEM-100CX scanning transmission electron microscope or a CAMBRIDGE MkIIA scanning electron microscope was used.

e. Trace Element Analysis

As in the case of environmental leaching tests of the Cu-Ni residues, 50 millilitersofthe centrifuged water after equilibration of the hydrolysis products, were placed in 125 milliliter polypropylene bottles, 0.95 ml of 10 to 1 dilution of concentrated ultrex grade nitric acid was added to each of the bottles as preservative, and the water samples delivered to the Regional Copper-Nickel Study for shipment to Barringer Research Ltd. of Toronto, Ontario, Canda for analysis of elemental composition of the samples.

IV. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. METALLURGICAL LEACHING OF THE CU-NI CONCENTRATE AND ENVIRONMENTAL LEACHING OF ITS LEACH RESIDUES

From the six hydrometallurgical extraction techniques discussed in an earlier section, sulfuric acid pressure leaching and ammonia pressure leaching were selected as being the most promising. An experimental program was therefore designed in order to subject the copper-nickel concentrate to these two leaching techniques in order to obtain their leach residues, and to examine the mineralogical composition, morphologies and environmental leaching characteristics of the same.

Hydrometallurgical Leaching

The concentrate used for the study contained chalcopyrite, cubanite, pentlandite and pyrrhotite as the chief sulfide minerals. The crude material was basically an altered troctolite consisting mainly of plagioclase, olivine and pyroxene.[147] Hence, the main constituents in the gangue are SiO_2, Al_2O_3, CaO and MgO. A partial analysis of the concentrate is given in Table 20. An elemental analysis of the concentrate by Barringer Research Ltd. is given in Appendix I.

From literature survey, it was noted that the chief parameters influencing the sulfuric acid leaching of sulfide concentrates are acid concentration, temperature, oxygen pressure and fineness of grind. With this in view, the experimental conditions were so chosen as to give the optimum results. The temperature of the process is dictated by the behavior of sulfur during leaching. The elemental sulfur produced during leaching forms a porous coating around the sulfide particles, and further reaction takes place through this coating. Hence, to ensure more efficient and faster rate of reaction, it has been found desirable to maintain the temperature of reaction below the melting point of sulfur (119°C) so as to obtain the final sulfur product as elemental sulfur. Therefore, a temperature of 100°C was chosen. It has been reported that higher temperatures such as 200-225°C have also been equally effective (Table 6), but gave sulfate as the end product of sulfur.[26]

The metallurgical leaching of the copper-nickel concentrates was carried out using samples ground to -325 mesh and -400 mesh size fractions, and the latter was found to be more effective. An oxygen overpressure of 400 psi was selected as being the optimum value from the data of other investigators. The acid concentration and retention time, however, were varied to give maximum extraction. It was found that in spite of using a higher acid concentration, extractions of more than 90 percent were not achieved. Hence, it was decided to add 3 g of NaCl per liter of solution on the basis of the reports by Subramaniam and Ferrajuolo[152] to promote a higher rate of extraction.

The experimental conditions and results of sulfuric acid leaching is given in Table 21. The extractions were calculated on the basis of the residue analysis. It can be noted from Table 21 that the leachate reports considerable amounts of sulfur. Sulfur in leachate of acid leach is contributed chiefly from the sulfates of copper, nickel, cobalt and iron. Free acid also may account for a part of the sulfur content in the leachate. Iron content in the leachate arises from the ferric and ferrous sulfate in solution, and reports in considerable amounts.

The partial chemical analysis of the acid leach residue is given in Table 22. A complete elemental analysis of the same from Barringer Research Ltd. is given in Appendix I. It is seen that the residue contains significant amounts of sulfur. A major portion of the sulfur content in the residue is in the elemental form, promoted by the conditions of leaching. Small amounts of unleached sulfides, and the sulfur associated with iron, may contribute to the remaining sulfur content. The iron in the residue is contributed by the residual iron sulfides and by the jarosites, basic ferric sulfates or ferric hydroxide produced during the leach.

The experimental conditions and results of ammonia leaching of the copper-nickel concentrates are shown in Table 21. The leachate in this case consists mainly of copper, nickel and cobalt ammines, besides ammonium sulfamate and sulfate. Small quantities of thiosulfate and polythionates also may be present. The above constituents contribute to the large sulfur content in the leachate. A partial chemical analysis of the ammonia leach residue is given in Table 23 and a complete elemental analysis of the same from Barringer Research Ltd. is given in Appendix I. The residue shows considerable amounts of iron. A major portion of this iron is accounted for by the ferric oxide produced during the leach. A minor portion of the iron arises from the unleached pyrrhotites which report directly in the residues.

TABLE 22. PARTIAL CHEMICAL ANALYSIS OF THE ACID LEACH RESIDUE

	%
Copper	0.98
Nickel	0.076
Cobalt	0.01
Iron	4.44
Sulfur	38.09

TABLE 23. PARTIAL CHEMICAL ANALYSIS OF THE AMMONIA LEACH RESIDUE

	%
Copper	0.84
Nickel	0.205
Cobalt	0.04
Iron	38.57
Sulfur	0.88

Thus the salient feature of the acid leach residue is its high sulfur content and that of the ammonia leach residue is its high iron content. The elemental sulfur which makes up the bulk of the sulfur in the residue is generally recovered and stored. The rest is made up by unleached minerals, jarosites and basic sulfates. Ferric oxide accounts for the high iron contents in the ammonia leach residue. It is noted that the iron content in the residue obtained is comparable to that in the leach residues of Sheritt Gordon process and Arbiter process (cf. Tables 3 and 4). The ferric oxide may be recovered from the residue, purified and used for the production of iron.

Environmental Leaching

The equilibration studies of the acid and ammonia leach residues were termed "environmental leaching" on account of their consisting of several compounds mixed together and thus resembling an actual plant discard. The final pH's of the equilibration tests performed on the acid leach residue have been plotted in Figure 50. The final pH in the first equilibration cycle reports at 4.1 gradually rising in subsequent cycles to a maximum of 6.6 and then decreases and stablizes at 4.0. The figure also shows the initial pH's of each cycle. Table 24 gives the concentrations of the ions released during each cycle of equilibration. The concentrations of sulfate ions in the centrifuged water were estimated by the barium sulfate precipitation technique but failed to show any precipitates. This indicated that the sulfate concentration of the water was below the detection limit of this estimation technique. The average values of ions reported in Table 24 have been calculated with a degree of confidence of 99%. The trace element analysis of the

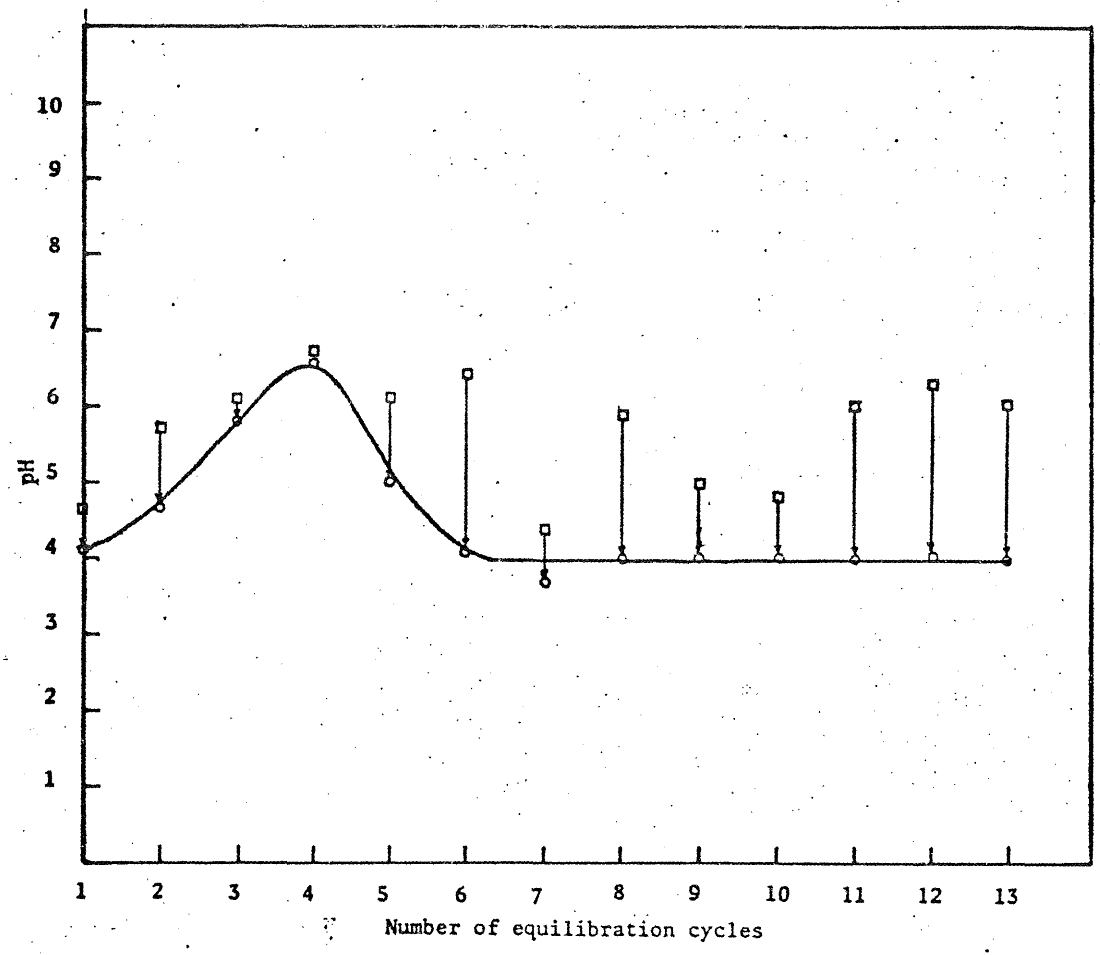


Fig. 50. Equilibration curve for acid leach residue

TABLE 24. RELEASE OF IONS IN ENVIRONMENTAL LEACHING STUDIES OF THE ACID LEACH RESIDUE

	Copper ppm	Nickel ppm	Cobalt ppm	Iron ppm
1.	2.8	0.5	0	0.67
2.	0.19	0.2	0	0.52
3.	0	0.3	0.05	0
4.	0	0.45	0	0
5.	0.38	0.65	0.05	0.05
6.	1.11	0.6	0	0.15
7.	0.79	0.69	0	0.77
8.	0.56	0.85	0	0.99
9.	0	0	0.05	0.05
10.	0.37	0.55	0.05	1.05
11.	0.07	0.48	0	0.2
12.	0.3	0.25	0	0.9
13.	0.3	0.3	0	0.7
Average	0.34±0.09*	0.45±0.05	0.02±0.005	0.45±0.09

*Entry No 1. was omitted for the calculation of average.

equilibrated distilled water from Barringer Research Ltd. is given in Appendix II.

The pH variation exhibited by the equilibration curve of the acid leach residue in Figure 50 was compared with the concentrations of released ions in Table 24. No significant correlation was found between the two. The reason for the rise and fall of the curve in the initial stages of equilibration is not known. It is noted that the initial pH of each cycle varied with one another, and exhibited a wavy pattern when the individual plots were joined.

Results of the environmental leaching on ammonia leach residue are shown in Figure 51 and Table 25. The first equilibration cycle has a final pH of 7.7 which dips to a pH of 5.1 in subsequent equilibration cycles and then rises and stabilizes at a pH of 7.0. The reason for this behavior is not known, and no correlation appears to be present between the pH variation of the equilibration curve and the concentrations of released ions. The initial pH's of each cycle also equilibrated, along with the final pH's, to the same value, as can be noted from Figure 51. Trace element analysis, from Barringer Research Ltd., of the equilibrated distilled water with respect to ammonia leach residue is given in Appendix II.

X-ray Diffraction Analysis

The x-ray diffraction patterns of the concentrates, acid and ammonia leach residues, including those of both before and after environmental leaching tests, are given in Figures 52 and 53. The diffraction pattern of the concentrates is repeated in Figure 53 for comparison. The acid leach residue showed the presence of considerable amounts of

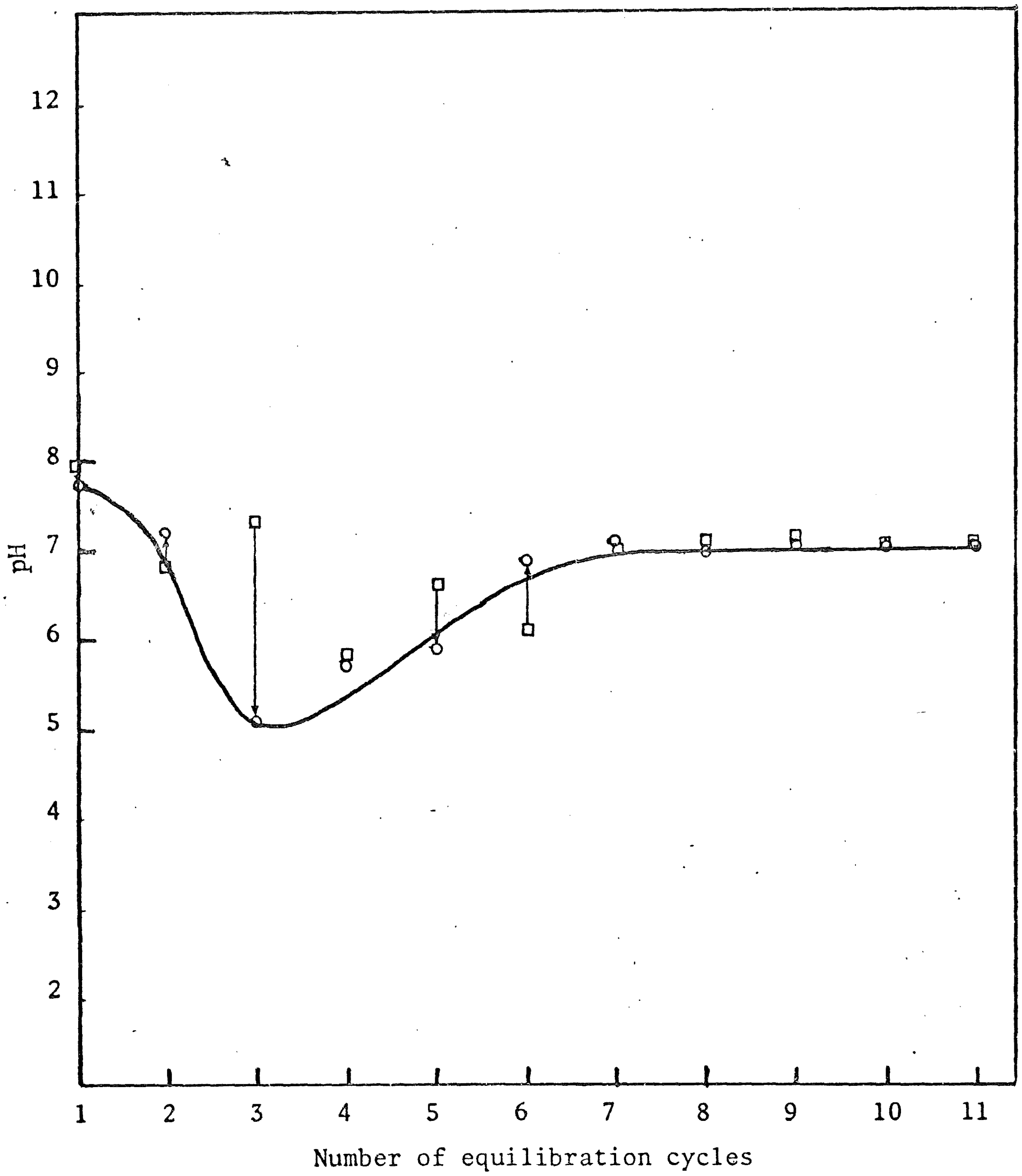


Fig. 51. Equilibration curve for ammonia leach residue

TABLE 25. RELEASE OF IONS IN ENVIRONMENTAL LEACHING STUDIES OF THE AMMONIA LEACH RESIDUE

	Copper ppm	Nickel ppm	Cobalt ppm	Iron ppm
	0	0.1	0	1
	0.99	0.1	0	0.2
	0.38	0.75	0.05	0.05
	0.02	0.26	0	0.05
	0	0.08	0	0
	0	0.15	0.05	0.2
	0	0.05	0	0.05
	0	0.07	0	0
	0	0	0	0
	0	0	0	0
	0	0	0	0
Average	0.13±0.09	0.14±0.06	0.01±0.0003	0.14±0.08

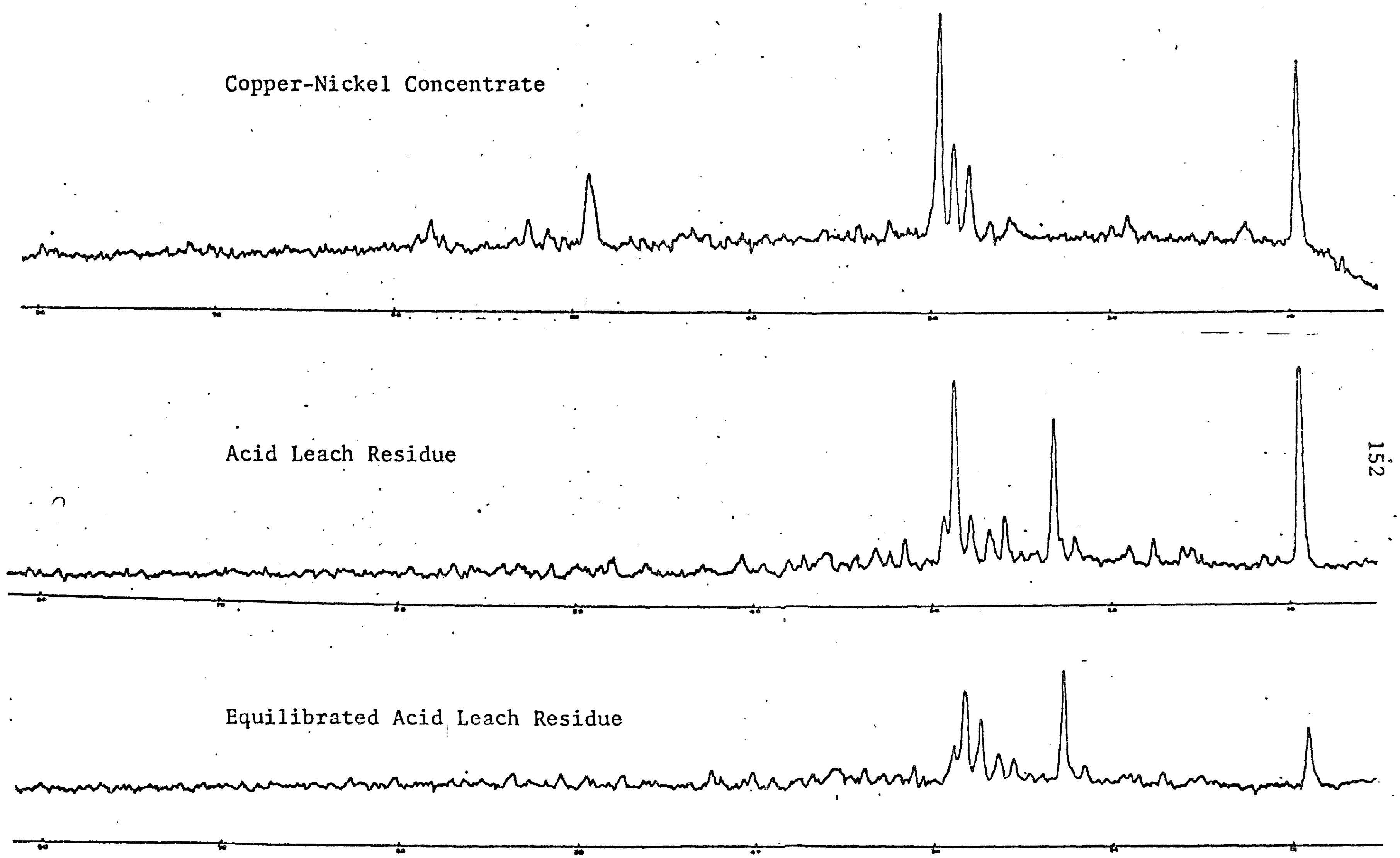


FIG. 52. X-RAY DIFFRACTOGRAPHS OF ACID LEACH RESIDUE, BEFORE AND AFTER EQUILIBRATION, AND THE CONCENTRATE

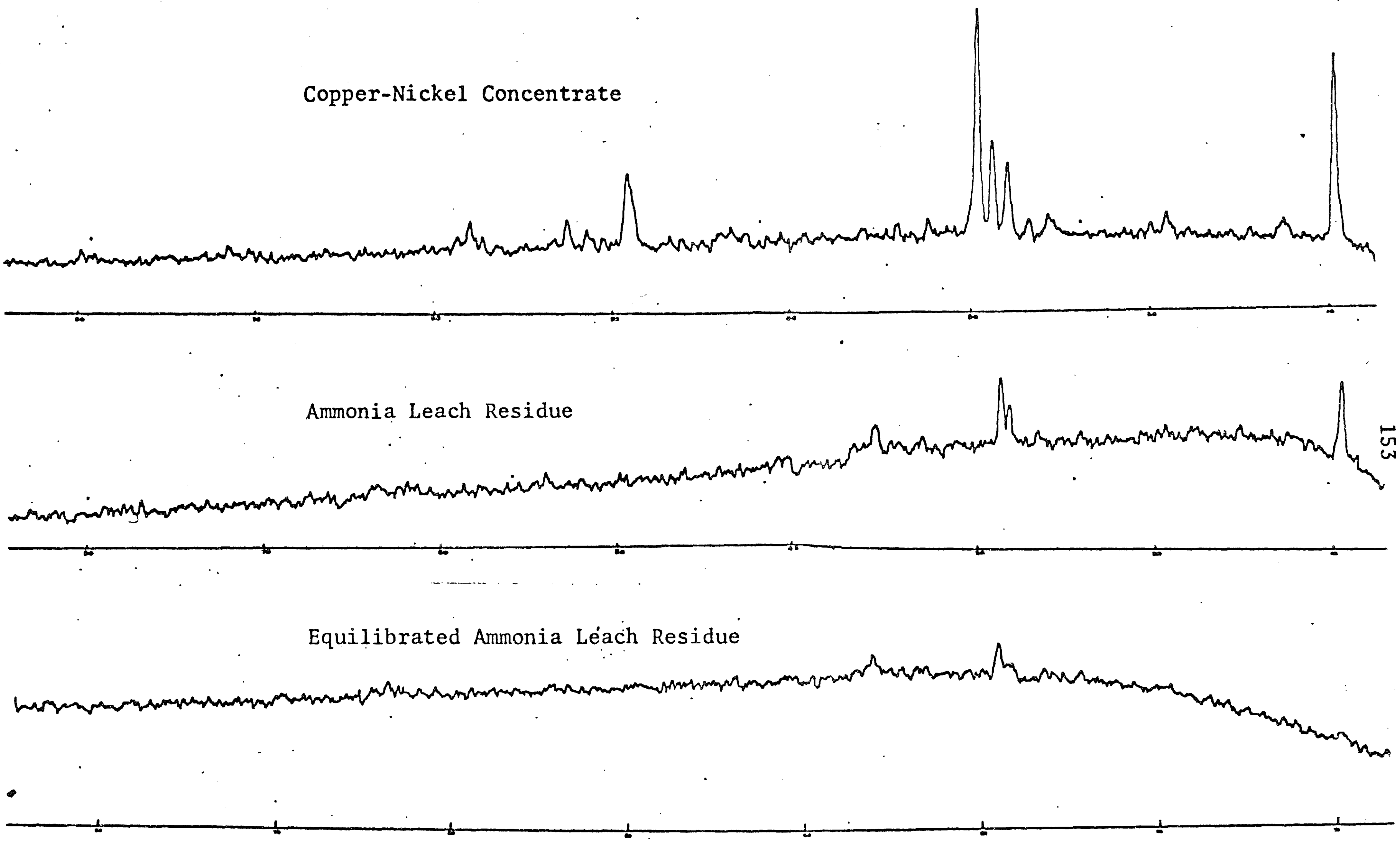


FIG. 53. X-RAY DIFFRACTOGRAPHS OF AMMONIA LEACH RESIDUE, BEFORE AND AFTER EQUILIBRATION, AND THE CONCENTRATE

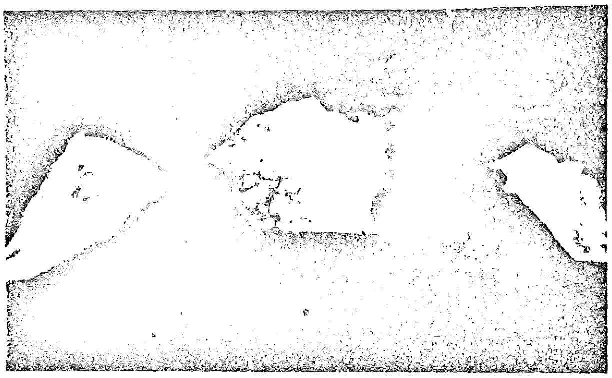
monoclinic sulfur and hydronium jarosite, with small amounts of natrojarosite. The ammonia leach residue was amorphous and hence a good diffraction pattern was not obtained. The x-ray diffraction patterns of each residue was compared with that of the corresponding equilibrated sample, and was found to show no significant change in either of the cases, indicating that no major change in composition or structure has taken place after the equilibration.

Scanning Electron Microscope Analysis

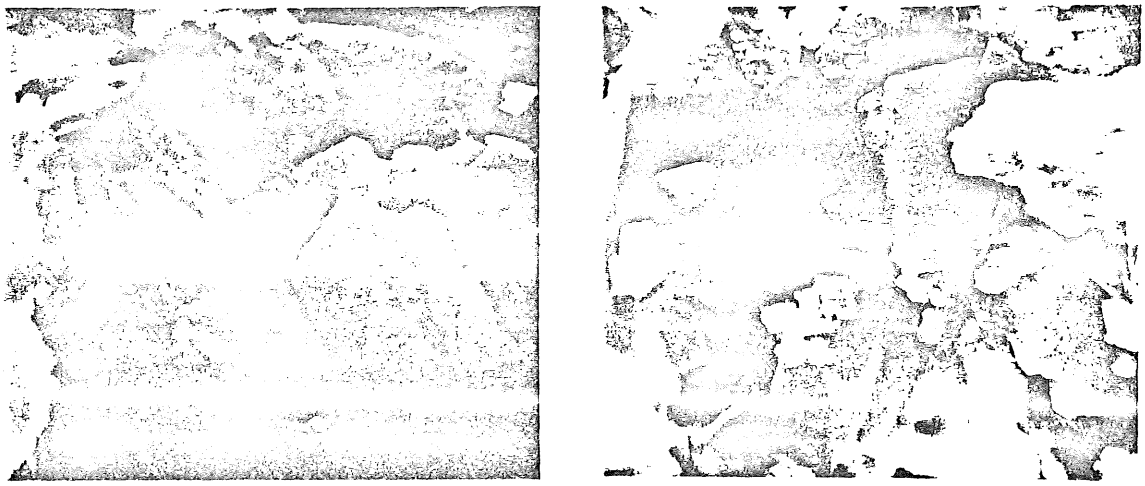
Electron micrographs of the concentrates, and acid and ammonia leach residues before and after equilibration are given in Figure 54. The acid leach residue before equilibration shows a platy tabular morphology which remains essentially the same after equilibration. The ammonia leach residue shows spheroidal particles which remain unchanged even after equilibration.

Discussion

Both acid and ammonia leach residues contain unleached sulfides of copper, nickel, cobalt and iron. Besides these, the acid leach residue contains hydronium jarosite and elemental sulfur in considerable amounts. The ammonia leach residue carries, in addition to the sulfides, significant quantities of ferric oxide. When equilibrated with distilled water, the residues have been found to release cations of copper, nickel, cobalt and iron in measurable quantities, as indicated in Tables 24 and 25. The presence of these cations in the equilibrated distilled water can be explained satisfactorily by the dissolution behavior of sulfides, oxidation, surface absorption, coprecipitation and related phenomena.

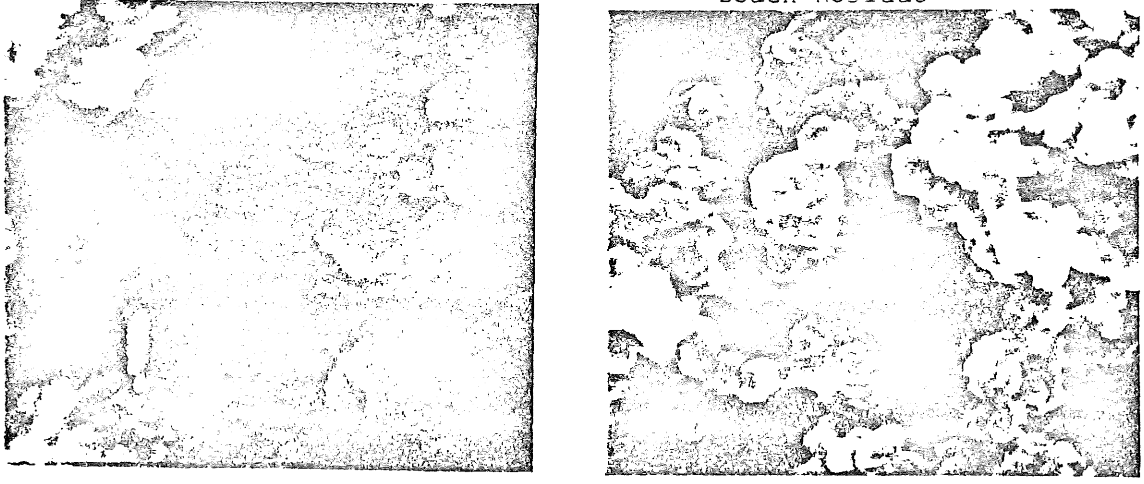


800X. Copper-Nickel Concentrate



5000X. Acid Leach Residue

5000X. Equilibrated Acid Leach Residue



30,000X. Ammonia Leach Residue

30,000X. Equilibrated Ammonia Leach Residue

FIG. 54. ELECTRON MICROGRAPHS OF THE ACID AND AMMONIA LEACH RESIDUES AND THE CU-NI CONCENTRATE.

The dissolution behavior of sulfides has been discussed by Kolthoff and Sandell.[120] From their discussion, the amounts of metal sulfide dissolved in water, which is equal to $[M^{++}]$, the concentration of metal ions, is given to be

$$[M^{++}] = \frac{S_{Ms}}{[S^{=}]} = \frac{S_{Ms}[H^{+}]^{2}}{10^{-20}[H_2S]} \qquad \ldots.(92)$$

Where S_{Ms} is the solubility product of the metal sulfide. If the solution is saturated at room temperature, $[H_2S]$ = constant = ca. 0.1. Hence, knowing the solubility product of the sulfide, the solubility of the sulfide in solutions saturated with hydrogen sulfide can be calculated for any hydrogen-ion concentration.

It is thus seen that the solubility of a metal sulfide in distilled water under the conditions of equilibration can be calculated from equation (92). However, Stumm and Morgan[154] have repeatedly pointed out that calculations of the solubility of a mineral on the basis of solubility product alone can be very misleading because the solubility is not exclusively governed by the solubility product. Various other equilibria besides the solubility equilibrium come into play. These include the acid-base equilibria of the cation and the anion of the solid, and equilibria describing complex formation. It is known, for instance, that all metal cations in water exist as aquo complexes,[154] and the complexes of cations such as Cu^{++}, Ni^{++} and Co^{++} are relatively more stable than many others.[120] When considered together with the solubility product, the acid-base equilibria and the complex forming tendency quantify the solubility of a solid in actual situations more accurately. This has been illustrated by Kolthoff and Sandell.[120]

Taking the acid leach residue as an example, the amount of copper expected to dissolve at the equilibrated pH of 4, assuming $[H_2S] = 0.1$ and the solubility product for CuS (4×10^{-36}), is calculated to be 4×10^{-23} moles per liter. However, in the actual equilibration test, assuming the average concentration of copper (Table 24), the copper dissolved is 5.35×10^{-6} moles per liter. Corresponding values for Ni and Co, assuming solubility products for NiS and CoS, are 1×10^{-12} and 7.66×10^{-5}, and 2×10^{-12} and 2.5×10^{-7} respectively. Similar calculations with ammonia leach residue also exhibits parallel results. These show that a greater amount of the cations have been released into the water than that can be theoretically calculated. However, the above theoretical calculations have been made based solely on the solubility products of the compounds specified, and hence when considered together with the acid-base equilibria and the equilibria of complex formations, the theoretical solubility will be significantly higher and closer to the actual data. Nevertheless, the large difference between the actual and theoretical values given above points to the fact that some other major phenomena are predominantly responsible for the release of the cations into the water. This is further examined in the light of known facts.

Oxidation of the sulfides by the dissolved oxygen in the aqueous solution has a strong possibility of occurrence. Oxidation can occur in either of two ways: the sulfides in the residue may first get oxidized and then dissolve into the aqueous media, or they may dissolve first and then get oxidized. It is probable that both these could be occurring simultaneously. Also, as a consequence, the sulfur species in the aqueous medium may exist as different sulfoxy compounds.

Kolthoff and Sandell[120] have stated that cations such as those of copper, zinc, magnesium, etc. get absorbed easily onto the surface of hydrous oxide precipitates of ferric iron. This fact has been supported by Stumm and Morgan[154] who further state that absorption of metal ions on the surface of hydrous oxides of iron takes place with the release of hydrogen ions or other cations. Transition and heavy metal ions are specifically attached to the surface of the hydrous oxides. Craigen et al.[121] have also reported on the high absorption properties of hydrous oxides of iron. These reports strongly suggest that the hydronium jarosite and the ferric oxide in the acid and ammonium leach residue respectively may be heavily contaminated with cations from the leach solutions and play an important role in the release of cations to the aqueous environment.

Besides surface absorption, occlusion of the cations during the growth of the precipitate is also another strong possibility for cation contamination. During precipitation when the solution contains an excess of lattice anions, occlusion of foreign cations in the precipitate tends to predominate, the amount of occlusion increasing with increasing concentrations of lattice anions in the solution.[120] This is especially true in the case of rapidly growing crystals. These conditions exist in the case of sulfuric acid leach where hydronium jarosite is precipitated from a sulfate solution containing copper, nickel and cobalt cations. Also, Walden and coworkers[155-157] have shown that precipitates can take up to a limited extent many foreign constituents in the form of solid solutions, even though the contaminant is not isomorphous with the

the host crystal. Under identical conditions, coprecipitation or occlusion of foreign ions is of the same order as their absorbability on the surface of the precipitate.

Thus it appears fairly certain that the acid and ammonia leach residues contain hydrous oxides of iron heavily contaminated with copper, nickel and cobalt ions either by surface absorption or coprecipitation. When the residues are suspended in water for equilibration, the absorbed cations enter the aqueous medium forming aquo complexes, hydrogen ions taking their place in the precipitate. It is also possible that both cations and the associated anions may dissolve in water and undergo oxidation. In the case of the ammonia leach residue, release of cations may occur due to the lowering of pH from that of the precipitate formation to the pH of equilibration.[154]

Hence, the release of copper, nickel, cobalt and iron into water from the acid and alkali leach residues may occur due to the dissolution of the residual unleached sulfides, their oxidation, or due to the absorption or coprecipitation and subsequent release of the cations from the precipitates. Comparing the concentrations of cations released from either of the residues (Tables 23 and 24) it can be at once noted that the concentrations of cations released from acid leach residue are about 2-3 times more than those released by the ammonia leach residue. Assuming that concentrations reported in the distilled water is predominantly due to the release of contaminated ions, this interesting fact suggests either or both of the two following interpretations. Hydronium jarosite may be more heavily contaminated by cations than ferric oxide. Also, it is possible that the release of absorbed ions may be facilitated more from the hydronium jarosite than from ferric oxide, and hence the amount of ions leaching out of the former is more than that of the latter. However, it is possible that the lower equilibration pH of the acid leach residue may be an additional factor causing this behavior. The behavior of iron in the residues throws more light on the difference in characteristics of hydronium jarosite and ferric oxide. It is seen from Table 24 and Table 25 that though ammonia leach residue has a much higher iron content than acid leach residue, the release of iron ions into water is more than three times in the case of acid leach residue than that of the alkali leach residue. Part of this may be due to the lower equilibrium pH in the case of acid leach residue. However, assuming the dissolution of unleached pyrrhotite to be comparable in both the residues, the above fact strongly suggests that ferric oxide is a much more stable constituent in the alkali leach residue than hydronium jarosite in the acid leach residue. This observation also ties in very well with the previous observations regarding the release of cations from acid and alkali leach residues. It thus appears that hydronium jarosite in acid leach residue is liable to cause more contamination and contribute to much more release of cations into water than its counterpart, ferric oxide, in alkali leach residue.

Surface absorption and coprecipitation, as discussed earlier, is also quite possible in the case of anions. Release of anions into water may be replaced by hydroxide ions which have a strong affinity for ferric iron.[154] The equilibrated and centrifuged distilled water was examined for the presence of $SO_4^=$ by the barium sulfate precipitation technique, but gave no results. This indicates that the sulfate ions, if any, released into the water had a concentration below the sulfate detection limit of the sample by the above technique. The detection limit of $SO_4^{=}$ can be calculated knowing the solubility product of barium sulfate and the concentration of barium chloride used. In the determination, a 10% $BaCl_2$ (0.48M) was made use of. The solubility product of $BaSO_4$ at room temperature is 1×10^{-10}. Hence the minimum amount of $SO_4^{=}$ necessary to precipitate $BaSO_4$ is calculated to be 1×10^{-5} ppm. However, in practice the detection limit is said to be about 1.0 ppm. Hence, in the equilibrated water the sulfate content was below 1.0 ppm. Sulfate release into the equilibrated water is possible only from the jarosite or basic ferric sulfate in the residue or by the oxidation of the sulfide ions or elemental sulfur. Since a considerable part of the sulfur in the residue associated with cations occurs as sulfides of copper, nickel, cobalt and iron, the major portion of sulfur species in the equilibrated water can be expected to consist of sulfides ($S^{=}$), bisulfides (HS^{-}), hydrogen sulfide (H_2S), sulfoxy compounds ($S_mO_n^{=}$), or sulfur complexes such as $FeHS^{+}$, $FeS_2^{=}$, etc.

Summing up, it was found that acid leach residue consisted predominantly of elemental sulfur and hydronium jarosite while ammonia leach residue contained considerable amounts of ferric oxide. During the leach, it appears that the cations such as those of copper, nickel and cobalt were absorbed onto the surface of the jarosite or ferric oxide precipitate and were thus carried into the leach residue. During equilibration, along with some possible dissolution and/or oxidation of the unleached sulfides, the cations may be released into the aqueous medium.

From the experimental observations it appears that ferric oxide in the ammonia leach residue is a more stable constituent with respect to release of ions than hydronium jarosite in the acid leach residue.

B. PREPARATION OF, AND EQUILIBRATION STUDIES ON, THE HYDROLYSIS PRODUCTS OF IRON

The hydrolysis behavior of iron is an important phenomena affecting various aspects of a hydrometallurgical process. Hence in order to understand this more fully, an experimental scheme was devised to synthesize pure hydrolysis products of iron from acidified ferric sulfate solutions, and to examine the mineralogy, morphology and equilibration characteristics of the hydrolysis products.

Preparation of Hydrolysis Products

Survey of published information on the preparation of hydrolysis products of iron from ferric sulfate gave some indication as to the general temperature range and level of acidity of their formation. Hydronium jarosite has been known to precipitate at all temperatures ranging from 25°C to 200°C at moderate acidity levels. At higher acidity levels (>50 g/ℓ H_2SO_4), and temperatures of more than 140°C, precipitation of basic ferric sulfate is favored. Ferric oxide precipitates at temperatures close to 200°C under low acid concentrations. Thus, conditions for the precipitation of the desired hydrolysis products were chosen with the general guidance of the above information obtained from the literature.

The experimental conditions employed for the preparation of the hydrolysis products are given in Table 26. These conditions are those which yielded pure precipitates of iron hydrolysis verified by x-ray diffraction analysis. The starting solutions for the precipitation of hydronium jarosite, basic sulfate and ferric oxide contained 25, 35 and

TABLE 26. CONDITIONS OF PREPARATION OF THE HYDROLYSIS PRODUCTS OF IRON

Compound	Concentration of $Fe_2(SO_4)_3$ g/ℓ	Concentration of H_2SO_4 g/ℓ	Temperature °C	O_2 Pressure psi	Retention Time Hours
Hydronium jarosite	89.3	5	95	120	6
Basic sulfate	125	62	200	150	4
Ferric oxide	62.5	0	200	200	12

Agitation speed 1000 rpm, solution volume 500 ml.

17.5 g/ℓ of ferric iron respectively. It can be noted that of the three hydrolysis products, precipitation of basic ferric sulfate required the highest amount of acid and that of ferric oxide the lowest. The partial chemical analysis of these precipitates is given in Table 27. The theoretical weight percentages of iron and sulfate in hydronium jarosite are 34.82 and 39.96 respectively. The iron and sulfate content of the sample prepared agreed very well with the theoretical values. Similarly, the reported iron and sulfate content of the basic sulfate sample, $Fe_2O_3 \cdot 2SO_3 \cdot H_2O$, agreed well with the theoretical percentages of 33.1 and 56.8 respectively. When compared with the theoretical value of the iron content in Fe_2O_3 (70%), the chemical analysis of the precipitated sample agreed fairly well.

Equilibration Studies

Equilibration tests carried out at the early stages were made to determine the effect of intense aeration on the equilibration behavior of the sample. Two samples of basic sulfate were suspended in distilled water and subjected to agitation under identical conditions except that to one of the samples air was supplied from a compressed air cylinder while the other sample was tested under conditions such that the only air accessible to the sample was that of the atmosphere. The pH values obtained as a function of time for each of the samples is plotted in Figure 55. It is seen that the curves match very closely. This indicates that there is little or no effect of extra aeration on the equilibration of basic sulfate, and it seems safe to assume the same to be true for other hydrolysis products of iron. Hence further equilibration tests on the products of iron hydrolysis were done without external

TABLE 27. PARTIAL CHEMICAL ANALYSIS OF HYDRONIUM JAROSITE, BASIC SULFATE AND FERRIC OXIDE

Compound	Total Fe %	Fe^{+2} %	$SO_4^{=}$ %	S %
Hydronium jarosite	34.86	0.09	42.78	-
Basic ferric sulfate	31.97	0.12	57.61	-
Ferric oxide	68.27	-	-	0.32

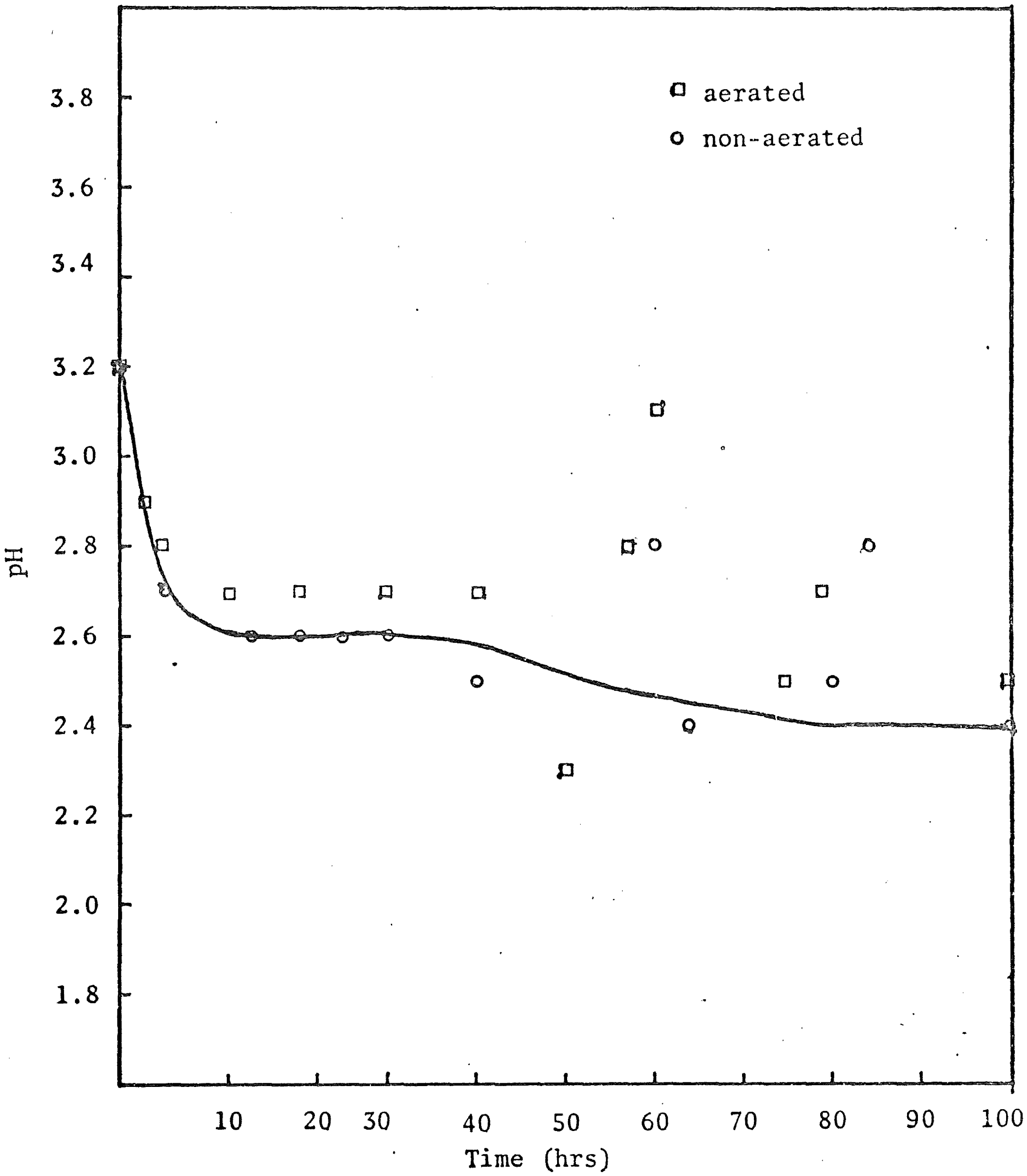


Fig. 55. Effect of aeration on equilibration of basic ferric sulfate

supply of air other than that in the atmosphere.

The equilibration curves of hydronium jarosite, basic ferric sulfate and ferric oxide are given in Figures 56-58. The final pH's of hydronium jarosite remained constantly at 3.4. The final pH's of basic ferric sulfate remained almost constantly at 2.7, while that of ferric oxide had initially a value of 6.5 but finally stablized at 7.0 Thus it can be noted that all the hydrolysis products of iron equilibrate easily and quickly to their final equilibration value, which remains almost constant throughout the equilibration. This fact therefore implied that the pure products of iron hydrolysis remain stable in distilled water when agitated for extended periods of time.

Tables 28-30 show the concentrations of ions released from the hydrolysis product samples during the equilibration tests. Hydronium jarosite releases decreasing amounts of iron until at the end of fourth equilibration cycle, no iron ions were detected in the supernatant water obtained after centrifuging the suspended solids. Basic ferric sulfate also releases decreasing amounts of iron for consecutive equilibration cycles, but the release of iron ions remains at significant levels even after equilibration. Ferric oxide releases very small quantities of iron and soon becomes undetectable in the supernatant water. Of the three hydrolysis products, basic sulfate reports the largest amounts of iron release averaging 113.2 ppm. Release of sulfate ions by hydronium jarosite and ferric oxide were not detected and hence could be present only below the detection limits of sulfate ion determination by the barium sulfate precipitation technique, which in practice is said to be about 1.0 ppm. Basic ferric sulfate, however, released considerable

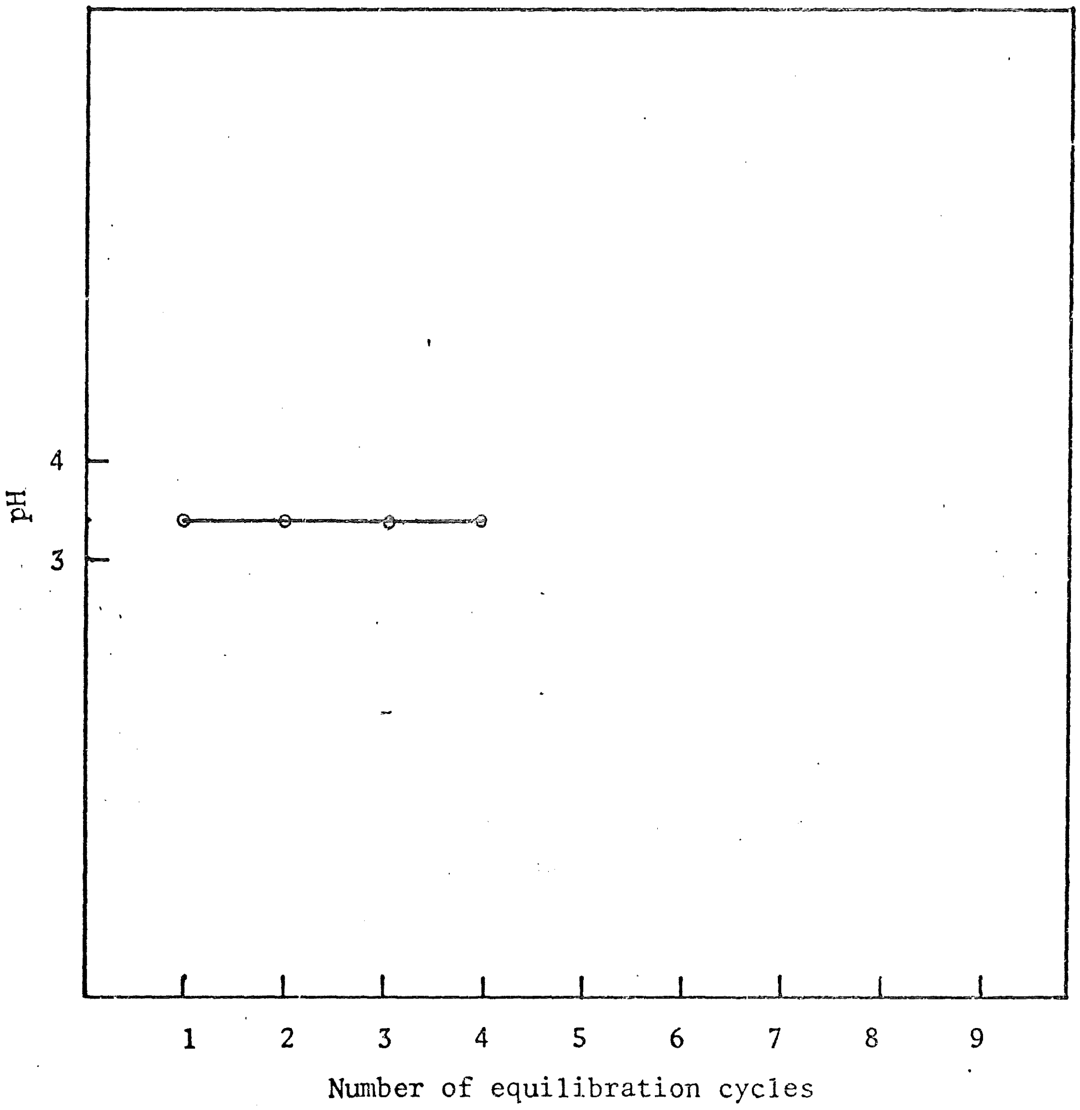


Fig. 56. Equilibration curve for hydronium jarosite

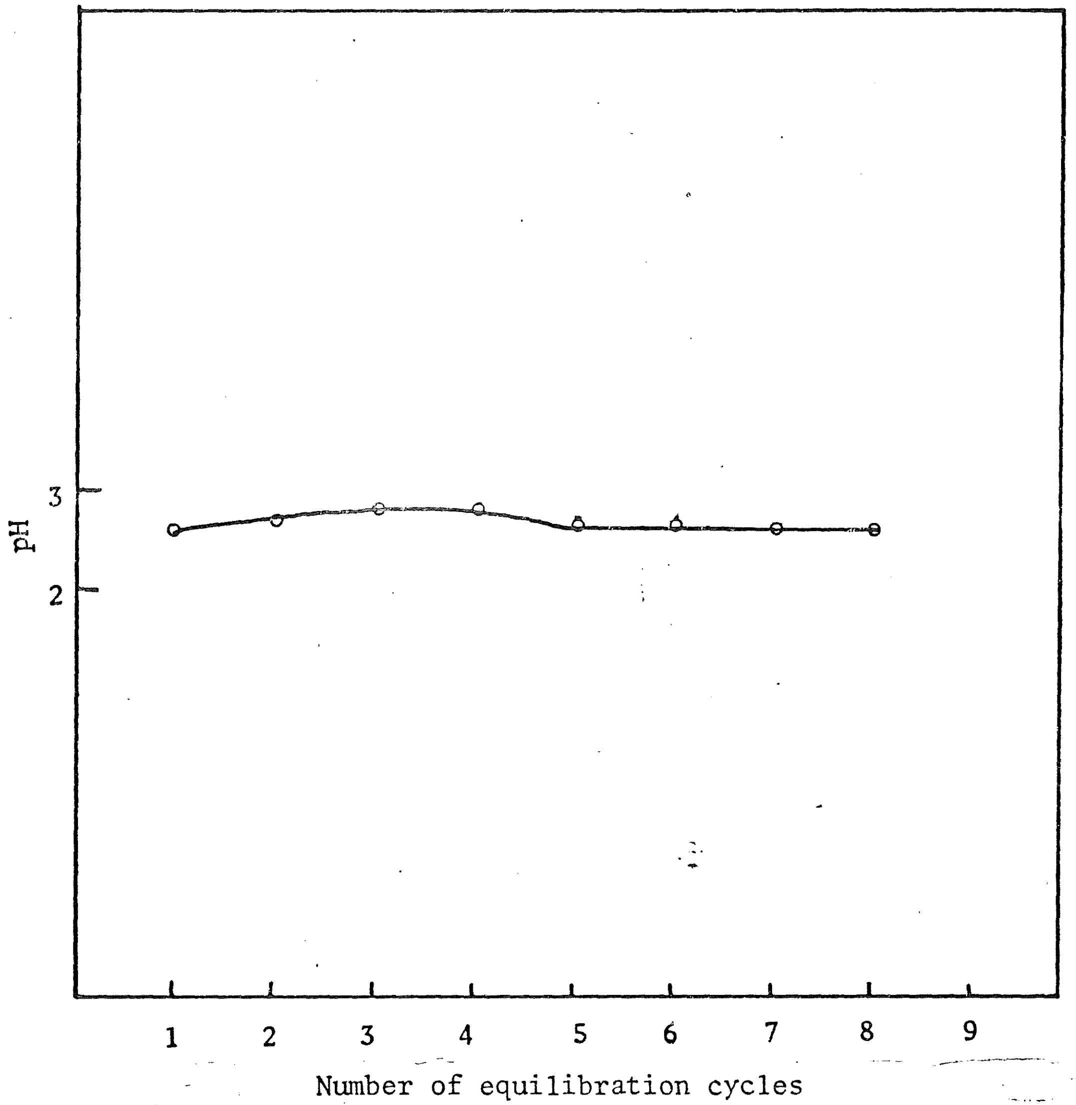


Fig. 57. Equilibration curve for basic ferric sulfate

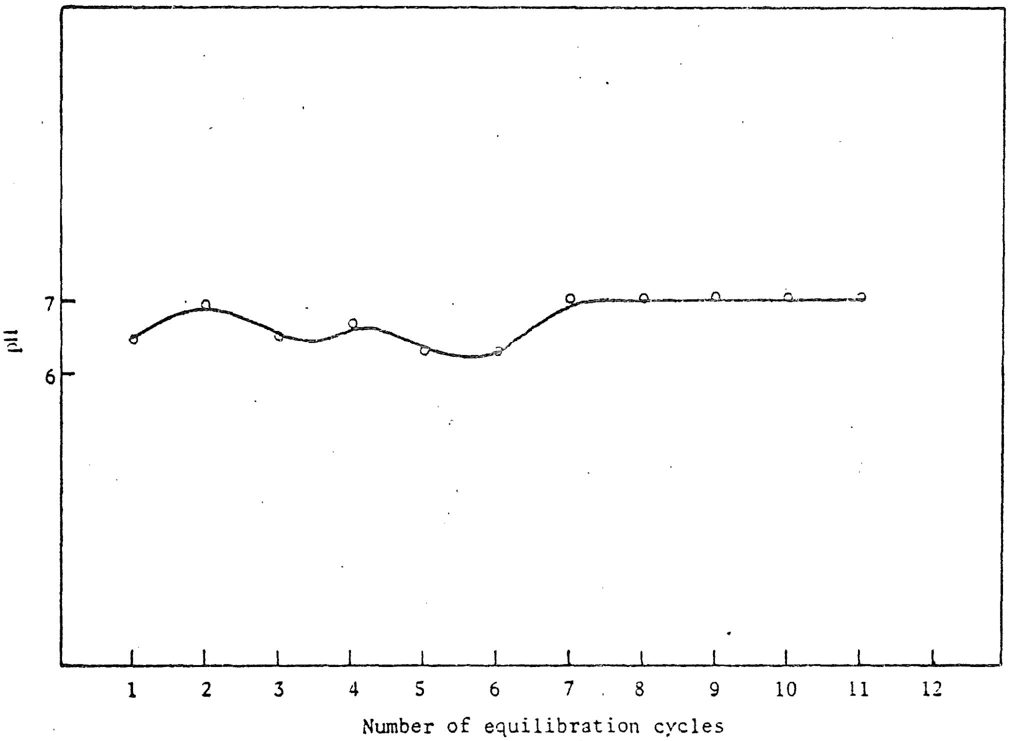


Fig. 58. Equilibration curve for Ferric oxide

TABLE 28. RELEASE OF IONS IN EQUILIBRATION STUDIES OF HYDRONIUM JAROSITE

No.	Iron ppm	$SO_4^=$ ppm
1.	3.1	0
2.	1.1	0
3.	2	0
4.	0	0
Average	1.55	

TABLE 29. RELEASE OF IONS IN EQUILIBRATION STUDIES OF BASIC FERRIC SULFATE

No.	Iron ppm	$SO_4^=$ ppm
1.	398	1,111
2.	125	329
3.	71.8	123
4.	76	329
5.	41	0
6.	45	0
7.	36	0
Average	113.2	270.2

TABLE 30. RELEASE OF IONS IN EQUILIBRATION STUDIES OF FERRIC OXIDE

No.	Iron ppm
1.	0
2.	0.05
3.	0.05
4.	0.08
5.	0
6.	2
7.	0
8.	0
9.	0
10.	0
11.	0
Average	0.02*

$SO_4^{=}$ ions were not detected.

*Entry No. 6 was omitted for calculation of average.

amounts of sulfate during the equilibration tests but the quantity released decreased to below the detection limits as the final pH's of the sample stabilized.

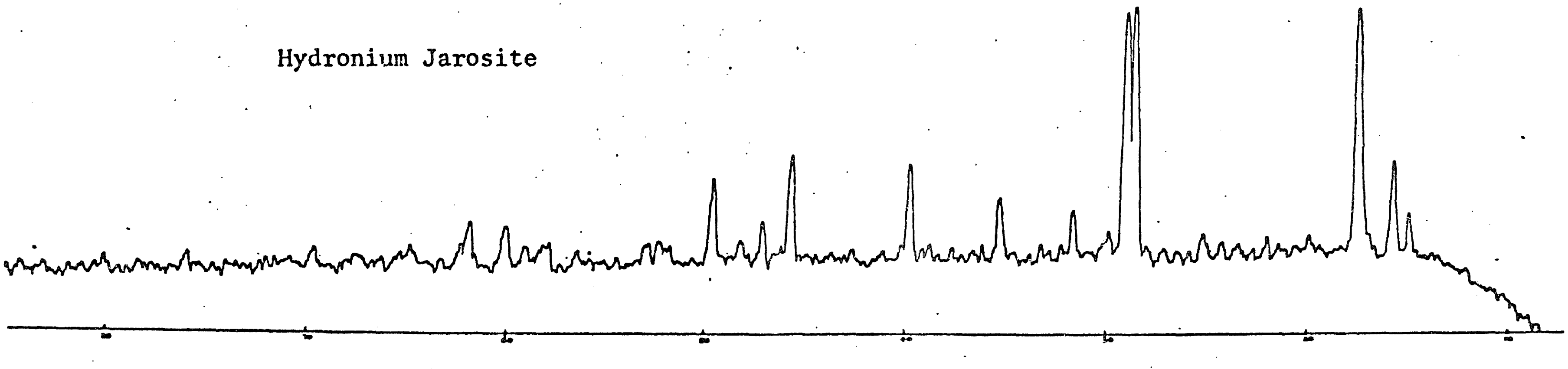
X-ray Diffraction Analysis

The identity and the purity of the hydrolysis products of iron namely, hydronium jarosite [$H_3O\ Fe_2(SO_4)_3(OH)_6$], basic ferric sulfate [$Fe_2O_3 \cdot 2SO_3 \cdot H_2O$] and ferric oxide [$\alpha - Fe_2O_3$], were established primarily by the x-ray diffraction technique, and secondarily by chemical analysis. The x-ray diffraction patterns of the samples both before and after equilibration are given in Figures 59-61. For every sample, the diffraction pattern of the one before equilibration was found to be identical to the one after equilibration. This, therefore, indicates that the equilibration has not produced any major changes in the composition or structure of the hydrolysis products.

Scanning Electron Microscope Analysis

Electron micrographs of the three hydrolysis products of iron before and after equilibration are given in Figure 62. The hydronium jarosite sample showed a tabular platy morphology which remained essentially the same even after the equilibration. The electron micrographs of basic ferric sulfate showed needle-shaped crystals. This morphological feature showed no significant change after equilibration. However, the needle-shaped crystals exhibited the tendency to stick together after equilibration, which was more or less the case with the crystals in every hydrolysis product examined. Ferric oxide showed spheroidal particles before equilibration with minor quantities of

Hydronium Jarosite



Equilibrated Hydronium Jarosite

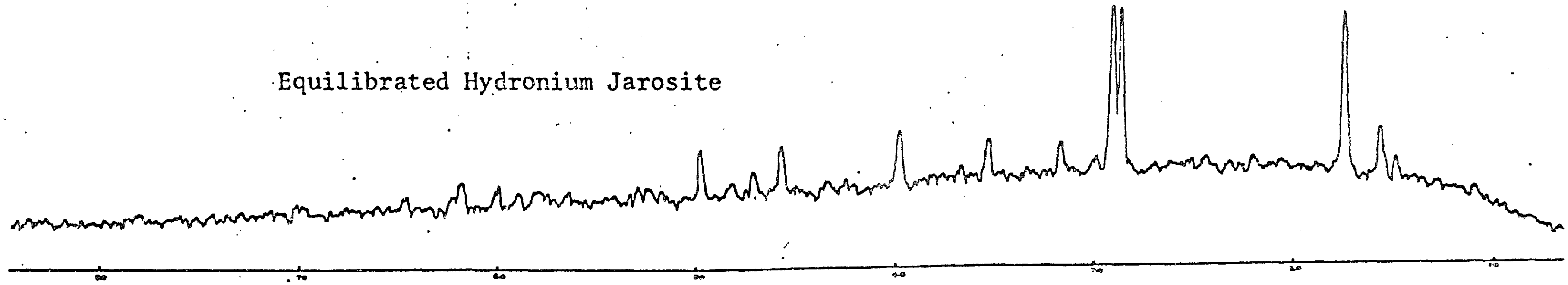
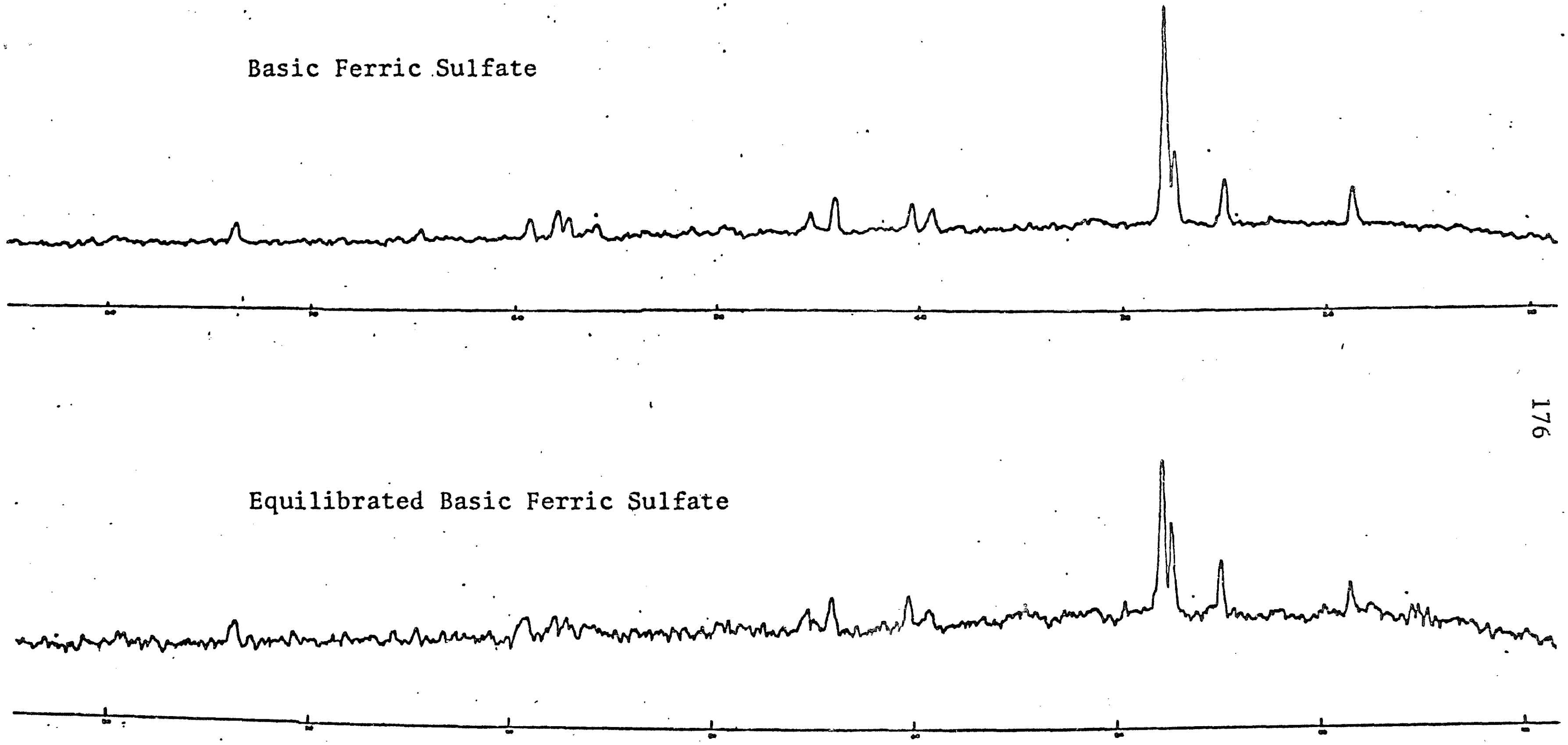
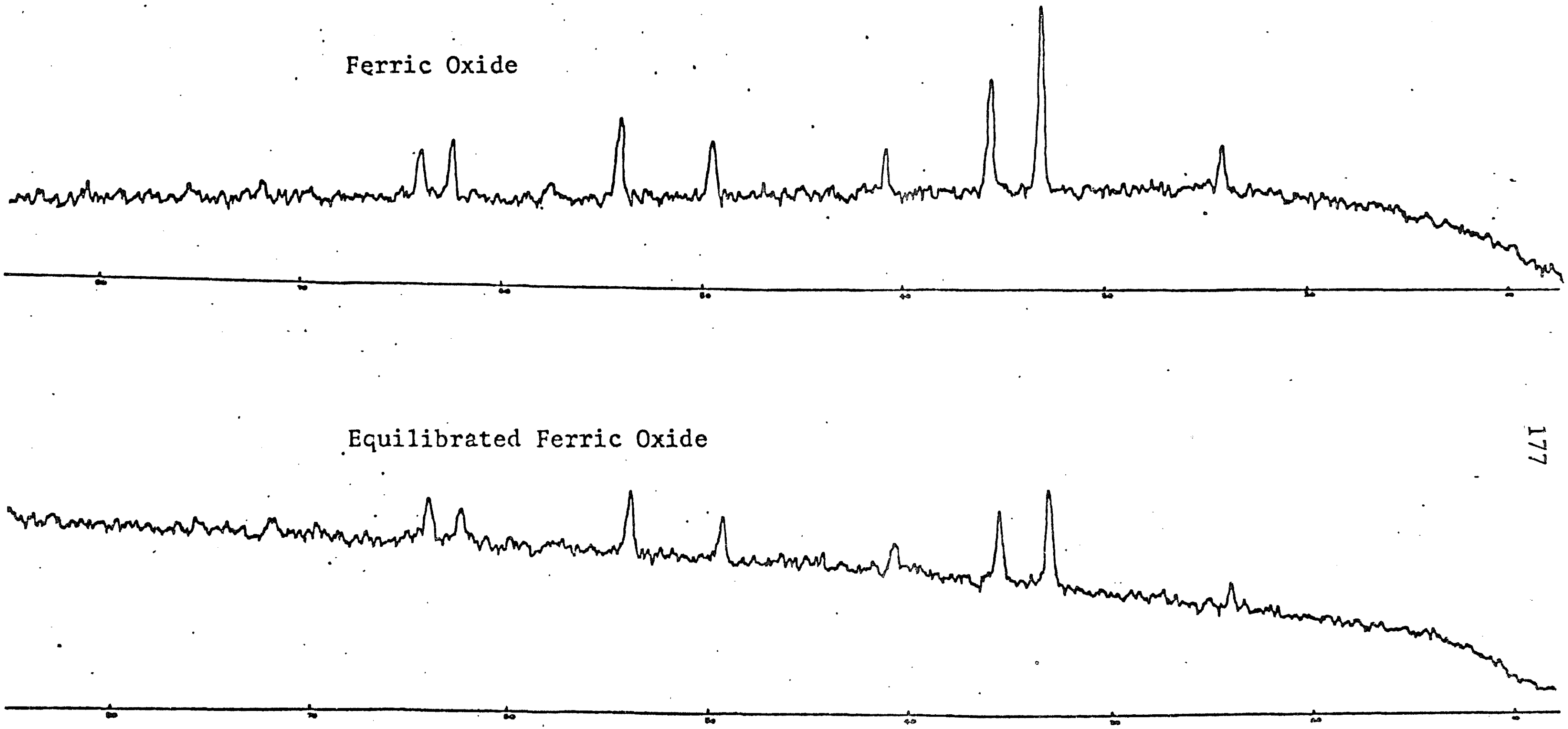


FIG. 59. X-RAY DIFFRACTOGRAPHS OF HYDRONIUM JAROSITE BEFORE AND AFTER EQUILIBRATION


Basic Ferric Sulfate

Equilibrated Basic Ferric Sulfate

FIG. 60. X-RAY DIFFRACTOGRAPHS OF BASIC FERRIC SULFATE BEFORE AND AFTER EQUILIBRATION



Ferric Oxide

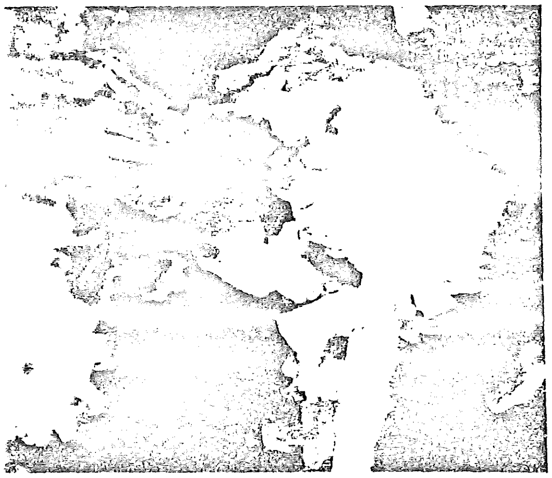
Equilibrated Ferric Oxide

FIG. 61. X-RAY DIFFRACTOGRAPHS OF FERRIC OXIDE BEFORE AND AFTER EQUILIBRATION

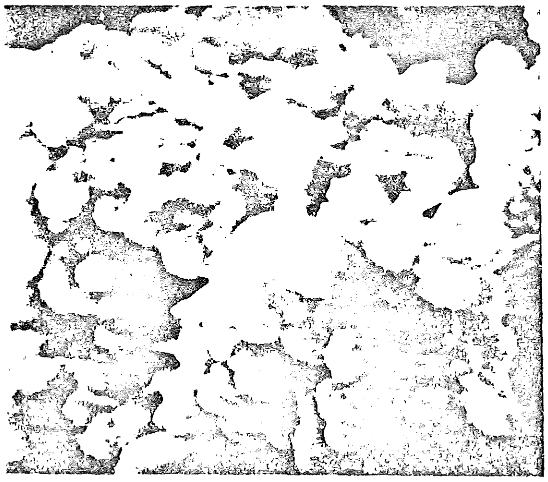
5000X. Jarosite

5000X. Equilibrated Jarosite

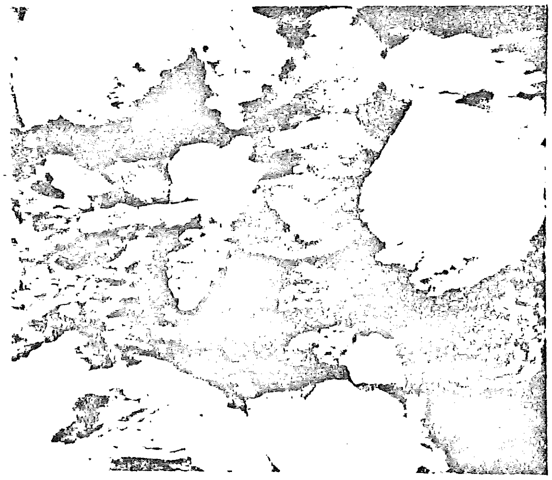
5000X. Basic Ferric
sulfate



5000X. Equilibrated Basic
Ferric Sulfate



5000X. Ferric Oxide



5000X. Equilibrated Ferric Oxide

FIG. 62. ELECTRON MICROGRAPHS OF HYDROLYSIS PRODUCTS OF IRON

radiating, acicular crystals. After equilibration, a larger proportion of the sample was made up of the acicular crystals along with the spheroidal particles. Thus, morphologically, ferric oxide on equilibration exhibits a tendency to change to basic sulfate, while hydronium jarosite and basic sulfate underwent no significant change. A notable fact that emerged from this electron microscope analysis was that each of the hydrolysis products showed entirely different morphologies, as can be seen in Figure 62.

Summary

The literature survey on hydrolysis of iron revealed a variety of conditions for the precipitation of each of the products. However, a general idea of the temperature and acidity level was apparent. Experiments conducted within this assumed ranges gave pure samples of the hydrolysis products as verified by x-ray diffraction techniques and chemical analysis. Each of the hydrolysis products was found to have a distinct morphology, different from the others. It is interesting to note that the morphology of hydronium jarosite as reported by Kunda and Veltman[122] is spheroidal in nature, while that which was obtained in this study showed a platy morphology. Thus the conditions of precipitation appears to have a strong influence on the morphology of the precipitate. The chemical analysis of the precipitates obtained revealed that the iron and sulfur contents of the precipitates matched closely with the theoretical values. Umetsu and Sasaki[117] have reported a sulfur content of 0.7 - 1.4% in the ferric oxide precipitated from pure ferric sulfate solutions. The sulfur content of the ferric oxide precipitated in this study was 0.32%.

It is immediately apparent, by an examination of the amounts of iron and sulfate release of the hydrolysis products, that basic sulfate dissolves to a certain extent in distilled water, the amount of ions released decreasing with time as the basic sulfate gets stabilized. The sulfate content of the hydronium jarosite and ferric oxide were below detection limits. It is not surprising that the sulfate release of ferric oxide was not detected, since the sulfate content in the sample was very low. Hydronium jarosite, however, may be expected to release some sulfate ions, corresponding perhaps to the amount of iron ions released.

Thus, in the overall analysis, it appears that though none of the three hydrolysis products underwent any major compositional or morphological changes after equilibration in distilled water, basic ferric sulfate released significant amounts of iron and sulfate ions, much more than those released by hydronium jarosite and ferric oxide. Hence, this observation appears to indicate the relative stability of these three compounds in water, with ferric oxide as the most stable of the three and basic ferric sulfate as the least stable, the jarosite having an intermediate stability value.

C. OVERALL DISCUSSION

Hydrometallurgical processes claim, as one of their merits, the obviation of air pollution by sulfur dioxide fumes. However, they give rise to leach residues which when ultimately dumped into the ground may release acid and heavy metal ions thus polluting the ground water. This fact makes it very important to study the environmental implications of leach residues of hydrometallurgical processes. The present study brings out some of the environmental aspects of the leach residues of acid and ammonia leaching treatments of the copper-nickel concentrates of the Duluth gabbro.

It was seen earlier that the acid leach residue gives rise to hydronium jarosites on which cations and anions get absorbed or coprecipitated. The ammonia leach residue, contains ferric oxide which also gets contaminated by cations and anions. The hydronium jarosite was found to be relatively more contaminated, and released cations to the aqueous environment much more than ferric oxide. This fact is confirmed also by tests on pure hydrolysis products. When the three hydrolysis products, hydronium jarosite, basic sulfate and ferric oxide were examined, it was found that basic sulfate released more ions than the other two, ferric oxide being the one which released the least amount of ions. Comparing the behavior of pure hydronium jarosite and ferric oxide in these tests, the results agreed with those of the tests on leach residue, in that hydronium jarosite was less stable, with reference to release of ions, than ferric oxide. Thus, it can be concluded that of the two, hydronium jarosite was more liable than ferric oxide to get contaminated with cations and anions, and release them into the environment. Extending this fact to the leach residues, it is clear that acid leach residue is more potentially hazardous to the environment than ammonia leach residue.

The equilibration tests also gave the final equilibrating pH's of the different products examined. It was found that the ammonia leach residue and pure ferric oxide equilibrated at the same pH (7.0). The equilibration pH of acid leach residue and pure hydronium jarosite were not much different (4.0 and 3.4 respectively). It was also found by equilibration tests with each of the pure hydrolysis products that the morphology of the products remained the same even after equilibration in distilled water. This was found to be true also in the case of leach residues. This adds further evidence to the possibility that the release of ions to the environment by the leach residues is due chiefly to the dissolution of the constituents in stoichiometric ratios, or surface absorption and coprecipitation of the cations and anions onto the precipitate and subsequent release of the same into the environment. The possibility of release of ions due to structural change in the precipitates thus appears to be less likely.

V. SUMMARY AND CONCLUSIONS

In order to study the metallurgical and environmental aspects of hydrometallurgical treatment of copper-nickel concentrate from Duluth gabbro, a detailed literature review of six hydrometallurgical extraction techniques was undertaken. From this review, three major areas of interest were identified as being important in the study. They were the hydrolysis of iron, oxidation behavior of sulfur in acid and basic solutions and sulfur disposal, and the solubility characteristics of silicate minerals. Literature reviews were made on each of these topics and their salient features and problems were brought to light. An experimental program was then designed to investigate the residues of the acid and ammonia leaching of the copper-nickel concentrate, and the preparation and behavior of the hydrolysis products of iron. From this experimental study, the following conclusions were made:

1. Hydronium jarosite was the chief iron product of the acid leach of the copper-nickel concentrate under the conditions of this study.

2. The leach residues of acid and ammonia leaching were contaminated by cations and anions from the leach solutions, acid leach residue being more affected than ammonia leach residue.

3. Hydronium jarosite in acid leach residue was more contaminated and released much more cations to the aqueous environment than its counterpart, ferric oxide, in ammonia leach residue.

4. Of the three hydrolysis products, hydronium jarosite [H_3O Fe_2 $(SO_4)_2$ $(OH)_6$], basic ferric sulfate [$Fe_2O_3 \cdot 2SO_3 \cdot H_2O$], and ferric oxide [$\alpha$ - Fe_2O_3], the basic sulfate released a larger amount of ions than the other two, ferric oxide releasing the least quantity.

5. The sulfate ion release of the acid and ammonia leach residues, hydronium jarosite and ferric oxide were below detectable limits.

6. The equilibration of the iron hydrolysis products were not affected by intense aeration.

7. Each of the three iron hydrolysis products exhibited distinct characteristic morphology.

8. The morphologies of pure hydronium jarosite and basic sulfate did not undergo any drastic change on equilibration, but that of ferric oxide exhibited a tendency to change toward the morphology of the basic sulfate.

9. Each of the hydrolysis products of iron equilibrated throughout at almost constant pH. The equilibrated pH of hydronium jarosite, basic ferric sulfate and ferric oxide were 3.4, 2.7, and 7.0 respectively.

10. The equilibrated pH of acid and ammonia leach residues were 4.0 and 7.0 respectively.

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ADDENDUM

Trace element analyses of the solids and liquids used in connection with the environmental leaching tests of the copper-nickel leach residues are reported and discussed in the Addendum because the data from Barringer Research Ltd. was not received before the completion of the main text. Appendix I gives the trace element analysis of the copper-nickel concentrate, acid leach residue and ammonia leach residue before and after equilibration. Appendix II gives the trace element analysis of the equilibrated distilled water of the environmental leaching tests of the acid and ammonia leach residues.

An examination of the trace element analysis in Appendix I revealed that there is little change in residue composition on equilibration. The elements have reported in the residue at various percentages of the concentrate and frequently have completely reported in the residue. Chromium and molybdenum contents of the concentrate, for example, have resisted leaching into solution, both in acid and ammonia systems, and have totally reported in the residues.

Appendix II shows the concentrations of various ions leached out into the distilled water from acid and ammonia leach residues. The concentrations of trace elements leached out are generally less than 1 ppm, and frequently of the order of ~0.05 ppm.

The trace element analysis thus shows that there is no compositional change in the leach residue on equilibration, and the trace elements leach out stoichiometrically. This is in agreement with the conclusions drawn from x-ray analysis and scanning electron microscope studies, and hence lends more support to the discussion in the text.

APPENDIX I. TRACE ELEMENT ANALYSIS OF THE CONCENTRATE, ACID LEACH RESIDUE AND AMMONIA LEACH RESIDUE BEFORE AND AFTER EQUILIBRATION - DATA FROM BARRINGER RESEARCH LTD.

		Acid Leach Residue			Ammonia Leach Residue		
Element	Concentrate %	Before Equilibration %	After Equilibration %	Distribution* %	Before Equilibration %	After Equilibration %	Distribution* %
Al	1.5	0.241	0.291	4.82	2.35	2.480	(100)**
Ba	0.015	0.0065	0.0061	13.0	0.124	0.101	(100)**
Be	n.d.	n.d.	n.d.	-	n.d.	n.d.	-
Ca	0.98	0.262	0.307	8.02	1.02	1.190	72.86
Cu	14.3	0.774	0.785	1.62	0.905	0.985	4.43
Fe	37.0	9.59	8.63	7.78	56.1	49.9	(100)**
K	0.104	0.037	0.054	10.67	0.161	0.170	(100)**
Mg	2.42	2.84	2.91	35.21	2.64	2.76	76.36
Mn	0.039	0.026	0.029	20.00	0.055	0.063	98.72
Na	0.26	0.49	0.41	56.54	0.590	0.6	(100)**
P	n.d.	n.d.	n.d.	-	n.d.	n.d.	-
Pb	0.01	0.018	0.015	54.0	0.007	0.008	49.0
Sr	0.0037	0.001	0.001	8.11	0.007	0.007	(100)**
Ti	0.058	0.078	0.081	40.34	0.082	0.085	98.97
V	0.0012	0.0015	0.0017	37.5	0.002	0.002	(100)**
Zn	0.033	0.02	0.0138	18.18	0.024	0.027	50.91
Th	n.d.	n.d.	n.d.	-	n.d.	n.d.	-
Ag	0.0039	0.0006	0.0006	4.62	0.002	0.002	35.9
Cd	n.d.	n.d.	n.d.	-	n.d.	n.d.	-
Co	0.103	0.005	0.0039	1.15	0.033	0.032	2.24
Cr	0.0056	0.079	0.0852	(100)**	0.036	0.245	(100)**
Mo	0.003	0.028	0.0210	(100)**	0.005	0.008	(100)**
Ni	2.67	0.053	0.0756	0.6	0.170	0.213	4.46
Zr	0.0015	0.0013	0.0014	26	0.004	0.003	(100)**

* percentage of the concentrate in the unequilibrated leach residue

** indicates that the element reports completely in the residue

APPENDIX II. RELEASE OF IONS FROM EQUILIBRATED DISTILLED WATER SAMPLE OF ACID AND AMMONIA LEACH RESIDUES - TRACE ELEMENT ANALYSIS FROM BARRINGER RESEARCH LTD.

	Equilibrated Distilled Water	
Element	Acid Leach Residue ppm	Ammonia Leach Residue ppm
Al	0.05	n.d.
B	0.008	0.024
Ba	0.004	n.d.
Be	n.d.	n.d.
Ca	0.4	0.34
Cu	0.350	0.018
Fe	0.631	0.050
K	n.d.	n.d.
Mg	n.d.	n.d.
Mn	0.0351	0.0060
Na	n.d.	n.d.
F	1.0	n.d.
Pb	0.2	n.d.
Si	0.571	0.710
Sr	n.d.	n.d.
Ti	n.d.	n.d.
V	n.d.	n.d.
Zn	0.13	n.d.
Th	n.d.	n.d.
Ag	n.d.	n.d.
As	n.d.	n.d.
Cd	n.d.	n.d.
Co	n.d.	n.d.
Cr	0.015	n.d.
Mo	n.d.	n.d.
Ni	0.23	0.35
Zr	n.d.	n.d.