MIRL Report No. 81

HYDROMETALLURGY OF COMPLEX SULFIDE ORES

Process Development

P. Dharma Rao, Editor

Mineral Industry Research Laboratory
School of Mineral Industry
University of Alaska Fairbanks
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(Reprinted August, 1991)

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Chapter 1

INTRODUCTION

Extensive exploration has resulted in delineation of a massive sulfide district on the north flank of the east-central Alaska range. The district covers approximately 400 square miles and contains numerous stratiform, transposed and some replacement type sulfide occurrences ranging in size from less than one million tons to over 20 milltion tons within a thick sequence of rift related metavolcanic and metasedimentary rocks comprising the Delta schist belt. Nerco Minerals Co. of Vancouver, Wa., controls a large block of claims, nearly 150 square miles of land, in the Delta district. The base and precious metal bearing massive sulfides are hosted by Devonian Age metavolcanics.

In 1984, Nerco Minerals Co. signed a cooperative agreement with the University of Alaska to conduct hydrometallurgical research. The principal objective of the agreement was to conduct bench scale research to study the problems of leaching the sulfide ore and the recovery of its valuable metals. Nerco has provided funding on an annual basis. Information contained in this publication is a result of this research.

Within the research program, complex sulfide ores are treated by ferric chloride leaching to dissolve zinc, lead, copper and silver. Leach residue is treated for gold recovery and the resulting leach liquor is directed to lead, copper, silver and zinc recovery steps. Lead chloride crystallization, solvent extraction and electrowinning of copper and zinc, and zinc powder cementation are the major technologies which will be applied to the metal recovery process. The barren solution is regenerated with chlorine gas produced in the electrowinning step and the regenerated solution is circulated back to the leaching step to complete the solution circuit. The use of ferric sulfate leaching has also been investigated.

This hydrometallurgy program is very important for Alaska for several reasons.

1. Alaska has numerous stratiform ores that are too finely disseminated to be amenable to standard physical beneficiation methods.
2. Sulfur in the ore is recovered as elemental sulfur, thus eliminating atmospheric pollution.
3. Hydrometallurgy results in a final metal product for domestic use or export, rather than a sulfide concentrate.
4. Hydrometallurgy permits construction of smaller scale installations than are possible with pyrometallurgy.
5. Alaska is blessed with numerous lode gold ores that would require cyanidation for gold recovery.

Success of the hydrometallurgy program is attributable to the vision of Lawrence E. Heiner, President, Nerco Mineral Co., who is responsible for initiating and funding the program, and to Chancellor O'Rourke, who has signed cooperative agreements with Nerco with a strong commitment for continuation of the hydrometallurgy research program. Special appreciation is due Dr. Donald J. Cook for his support of the program. The execution of the program is done under the constant vigil and guidance of Mr. Barry Hoffmann, Vice President, Nerco Minerals Co.. Dr. Raymond Price has been most helpful in guiding our solvent extraction research, during our meeting at Fairbanks, as well as through regular dialog. The help of Mr. Dan Walsh in the mineral processing portion of the program and in editing manuscripts is gratefully acknowledged. Special thanks are due Mrs. Cathy Farmer and Ms. Carol Wells for typing the manuscript.

Chapter 2

HYDROMETALLURGY OF THE DELTA SULFIDE ORES

First Stage Research

F. Letowski, K.T. Chou and P.D. Rao

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ABSTRACT

This report presents the results of hydrometallurgical research carried out from September 16, 1985 to June 30, 1986 on metals recovery from complex sulfide ores from the Delta deposit near Tok, Alaska. The leaching characteristics performed for 6 different ore samples indicate that the most valuable components form the following order: Zn > Au > Pb > Ag > Cu > S°. Further study demonstrates that direct leaching of the ore is effective both in chloride as well as in sulfate oxidizing solutions coupled with separating of leached solid components by flotation. Three variants of the ore processing with ferric chloride or ferric sulfate leaching are analyzed: one flowsheet with direct ore leaching in ferric chloride solution followed by leaching-flotation step, with subsequent zinc separation in a solvent extraction step and electrolysis in chloride solution; and two flowsheets of direct ore leaching with ferric sulfate solution followed by a leaching-flotation step, with zinc sulfate electrolysis and other metals recovery in chloride leaching steps. In two last flowsheets silver is recovered during the chloride leaching steps and gold from flotation products during the cyanide leaching. Preliminary economic and technical evaluation is presented.

The engineering study on apparatus for the fast leaching- flotation processing and on better accumulation of gold and silver in one semi-product are concluded for the next year of research.

2.1 Introduction

Most nonconventional hydrometallurgical methods of the processing of complex sulfide ores are based on metals extraction from bulk flotation concentrates [2.11-2.11]. The recovery of zinc, lead and copper by froth flotation, even as a relatively rich concentrate, presents today a rather routine problem. However, gold and silver, which are often associated with pyrite, can be rejected to the tailings during flotation. If the value of the rejected precious metals is high, additional leaching of tailings for their recovery (Figure 2.1,a) must be applied [2.12,2.13].

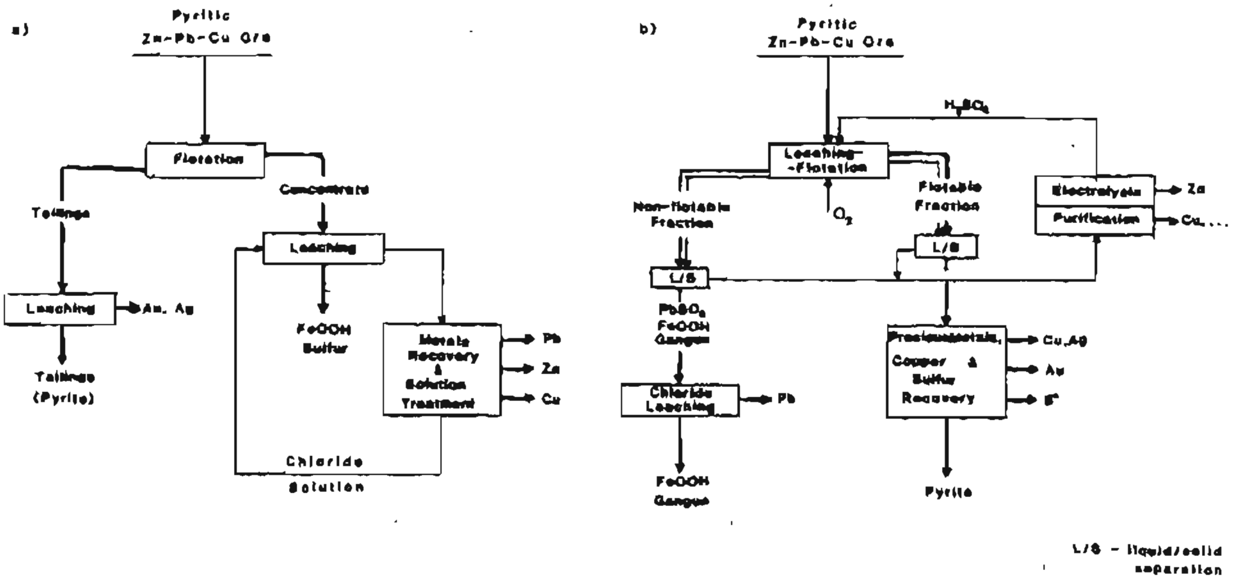

Figure 2.1. Hydrometallurgy of complex sulfide ores (gold and silver are associated with pyritic matrix):
a) Classical concept of hydrometallurgical processing of concentrate (example of chloride leaching)
b) Leaching-Flotation processing of ore (example of sulfate leaching).

Just such a situation occurs with the pyritic deposit of complex sulfide ores found near Tok, Alaska [2.14]. The gold and silver are predominantly associated with pyrite and their recovery in flotation concentrate is very low. Because their loss is not acceptable from an economic point of view, another possibility for processing the ore has been studied by the Mineral Industry Research Laboratory (MIRL) of the University of Alaska-Fairbanks. During initial investigations, three possible scenarios of hydrometallurgical processing of the Delta sulfide ores were discussed:

1) Bulk flotation concentrate production and their hydrometallurgical treatment;

2) Direct hydrometallurgical treatment of ore; and

3) Activation of pyrite by thermal shock and quasi-instantaneous leaching.

The conclusion of the preliminary analysis was that the second scenario is most favorable. Gold and silver - remaining in solid residues after leaching of the Delta ores can be concentrated by flotation in a separate fraction. Such a flotation associated with leaching in the ferric sulfate solution [2.15] allows for:

- selective extraction of zinc as soluble zinc sulfate;

$$ZnS(s) + Fe_2(SO_4)_3(aq) = ZnSO_4(aq) + 2FeSO_4(aq) + S^\circ(s) \quad (2.1)$$

- separation of insoluble lead sulfate, formed during galena oxidation by ferric sulfate solution, in the non-flotable fraction:

$$PbS(s) + Fe_2(SO_4)_3(aq) = PbSO_4(s) + 2FeSO_4(aq) + S^\circ(s) \quad (2.2)$$

- separation of other unreacted sulfides and sulfur in the flotable fraction;
- regeneration of the leaching agent under elevated oxygen pressure (30-120 psi) with simultaneous precipitation of iron excess in the form of goethite and its separation in the non-flotable fraction:

$$6FeSO_4(aq) + 3/2\ O_2(g) + H_2O(l) = 2FeOOH(s) + 2Fe_2(SO_4)_3(aq) \qquad (2.3)$$

Extraction of zinc, the principal valuable component of the complex sulfide ores, with the simultaneous separation of lead sulfate during direct ore processing and possible accumulation of precious metals dispersed in sulfide matrix, will be probably advantageous if technical problems were resolved. A simplified sketch of such processing is shown in Figure 2.1,b.

The possibility of separating by differential flotation valuable elements contained in residues after complex sulfide ore leaching, is also referred by Morin et al. [2.16]. Fugleberg et al. [2.17] describes the direct leaching and flotation of a black schist ore (Ni, Zn, Cu, Co sulfides) . Wakamatsu et al. [2.18] presents a study on complex sulfide concentrate leaching with 60% (vol.) sulfuric acid. This allows for a near total zinc dissolution (99% of recovery) while chalcopyrite remains at all in the solid residue. After filtration, the insoluble lead sulfate is separated from chalcopyrite by routine differential flotation. Also Mantsevich et al. [2.19] presents a paper on oxidative leaching and flotation of nickeliferrous pyrrhotite concentrates. None of these publications, nor any recently published paper addresses the application of a leaching-flotation process for recovering or concentrating precious metals.

During 1986, research initiated by MIRL to study the recovery of metals from the Delta sulfide ores has been comprised of the following tasks:

1. A study of the ore leaching kinetics with chloride and sulfate solutions.
2. A laboratory study of the leaching-flotation process.
3. An engineering study of an iron oxidation processes.
4. A general study of proposed process-flowsheets.

Results of the above research are presented in this report.

2.2 Chemical Characteristics of Ore

Six bulk samples of ore were collected from the Delta Massive Sulfide belt [2.14]. The concentration of metals and sulfur in the samples is presented in Table 2.1.

The chemical characteristic of the ore samples is presented in Table 2.2. It is based on metals and sulfur content and on reactivity of the ore samples during digestion in three different solutions:

- aqua regia, at temp. 90-95°C;
- sulfuric acid, conc. 10%, at 80-90°C;
- hydrochloric acid, conc. 10%, at 70-80°C.

Because the ore samples are characterized with respect to their chemical reactivity only, the chemical symbols of substances do not necessarily correspond to their mineralogical formations and the quantitative characteristics presented in Table 2.2 differ slightly from the mineralogical description of the ore samples presented previously in the Research Grant Proposal [2.20].

In the tests of chemical reactivity, 1-3 grams samples of ore were digested in aqua regia (conc. HNO_3: conc. HCl as

Table 2.1. Elemental composition of Delta ore samples

Sample No.	Description	Quant. lbs	Zn %	Pb %	Cu %	Au ppm	Ag ppm	As %	Fe %	Total Sulfur %
1	LP Upper	330	6.63	2.83	0.38	3.48	92.7	0.56	32.25	34.72
2	LP Lower	200	7.34	2.98	0.40	2.61	102.9	0.91	32.11	35.56
3	DD South	150	0.16	0.06	0.80	0.75	8.1	0.02	47.33	41.58
4	Trio	300	7.50	7.30	1.35	3.98	118.8	6.99	25.03	27.52
5	DD North	226	2.68	1.20	1.50	1.93	34.5	0.73	43.07	41.73
6	DD North	160	8.63	0.08	1.18	0.62	7.8	0.02	44.20	31.07

Table 2.2. Contents of sulfides and other components in the ore samples

Sample				Weight percent							
		ZnS	PbS	FeS	$CuFeS_2$	FeAsS	FeS_2	Fe(ox)	Ca	Insoluble Residue	Total Identified
#1	LPU	9.88	3.25	1.54	1.10	1.22	55.86	4.52	0.35	15.2	92.92
#2	LPL	10.94	3.45	1.97	1.16	1.97	56.11	3.71	0.74	13.52	93.57
#3	DDS	0.34	0.07	38.5	2.31	0.03	47.93	—	0.03	4.79	94.0
#4	TRIO	11.18	8.42	2.36	3.89	15.14	32.75	1.91	4.35	4.67	84.67
#5	DDN	3.99	1.39	23.01	4.33	1.58	56.20	0.44	6.10	1.76	98.80
#6	DDN	12.71	0.10	53.55	3.41	0.03	11.50	3.77	0.02	6.56	91.65

1:3), 10-20g samples in 10%-sulfuric acid and 10g samples were digested in 10% hydrochloric acid.

Only in the case of sample #3 (DDS) the balance of total iron is negative. 1.3% of iron is lacking for equilibrating its total concentration with concentration of copper as $CuFeS_2$, arsenic as FeAsS and iron "soluble" in 10% HCl - identified as FeS.

In other samples an excess of 0.4 to 4.5% of iron was not equilibrated with sulfidic sulfur. This iron excess is arbitrarily identified as a non-sulfidic iron, probably in oxide or carbonate form (Table 2.2). Relatively high concentration of calcium probably from carbonaceous rock was found in sample #4 (TRIO) - 4.35% Ca and #5 (DDN) - 6.10% Ca. The highest percent of insoluble residue after aqua regia digestion was found in sample #1 (LPU) - 15.2% and #2 (LPL) - 13.52%.

Mass balance of the identified components (last column in Table 2.2) range from at 84.7% for sample #4 (TRIO) to 98.8% for #5 (DDN). In the case of the sample #5, this is probably too large a value since when oxidized iron and total calcium occur as carbonates, the mass balance for the sample sums to 108.4%.

The loss of weight for the samples during the digestion tests in aqua regia, HCl and H_2SO_4 solutions as well as during 4 hour-leaching in ferric chloride and ferric sulfate solutions is shown schematically in Figure 2.2. For the sample #1 (LPU) and #2 (LPL) the loss of weight is a function of the following order:

Aqua regia >> $FeCl_3$ > $Fe_2(SO_4)_3$ > HCl > H_2SO_4

The higher dissolution of components in samples 3, 5, and 6 in reductive (HCl) or nonoxidative (H_2SO_4) than in oxidative ($FeCl_3$, $Fe_2(SO_4)_3$) conditions can be explained by the high concentration of iron sulfide FeS in the ore samples. This sulfide is easy to decompose with the evolution of gaseous hydrogen sulfide (H_2S).

Sample #4 (TRIO) is characterized by a higher loss of weight in chloride solution than in sulfate solution. In the sulfate solution galena is transformed to insoluble lead sulfate and in the chloride solution total lead forms soluble chloride complex.

The metals extraction from the ore samples during leaching with sulfuric acid, hydrochloric acid, ferric chloride and ferric sulfate solutions presented in Table 2.3 is a supplementary illustration of chemical properties of raw material.

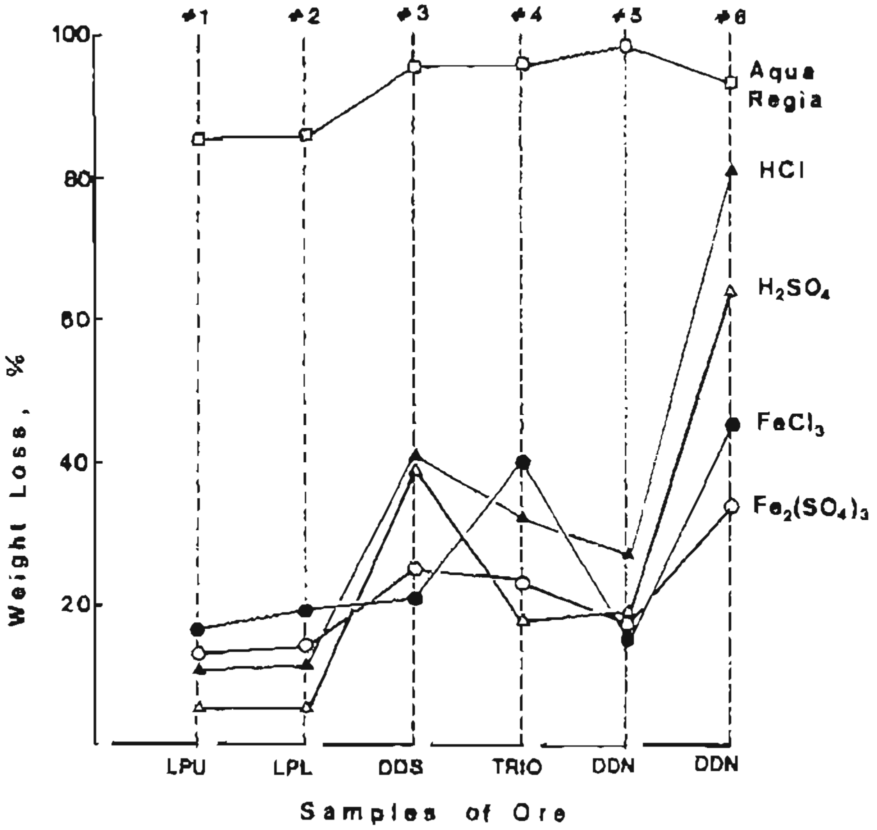

Figure 2.2. Loss of weight of the ore samples during digestion in different solutions. Test conditions - see Table 2.3.

Table 2.3. Metal extraction from the ore samples by different solutions:
10% H_2SO_4 at 80-90°C; 10% HCl at 70-80°C; $Fe_2(SO_4)_3$ 1.2M at 90°C; $FeCl_3$ 1.8M at 90°C

Metal Extracted	Extracting Solution	Extraction degree, % *)					
		#1 (LPU)	#2 (LPL)	#3 (DDS)	#4 (TRIO)	#5 (DDN)	#6 (DDN)
Zn	H_2SO_4	28.6	25.1	100	3.8	16.3	52.7
	HCl	81.4	23.4	100	6.3	100	100
	$Fe_2(SO_4)_3$	97	97	–	98.0	94	98.0
	$FeCl_3$	95	98	88.7	97.23	85	74.0
Pb	HCl	96.8	158.1	Total	Total	Total	Total
	$FeCl_3$	96.2	96.7	92.2	83.2	100	96.9
Cu	HCl	4.5	3.0	1.1	1.2	11.9	35.8
	$Fe_2(SO_4)_3$	75	80	3.0	34	37	23
	$FeCl_3$	61.2	80	37.7	15.5	45.5	28.3
Fe	H_2SO_4	3.4	7.5	56.9	5.1	39.9	118.9
	HCl	3.0	3.9	62.6	6.1	33.0	77.8
	$Fe_2(SO_4)_3$	15	22	32	5	47	54
	$FeCl_3$	1.52	n.i.	n.i.	7.6	n.i.	80
As	H_2SO_4	<1	<1		2.5	<1	–
	HCl	8	5	–	1.7	<6	–
	$Fe_2(SO_4)_3$	n.i.	n.i.	n.i.	22.5	n.i.	n.i.
Ag	HCl	27.1	30.7	18.5	12.1	84.9	79.5
	$FeCl_3$	85.2	83.2	60	24.2	86.7	75

*) after 8h of digestion with excess of the solution
n.i. not identified

2.3 Tests of Ore Leaching with Ferric Sulfate Solution

The following tests of ferric sulfate leaching were performed at laboratory scale:

- a long-time, static-bed leaching test, of ore sample #1 (LPU), fraction size 10-14 mesh;
- tests of zinc extraction from different size fractions of ore sample #1 (LPU):

  60 - 150 mesh
  150 - 270 mesh
  270 - 400 mesh
  325 - 400 mesh
  < 400 mesh

- a three-step leaching test of the 325-400 mesh fraction of ore sample #1 (LPU);

- tests of zinc, copper and iron extraction from the fraction 325-400 mesh of the six investigated ore samples.

The long-time leaching test in a static bed condition was carried out in a glass column (24 inch height, 3/4 inch diameter) filled with 314.1g of ore sample #1, fraction 10-14 mesh. 4L of acidic ferric sulfate solution, initially containing 23.8 g/L Fe in 7.5% $H2SO_4$ was continuously circulated upwards the column during 27 days, with average flow rate of 0.4-0.6 L/h. The temperature of the column was kept at 20-23°C. Concentrations of zinc, copper, and iron were analyzed and pH was measured in 10 ml samples of solution taken during the experiment. The results of the test are shown in Figure 2.3.

To determine the degree of transformation of galena PbS, to insoluble lead sulfate $PbSO_4$, additional chloride leaching of the ore bed was performed after completing the 27 day sulfate leaching test. 1.58 liter of leaching solution containing 240 g/L $CaCl_2$ and 1% HCl was used. The chloride leaching test was conducted during 24 hours in the same conditions of circulation as the sulfate leaching test. These results are also shown in Figure 2.3.

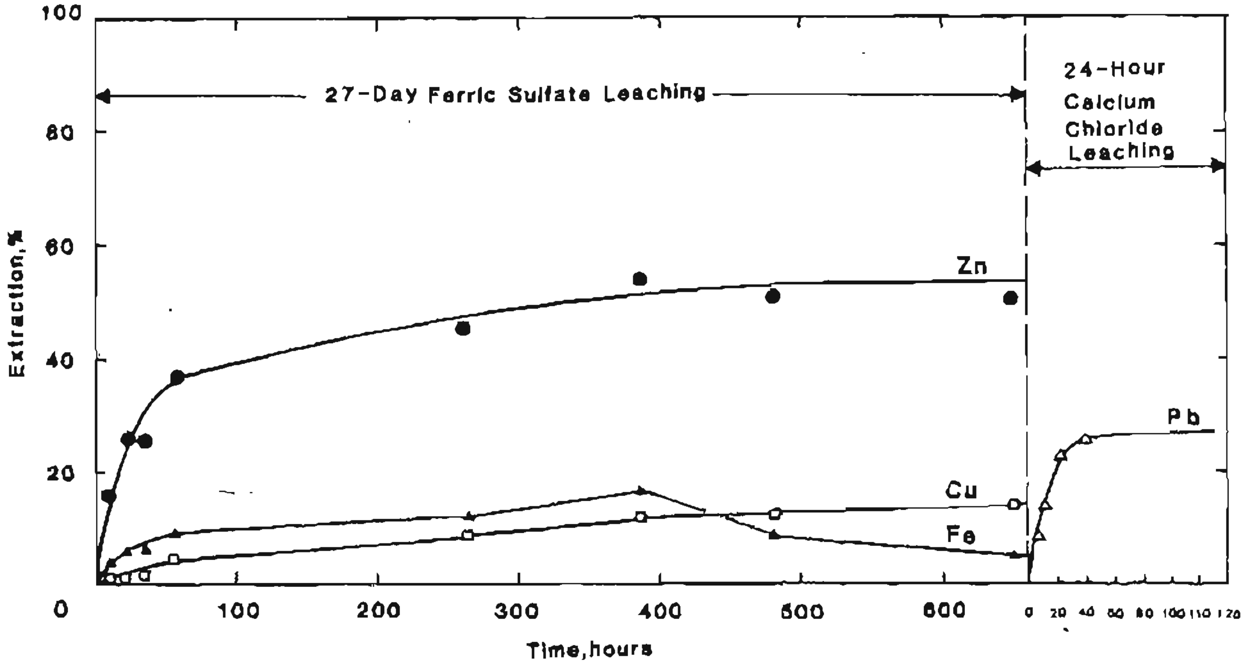

Figure 2.3. Extraction of metals in the column-leaching test in ferric sulfate - sulfuric acid solution and in calcium chloride - hydrochloric acid solution at temp. 20-22°C; - ● zinc, □ - copper, ▲ - iron, △ - lead. (Other conditions in the text.)

After both tests the bed of ore was washed in the column by water and the concentration of metals found in the wash-water was taken into account during mass balance calculations.

Other tests of leaching were carried out in a 1 liter Corning-glass reactor with a cover and other standard equipment under steady state hydrodynamic conditions (mixing) at constant temperature.

Results of zinc extraction from different size fractions of sample #1 are shown in Figure 2.4 and specific conditions of these leaching tests are collected in Table 2.4.

The results of the 3-step leaching experiment carried out on the fine fraction (325-400 mesh) of sample #1 are presented in Figure 2.5 and in Table 2.5.

The concentration of ferrous ions was calculated from a standardized $[Fe3^{+}]/[Fe^{2+}]$ = f(potential, mV) graph or calculated from the balance of sulfidic sulfur oxidation during leaching.

Results of the tests on metal extraction from the fine fractions (325-400 mesh) of the six investigated ore samples are presented in Figures 2.6-2.12.

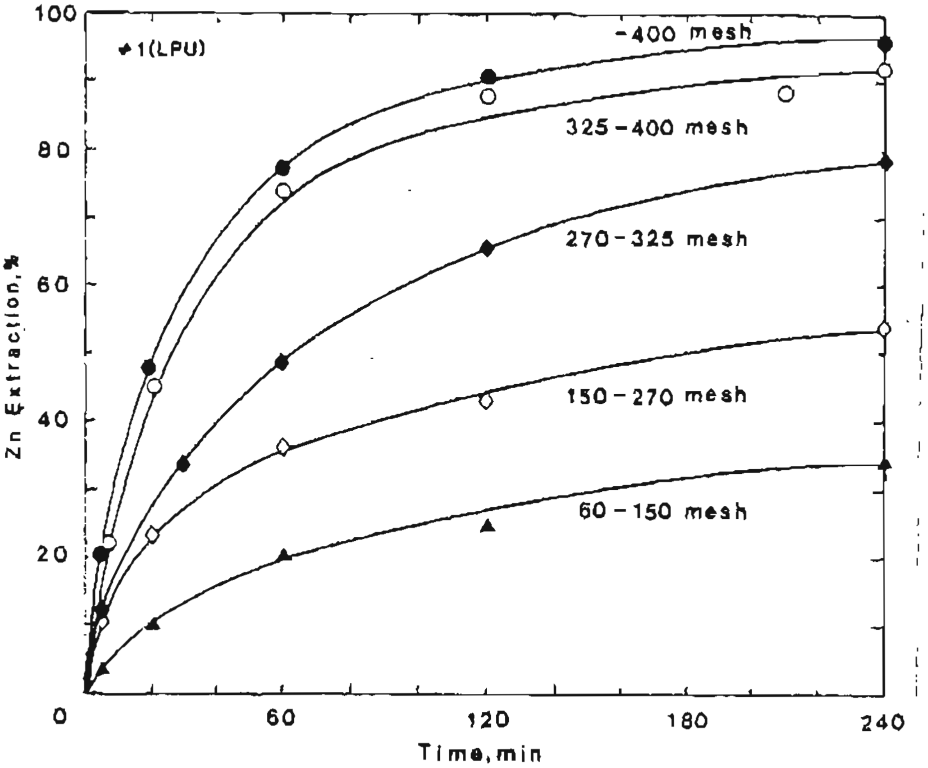

Figure 2.4. Effect of size fraction of the ore on zinc extraction. Ore sample #1 (LPU). Conditions of leaching - see Table 2.4.

Table 2.4. Leaching conditions of different fractions of ore sample #1. Temperature 90°C, stirrer rotation 250-300 min-1. Loss of weight of ore sample after 4 h of leaching is presented in the last column.

Size fraction of ore (mesh)	Initial solid/liquid ratio (g/ml)	Initial Concentrations[1] Fe[2] (g/L)	Zn (g/L)	Cu (g/L)	H_2SO_4 (%)	Loss of weight (%)
60-150	60/700	69	6.6	0.2	2.4	11.28
150-270	60/700	69	6.6	0.2	2.4	12.78
270-325	50/700	52	5.6	0.3	1.2	14.42
325-400	30/700	50	9.2	0.3	1.2	17.44
<400	60/700	52	5.6	0.3	2.4	19.35

1) Conc. in solutions after regeneration under oxygen pressure (see p. 34)

2) Total iron concentration, with $[Fe^{2+}] < 10\%$ of total iron

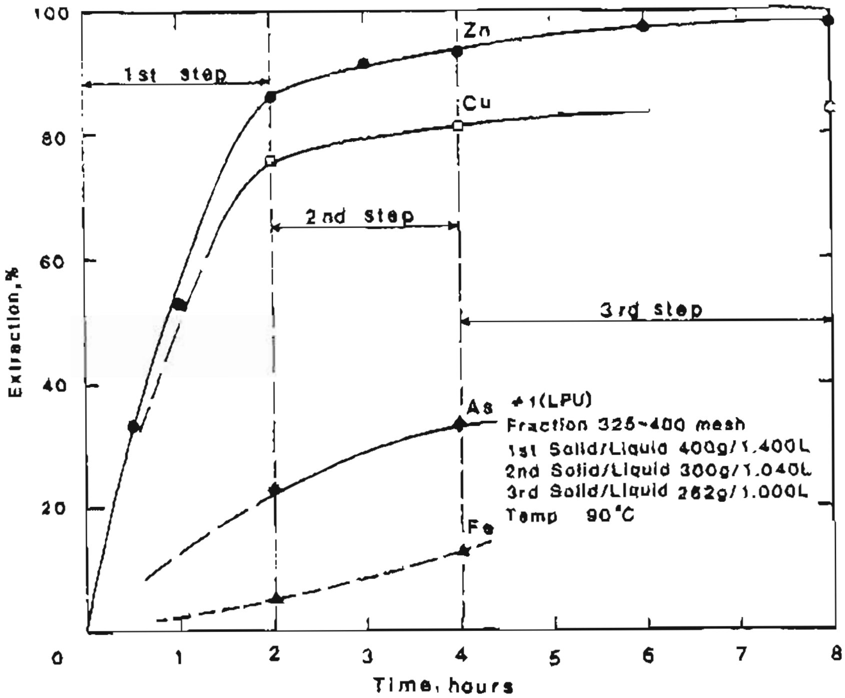

Figure 2.5. Metals extraction during 3-step ferric sulfate leaching of the fine fraction of ore sample #1: ● - zinc, □ - copper, ♦ - arsenic, ▲ - iron.

Table 2.5. Some conditions and results of 3-step leaching of the fine fraction (325-400 mesh) of sample #1. Kinetic of leaching and other conditions are shown in Fig. 2.5.

Step of Leaching		Concentrations (g/L)				Extraction (%)				Loss of weight %
		Fe^{3+}	Fe^{2+}	Zn	Cu	Zn	Cu	As	Fe	
1st	Initial*	79.2	42.8	24.1	0.82					
	Final	40.7	88.3	40.5	1.74	86.3	75	23	5	14.6
2nd	Initial*	79.2	42.8	24.1	0.82					
	Final	77.0	52.2	25.7	0.92	93.2	81	33	12	20.6
3rd	Initial*	129.6	—	—	1.18					
	Final	126	~6	1.3	1.20	96.0	82	nd	nd	26.3

* in 1% H_2SO_4 solution

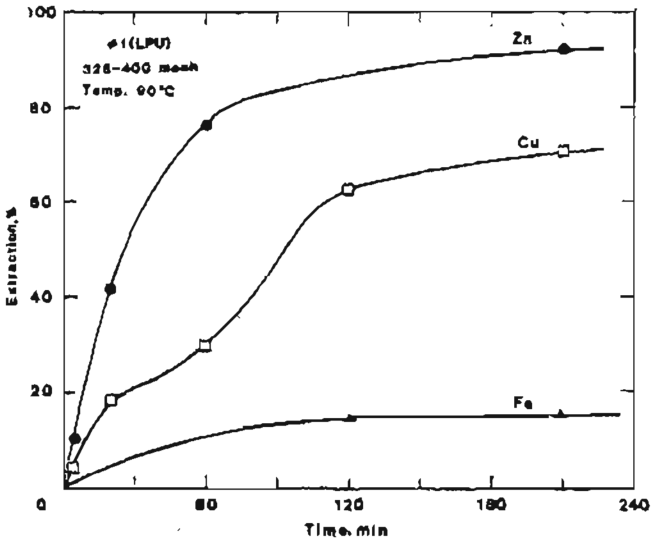

Figure 2.6. Ferric sulfate leaching of ore sample #1,; weight of sample 30 g; solution 0.7L; initial concentration: Fe^{3+} 46.1g/L, Fe^{2+} 25.3g/L, Zn 18.9g/L, Cu 0.45g/L, H_2SO_4 1%. Loss of the sample weight during leaching 17.07%.

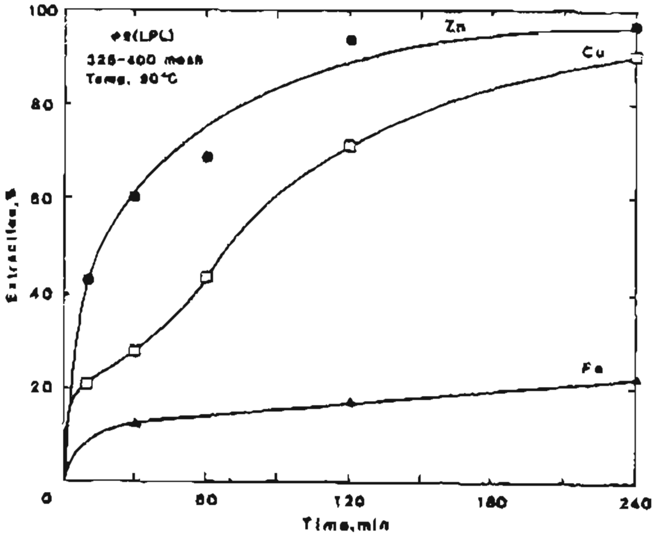

Figure 2.7. Ferric sulfate leaching of ore sample #2; solid/liquid = 50 g/0.7 L; initial concentration: Fe^{3+} 40.9g/L, Fe^{2+} 26.7g/L, Zn 13.45g/L, Cu 0.38g/L, H_2SO_4 1%. Loss of the sample weight during leaching 20.56%.

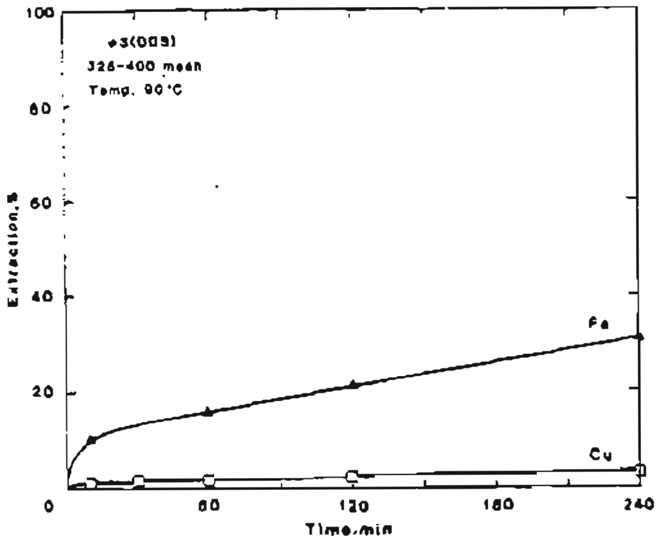

Figure 2.8. Ferric sulfate leaching of ore sample #3; solid/liquid = 50 g/0.7 L; initial concentration: Fe^{3+} 46.0g/L, Fe^{2+} 23.2g/L, Zn 13.56g/L, Cu 0.04g/L, H_2SO_4 1%. Loss of the sample weight during leaching 25.09%.

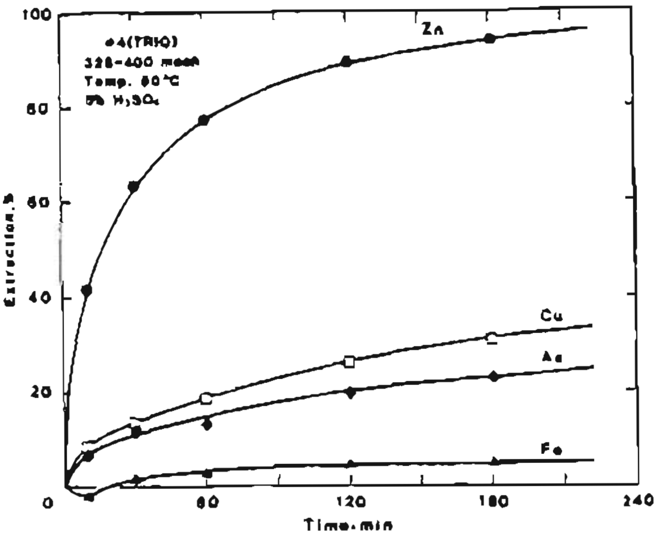

Figure 2.9. Ferric sulfate leaching of ore sample #4; solid/liquid = 50 g/0.7 L; initial concentration: Fe^{3+} 20.2g/L, H_2SO_4 5%. Loss of the sample weight during leaching 40%.

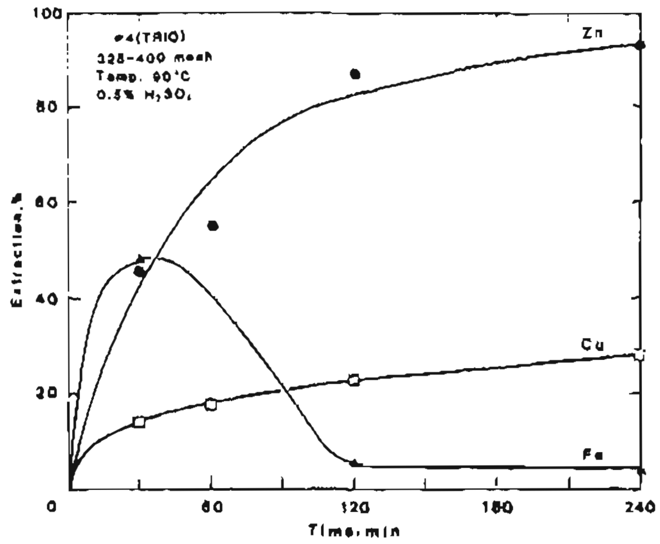

Figure 2.10. Ferric sulfate leaching of ore sample #4; solid/liquid = 50 g/0.7 L; initial concentration: Fe^{3+} 108.0g/L, Fe^{2+} 30.4g/L, Zn 16.72g/L, Cu 0.512g/L, H_2SO_4 <0.5%. Loss of the sample weight during leaching 20.06%.

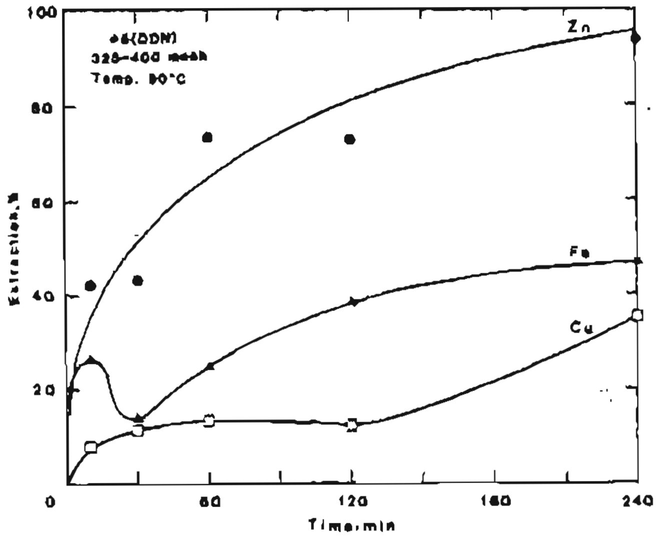

Figure 2.11. Ferric sulfate leaching of ore sample #5; solid/liquid = 50 g/0.7 L; initial concentration: Fe^{3+} 99.2g/L, Fe^{2+} 29.0g/L, Zn 15.9g/L, Cu 0.526g/L, H_2SO_4 1%. Loss of the sample weight during leaching 15.0%.

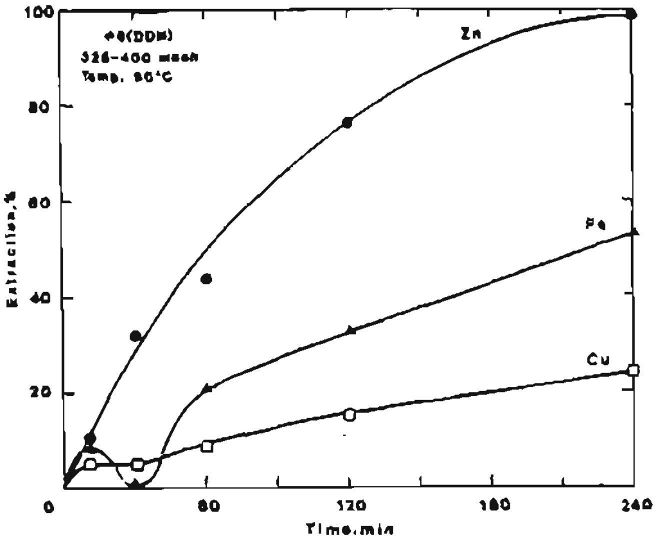

Figure 2.12. Ferric sulfate leaching of ore sample #6; solid/liquid = 50 g/0.7L; Initial concentration: Fe^{3+} 113.8g/L, Fe^{2+} 30.4g/L, Zn 16.6g/L, Cu 0.57g/L, H_2SO_4 1%. Loss of sample weight during leaching 34.8%.

Pure ferric sulfate solution in 5% sulfuric acid was applied as a leaching agent only in the tests carried out on sample #4 (Figure 2.9). In other cases, the leaching tests were performed with solutions containing elevated concentration of zinc sulfate and ferrous sulfate, and not higher than 1% concentration of sulfuric acid. The tests conducted with a low acid concentration are characterized by a decrease of copper extraction rate or by hydrolytic copper precipitation from the solution during the first hour of leaching. At 90°C this phenomenon is a function of iron concentration and pH of solution and occurs even when the copper concentration in solution is below 1 g/L (Figure 2.13).

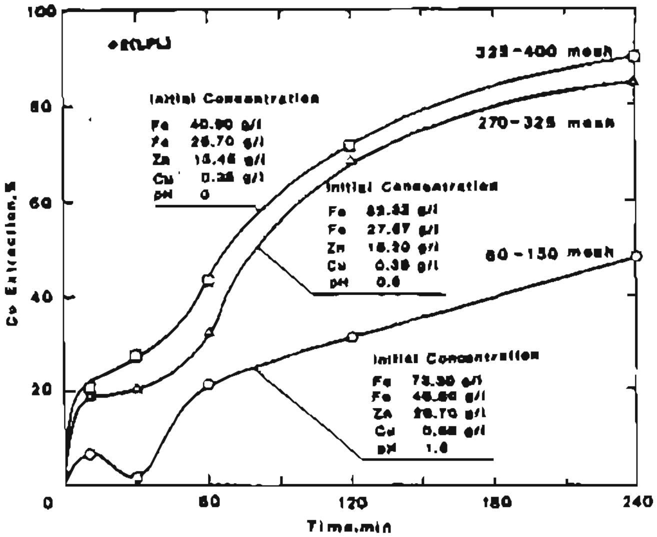

Figure 2.13. Ferric sulfate leaching of ore sample #2. Effect of iron(III) concentration and pH of leaching solution on copper extraction from 3 different size fractions of the ore at 90°C. Solid/liquid = 50 g/0.7L

Secondly, hydrolytic iron precipitation was observed during leaching of samples #5 and 6 with solution containing high concentration of ferric ions. Iron concentration in solution increases much more because of the fast decomposition of iron sulfide FeS (Figures 2.11 and 2.12). Another cause of iron precipitation during the leaching of sample #4 might be its high arsenopyrite - FeAsS concentration (Figures 2.9 and 2.10). Arsenates of iron(II) and iron(III) can be easily precipitated from low acidity solutions (Figure 2.10).

In the case of sample #3, high concentration of iron sulfide FeS (see Table 2.2), caused fast and total reduction of ferric sulfate long before leaching was completed. Under the test conditions (Figure 2.9) only fifty percent of the FeS was decomposed due to the lack of leaching agent.

2.4 Tests of Ore Leaching with Ferric Chloride Solution

The leaching of complex sulfide ores with ferric chloride solution leads to dissolution of lead together with zinc and copper.

Ferric chloride leaching tests were conducted in a 1 L Corning-glass reactor under the same operational conditions as for sulfate leaching. During some initial experiments the temperature was kept at 80°C.

The high concentration of chloride ions necessary to keep the extracted metals in soluble form, was achieved by calcium chloride and magnesium chloride addition. Total chloride ions concentration supplied from these sources was 2.54 mol/L. The leaching tests were performed on the size fraction of 140-270 mesh of the six ore samples (Figures 2.14-2.19).

Metals extraction and loss of weight of the samples after 4 hours of leaching is compared in Table 2.6.

Two stage leaching tests were performed on sample #1 and 2 (Figures 2.14 and 2.15). Results indicate that prolongation of leaching time for an extra 2-4 hours raises the yield of metals extraction.

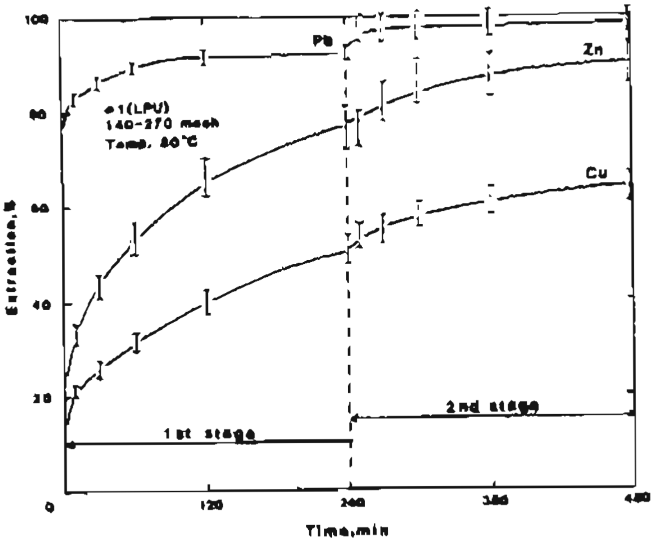

Figure 2.14. 2-stage ferric chloride leaching of ore sample #1; solid/liquid = 75 g/0.6L (1st stage) and 56.5 g/0.6L (2nd stage); Initial concentrations: [$CaCl_2$] = 58g/L, [$MgCl_2$] = 79g/L, [HCl] = 0.4g/L, [Fe^{3+}] = 99.8g/L (1st stage) and 64g/L (2nd stage).

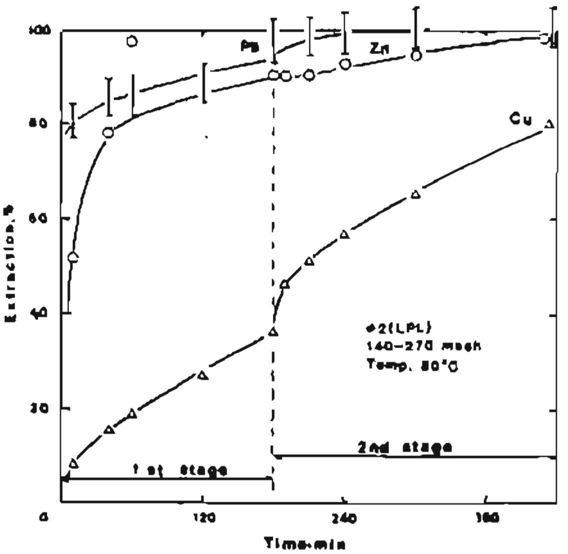

Figure 2.15. 2-stage ferric chloride leaching of ore sample #2; solid/liquid = 55 g/0.6L (1st stage) and 42 g/0.6L (2nd stage); initial concentrations: [$CaCl_2$] = 58g/L, [$MgCl_2$] = 79g/L, [HCl] = 0.4g/L, [Fe^{3+}] = 64g/L.

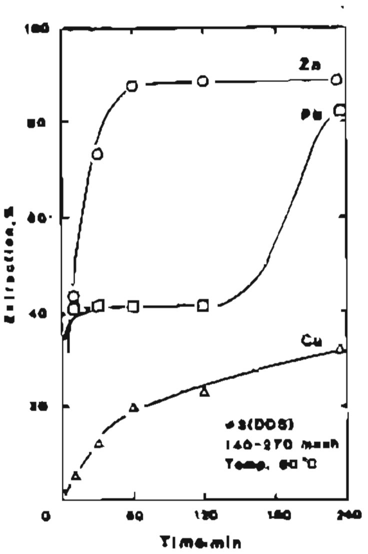

Figure 2.16. Ferric chloride leaching of ore sample #3;solid/ liquid = 50 g/0.64 L; initial concentrations: [$CaCl_2$]=58g/L, [$MgCl_2$]=79g/L, [Fe^{3+}]=90g/L, [HCl] = 4g/L .

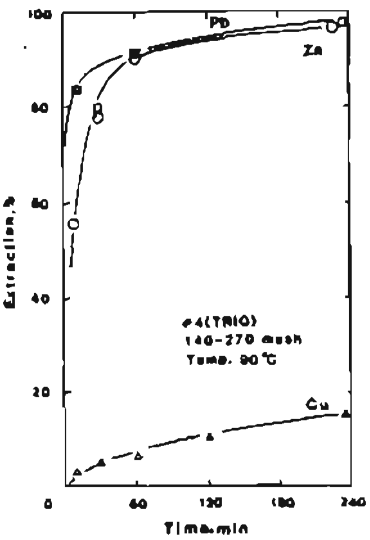

Figure 2.17. Ferric chloride leaching of ore sample #4;solid/ liquid = 50 g/0.6 L; initial concentrations: [$CaCl_2$]=58g/L, [$MgCl_2$]=79g/L, [Fe^{3+}]=90g/L, [HCl] = 4g/L.

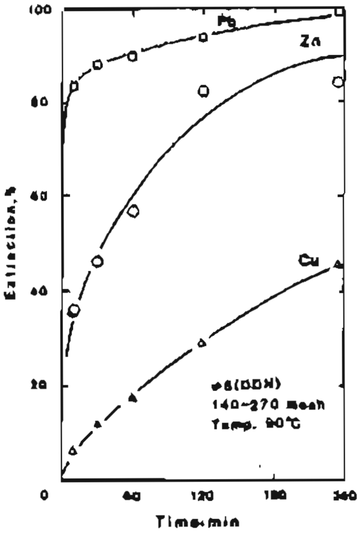

Figure 2.18. Ferric chloride leaching of ore sample #5;solid/ liquid = 50 g/0.6 L; initial concentrations: [CaCl$_2$]=58g/L, [MgCl$_2$]=79g/L, [Fe^{3+}]=90g/L, [HCl] = 4g/L .

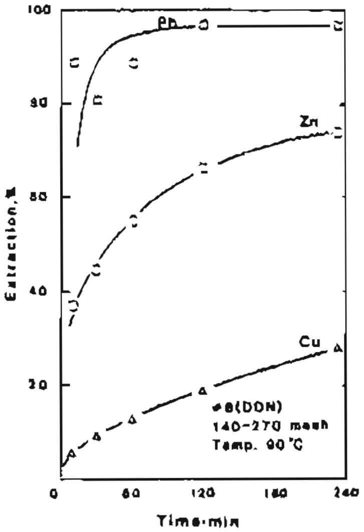

Figure 2.19. Ferric chloride leaching of ore sample #6;solid/ liquid = 20 g/0.6 L; initial concentrations: [CaCl$_2$]=58g/L, [MgCl$_2$]=79g/L, [Fe^{3+}]=94g/L, [HCl] = 4g/L .

Table 2.6. Metals extraction and loss of the samples weight after 4 hours of leaching. Fraction 140-270 mesh. Other conditions: see Figures 2.14-2.19.

	Metals Extraction (%)					Loss of weight (%)
Sample	Fe	Zn	Pb	Cu	Ag	
#1 - LPU[1)]	1.52	94.85	96.19	61.16	85.24	15.82
#2 - LPL[1)]	-7.6[2)]	98.57	96.70	80.00	83.16	18.89
#3 - DDS	-9.9[2)]	88.75	83.95	32.75	60.00	21.52
#4 - TRIO	7.6	97.23	97.01	15.50	24.19	41.20
#5 - DDN	0.0	85.07	100.00	45.47	86.67	15.70
#6 - DDN	79.9	74.32	96.88	28.26	75.00	46.80

1) All results after 2-step leaching
2) Percent of iron precipitated from solution as an excess in relation to the initial content of iron in the ore sample

The results of lead extraction from sample #3 differ from that in other cases (Figure 2.16). This anomalous course of leaching is difficult to explain. The most probably reason is that the detection level during lead analysis by AAS (Atomic Absorption Spectrometry) technique is below the low Pb concentration in the sample (see Table 2.1).

Iron extraction is very low or some part of iron precipitates from solution at low acid concentration (Table 2.6). However, when pH ≤ 0, iron dissolved from the solid sample remains in solution. Such a situation characterizes the test with sample #6, when hydrochloric acid concentration was 14 g/L HCl and about 80% of total iron in sample occurs as "soluble" FeS.

Silver extraction is high. It fluctuates from 24% (sample #4) to 83-87% for the samples #1, 2 and 5 (Table 2.6). Some regularity with copper extraction is observed.

2.5 Tests of the Leaching-Flotation Process

The leaching-flotation tests were carried out on sample #1 (LPU) and #4 (TRIO). Several characteristics of the samples were described in Section 2.2. The quantitative compositions of the samples werepresented in Tables 2.1 and 2.2 and the leachability of the samples in ferric sulfate solution is described in Section 2.3.

The leaching-flotation tests were conducted in the same typical laboratory Pyrex-glass reactors (volume 1 or 2L) as were used in the leaching tests (see Sections 2.3 and 2.4).

The leaching tests were easy to shift into the leaching-flotation tests by introducing air or oxygen into the reactor and dispersing it in leaching suspension. The laboratory reactor equipped for the leaching-flotation tests is presented schematically in Figure 2.20.

The froth of the flotable fraction of solids was transported through glass tube-connector to the next step-reactor or was collected in a Büchner funnel, filtered and prepared for analysis. The non-flotable fraction was retained in the form of suspension in the lower part of the reactor or sedimented at the reactor bottom. This fraction could be transported to another reactor using a peristaltic pump. The simplified flowsheet of a 3-step leaching-flotation tests is shown in Figure 2.21.

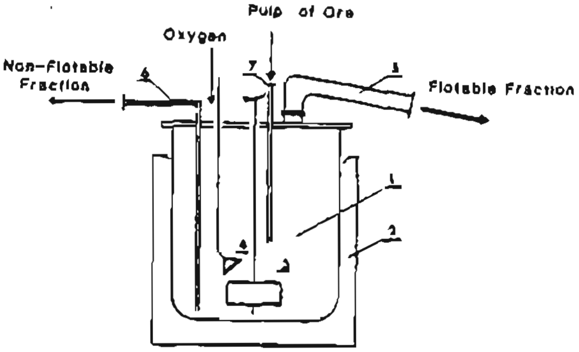

Figure 2.20. Laboratory reactor for leaching-flotation tests:
1. Glass reactor
2. Heater
3. Stirrer
4. Gas dispersion tube (medium porosity)
5. Outlet of foam (flotable fraction)
6. Outlet of non-flotable fraction
7. Inlet of ore pulp

In these experiments the pulp of ore in the leaching solution was transported continuously to the first reactor. From the 1st reactor only flotable fraction was transported in a froth flow formed by dispersed in solution oxygen, to the second reactor and afterwards in the same manner from second to the third reactor. At the same time, the non-flotable fraction was transported as a suspension in the leaching solution from the third reactor to the second and subsequently to the first reactor by means of peristaltic pumps.

Three leaching-flotation (L-F) tests were carried out with ore sample #1 (LPU) and two with ore sample #4 (TRIO). The 1st, 2nd and 5th L-F test followed the initial sulfate leaching step (Figure 2.22). The 3rd and 4th L-F tests were followed

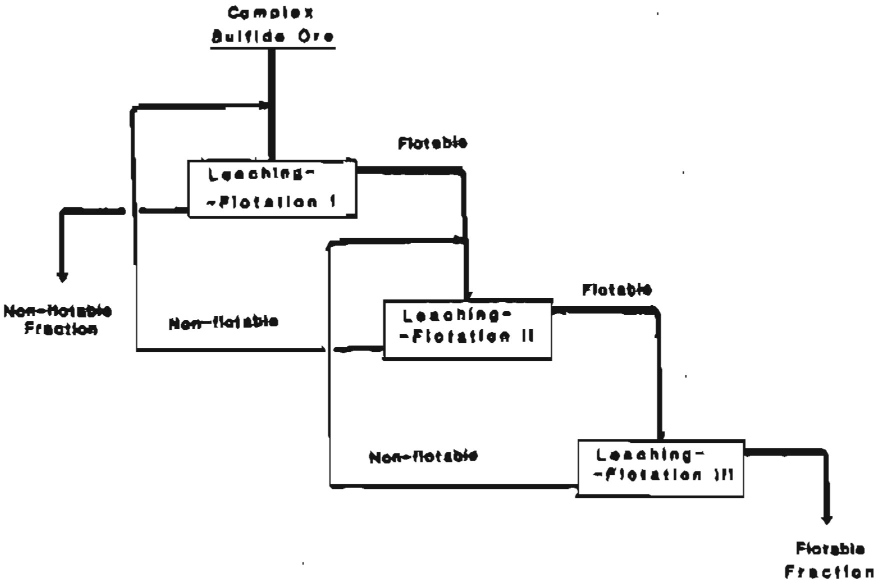

Figure 2.21. Simplified flowsheet of 3-step leaching-flotation test.

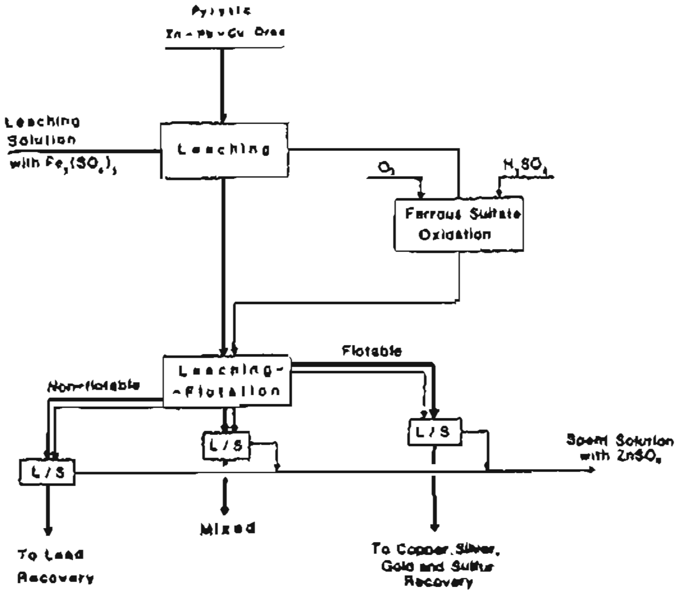

Figure 2.22. Arrangement of the 1st, 2nd and 5th L-F tests. Leaching-flotation steps follow initial sulfate leaching step.

by sulfate leaching of the flotable fractions and by chloride leaching of the nonflotable fractions (Figure 2.23).

General conditions of the leaching-flotation tests are presented in Table 2.7.

The 1st and 5th experiments were performed with small solid samples in the one, 1L volume unit (Figure 2.20). The flotation products were cleaned in additional flotation steps, according to schematic flowsheet shown in Figure 2.24. The intermediary fractions were collected together as a "MIXED" fraction.

Results and other conditions of the tests are summarized in Tables 2.8 and 2.9.

The direct, leaching-flotation treatment of the ore was applied in the 3rd and 4th experiments. During the 2-hour 3rd experiment, 79% of the zinc and 33.5% of the copper were extracted from the ore sample #1 to the solution and 77.5% of the lead was found in the nonflotable fraction. The copper remaining in solid phase was collected in the flotable fraction together with 82% of the total iron, 90% of the silver and 96.6% of the elemental sulfur.

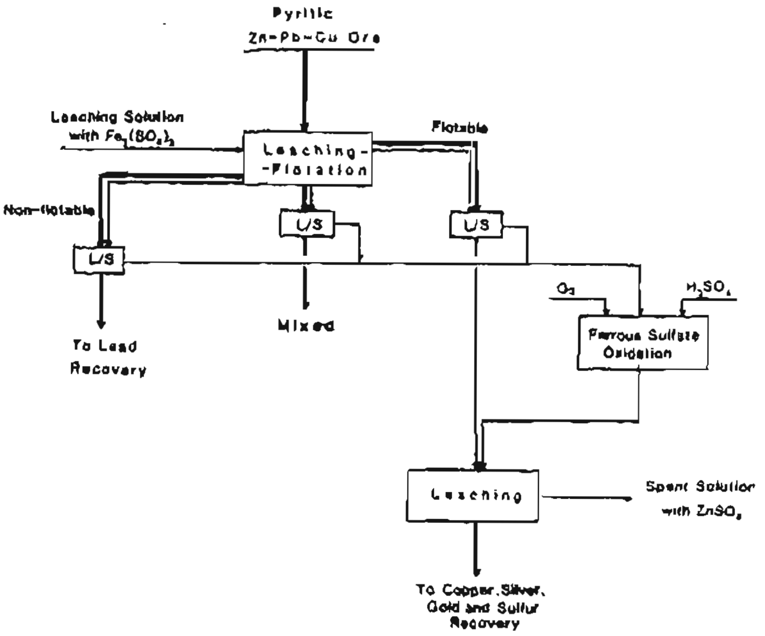

Figure 2.23. Arrangement of the 3rd and 4th L-F test. Sulfate leaching follows leaching-flotation step.

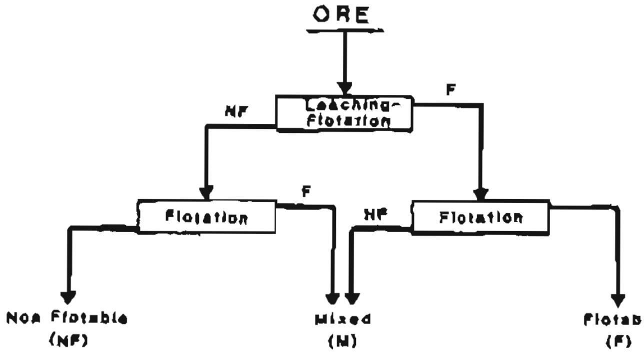

Figure 2.24. Scheme of the leaching-flotation batch experiments.

Table 2.7. General conditions of the leaching-flotation (L-F) tests in ferric sulfate solution at 90°C

Sample		#1 (LPU)			#4 (TRIO)	
Specification \ Test		1st	2nd	3rd	4th	5th
Initial weight of sample(g)		150.45	567[1]	1200	367	177.1
Sample weight before L-S step[2] (g)		129.87	500	1200	367	137.0
Size fraction (mesh)		140-325	325-400	140-325	140-270	325-400
Total volume of solution (L)		0.8[3]	2.8	3.0	3.33	1.8[4]
Initial concentration (g/L) and pH in solution	Fe^{3+}	45.3	74.7	70.0	84.4	20.0
	Fe^{2+}	9.3	27.3	27.2	9.5	—
	Zn	4.8	14.2	14.1	5.2	—
	Cu	0.31	0.78	0.76	0.19	—
	pH	–	0.75	0.85	1.2	0.91
Experimental arrangement[5]		A-1	A-2	B-2	B-2	A-1
Time of experiment		20 min	1 hr	2 hr	1 hr	30 min

1) Calculated; only 500 g of solid was directed to L-S step from 712 g of the total sample weight before leaching (see remark 5).

2) See remark 5

3) 0.5 L of solution +0.3 L of wash water

4) 1.0 L of solution +0.8 L of wash water

5) A - according to scheme in Fig. 2.22
B - according to scheme in Fig. 2.23
1 - bath process, according to Fig. 2.24
2 - 3-step continuous process, according to Fig. 2.21

Table 2.8. Leaching-flotation tests of sample #1 (LPU):

a) Mass distribution and metal concentrations in the flotation fractions and leach solution

	Specification	Fraction distribution (%)	Concentration (%)[1]						
			Zinc	Lead	Copper	Iron	Sulfur[2]	Silver	Gold
1st Experiment	Raw Material[3]	100	1.02	3.23	0.21	35.65	4.3	106ppm	3.42ppm
	Non Flotable Fraction (NF)	9.8	0.25	18.55	0.12	3.12	1.61	138ppm	0.17ppm
	Mixed Fraction (M)	3.3	–	–	–	32.12	3.85	45ppm	–
	Flotable Fraction (F)	76.3	0.65	1.8	0.25	50.50	5.25	106ppm	4.09ppm
	Solution	11.6[4]	From 4.80 to 6.11 g/L	–	–	From 54.6 to 59.5 g/L	–	–	–
2nd Experiment	Raw Material[3]	100	4.30	3.35	0.27	30.4	2.04	105ppm	nd
	NF	14.63	0.06	14.89	0.06	0.2	–	93ppm	–
	M	8.94	0.08	4.74	0.02	9.2	1.7	92ppm	nd
	F	68.46	2.45	1.33	0.33	43.2	7.19	176ppm	nd
	Solution	7.98[4]	From 14.2 to 19.4 g/L	–	nd	nd	–	–	–
3rd Experiment	Ore	100	6.63	2.83	0.38	32.2	–	92ppm	3.48ppm
	NF	11.86	1.58	18.49	0.15	35.9	0.51	72ppm	nd
	M	2.71	1.90	1.92	0.14	41.7	1.40	70ppm	nd
	F	73.37	1.76	0.83	0.30	33.7	3.82	130ppm	2.17ppm
	Solution	12.06[4]	From 14 to 35 g/L	–	nd	From 760 to 1270 mg/L	–	–	–

b) Metals partition among flotation fractions and solution (%).

1st	Non Flotable Fraction (NF)	2.4	56.3	0.3	0.8	3.7	14.2	49.6
	Mixed Fraction (M)	–	1.7	1.4	2.7	3.0	1.6	0.4
	Flotable Fraction (F)	48.0	42.0	48.1	96.5	93.2	84.2	49.6
	Solution	49.6/96[5]	–	50.7[6]	-2.8[7]	–	–	–
2nd	NF	0.2	66.5	3.2	0.1	–	9.58	nd
	M	0.2	12.9	0.7	2.7	3	5.76	nd
	F	39.0	20.6	83.6	97.2	97	84.66	nd
	Solution	60.6/96.9[5]	–	12.1/84.1[5]	nd	–	–	–
3rd	NF	2.8	77.5	4.7	8.78	2.1	8.1	nd
	M	0.8	1.8	0.96	5.32	1.3	1.8	nd
	F	19.5	21.4	57.9	81.65	96.6	90.1	64
	Solution	79.0	–	33.5	4.24	–	–	–

1) Precious metals concentration is expressed in ppm.
2) Elemental sulfur
3) After sulfate leaching before L-F step (see Table 2.7 - Experimental arrangement case A)
4) Loss of sample weight during L-F process
5) Metal extraction in the L-F step only(%)/cummulative extraction after L-F step (sulfate leaching and L- F step(%))
6) Cummulative extraction
7) Iron precipitation from solution during L-F step, as 102.8% excess in relation to the initial content of iron in the raw material
nd Not determined

Table 2.9. Leaching flotation test of sample #4 (TRIO)

a) Mass distribution and metal concentrations in the flotation fractions and leach solution

	Specification	Fraction Distribution, %	Concentration (%)					Conc. (ppm)	
			Zinc	Lead	Copper	Iron	Sulfur[2]	Silver	Gold
4th Experiment	Ore	100	7.50	7.3	1.35	25.0	–	118.8	3.98
	NF	60.9	4.04	8.9	0.5	27.7	nd	55.5	3.04
	M	1.5	5.14	11.6	0.6	22.3	nd	96.5	nd
	F	37.5	9.8	3.1	2.7	40.2	nd	232	2.96
	Solution	nd	From 5.2 to 5.8 g/L	–	From 0.19 to 0.29 g/L	nd	–	–	–
5th Experiment	Raw Materials[3]	100	0.95	12.83	1.76	31.4	7.3	158.7	5.3
	NF	23.12	0.03	27.6	0.04	0.16	0.5	207.3	nd
	M	12.74	nd	nd	nd	nd	(3.2)	(167.4)	nd
	F	51.91	1.18	2.5	0.46	nd	18.4	127.6	nd
	Solution	12.21[4]	1.26 g/L	–	0.07 g/L	3.7 g/L	–	4.0	–

b) Metals partition among flotation fractions and solution (in weight percent)

		Zinc	Lead	Copper	Iron	Sulfur	Silver	Gold
4th	NF	36.7	83.7	24.0	52.9	nd	32.1	52.7
	M	1.1	2.7	0.8	1.0	nd	1.4	nd
	F	55.0	18.1	83.8	47.3	nd	82.9	31.5
	Solution	7.9	–	6.9	nd	–	–	–
5th	NF	0.6	65.48	0.5	0.11	1.1	23.0	nd
	M	(6.6)	(21.29)	(4.9)	nd	(4.1)	10.2	nd
	F	36.1	13.23	13.3	nd	94.8	31.8	nd
	Solution	56.7/92.7[5]	–	81.3[6]	8.4	–	nd	–

Notes 2-6 as in Table 2.8
Values in paranthesis are balanced to 100%
NF - Non Flotable fraction; M - Intermediate (Mixte) fraction;
F - Flotable fraction; nd - not determined

Results of the 4th experiment, conducted with sample #4, was significantly different. Extraction of zinc and copper during the L-F process was very low - 7.9% for zinc and 6.9% for copper. Relatively high accumulation of copper and silver, higher than 80%, was found in the flotable fraction. Lead remained predominantly in the non-flotable fraction.

Other L-F experiments were preceded by the sulfate leaching step. Because acceptable zinc extraction requires several hours of leaching, the continuous and simultaneous action of much faster flotation is troublesome. The continuous flotation causes too fast removal of nonreacted sulfides from the reactive medium. This is exactly the reason that in the 1st, 2nd and 5th experiment, the L-F process followed the 2-4 hour sulfate leaching step, without simultaneous flotation. In the 1st and 2nd experiment, total zinc extraction was about 96%, while copper 50.7% and 84.1% respectively. As in previous experiments, the "nonsoluble copper" was easy to concentrate in the flotable fraction and lead in the nonflotable fraction. The result from the 1st experiment, where partition of lead between principal fractions was equilibrated, is exceptional. The

5th L-F experiment was also proceeded by sulfate leaching and the resulting distribution of zinc, lead, copper and sulfur were similar to those of other L-F experiments.

The partitioning of silver and gold was not uniform over all experiments. Silver was concentrated in the flotable fraction as well as in the nonflotable fraction. Nor was any regularity of gold distribution observed. Perhaps this irregularity is caused by the limited accuracy in analyzing for the low concentration of silver and gold. The mass balances of silver and gold based on AAS analyses and presented in Tables 2.8 and 2.9 show an excess of about 15% of these metals in comparison to their concentration in the ore samples. In order to explain the cause of this behavior exhibited by silver and gold, additional L-F tests, as well as sulfate or chloride leaching tests, were performed on the separated "bulk" fractions after the 1st and 4th L-F experiments. Precious metals distributions over these multistage leaching-flotation tests are presented in Figures 2.25 and 2.26.

Based on these results it is difficult to state the best conditions for the concentration of precious metals and for their accumulation into one product of the leaching-flotation process. One valuable observation is that silver is accumulated in the flotable fraction rather than in the "heavy" nonflotable fraction, which contains the nonflotable portion of pyrite. Additional sulfate leaching tests carried out with the flotable fraction of sample #1 and with the nonflotable fraction of sample #4, after the L-F step, are described in Chapter 2.6.

The flotable fraction from the 3rd experiment (Tables 2.7 and 2.8) was leached with the solution from the L-F step, after the solution had been regenerated under elevated oxygen pressure.The resulting zinc and copper extractions are

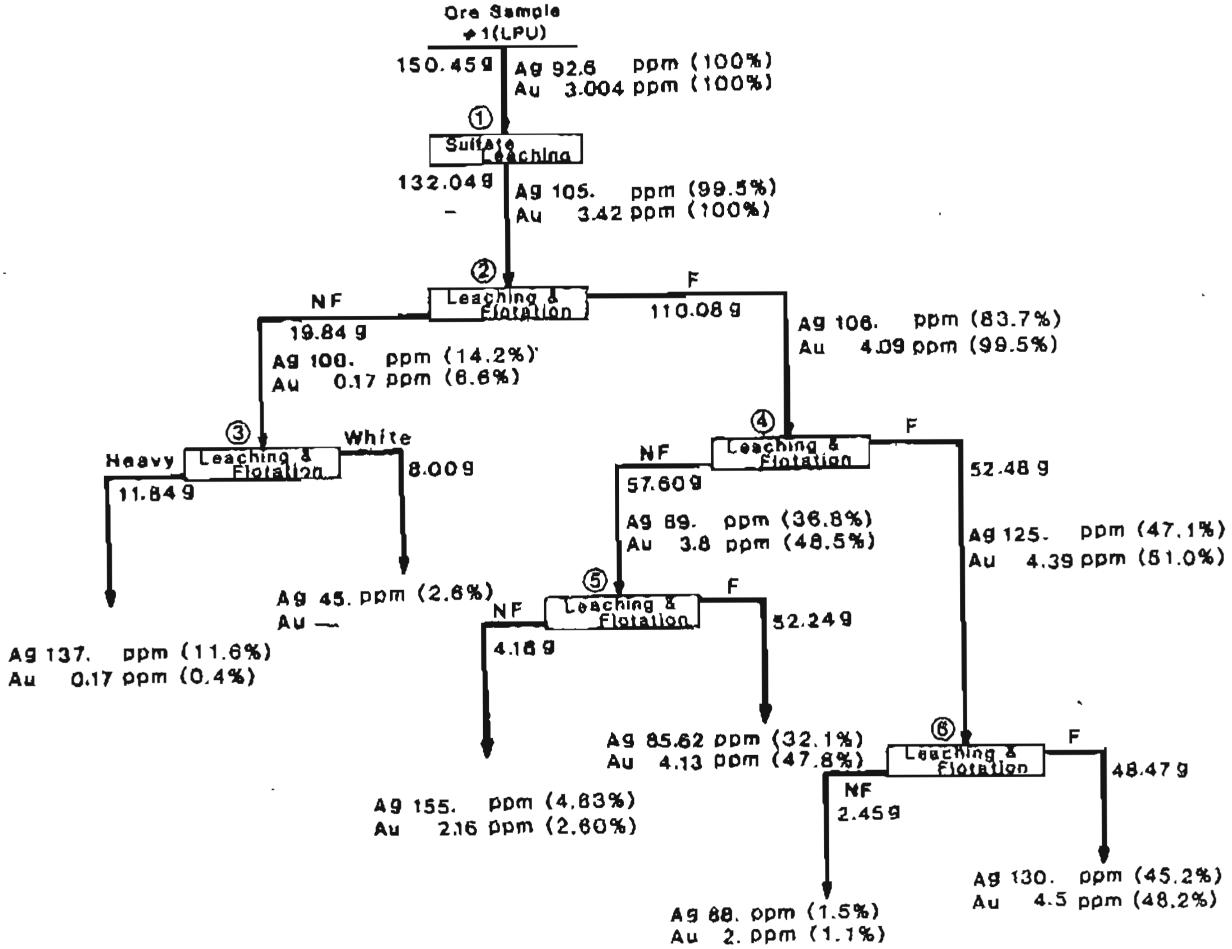

Figure 2.25. Multistage leaching-flotation test. Precious metals concentration and partition in the flotation products. Other metals distribution in 1st L-F step - see 1st experiment in Table 2.8.

presented together in Figure 2.27, along with those of the preceding L-F process, described earlier. 80% of zinc and 45% of copper were extracted after two hours of the L-F process. After four additional hours of leaching with the regenerated solution, total zinc recovery reached 96% and copper 57%. After an additional four hours, 99% of zinc and 65% of copper were recovered.

A strong acceleration of zinc extraction can be achieved during leaching under oxygen pressure. Results of such leaching following the L-F process are also indicated in Figure 2.27 by the dashed lines. After two hours 98.5% of total zinc and 64% of total copper were recovered.

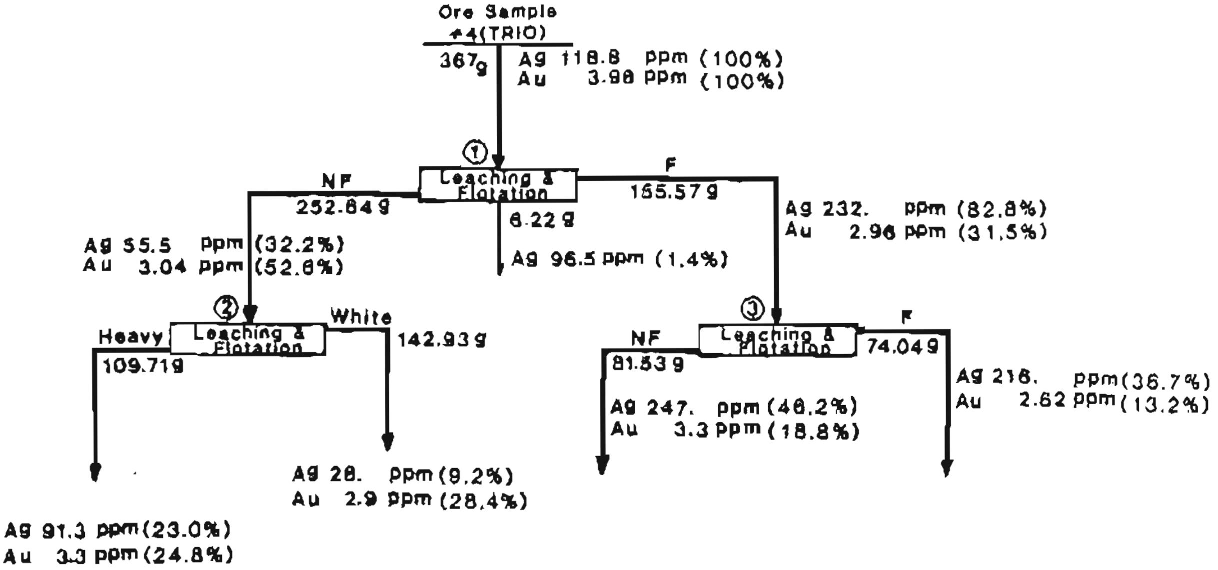

Figure 2.26. Multistage leaching-flotation test. Silver and gold concentrations (ppm) and distribution (%). Other metal distribution in 1st L-F step - see 4th experiment in Table 2.9.

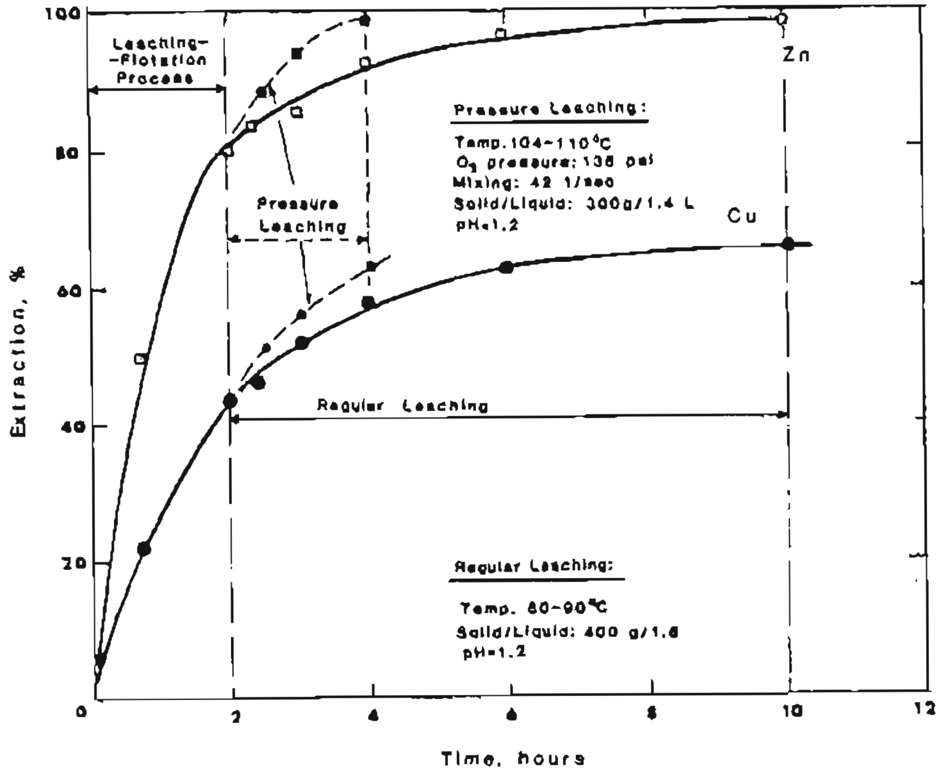

Figure 2.27. Zinc and copper extraction during leaching-flotation and leaching tests. Dashed line: pressure leaching test (other conditions - see text and Tables 2.7 and 2.8).

The nonflotable fraction from the 4th experiment (Tables 2.7 and 2.9) was leached with 20% sulfuric acid. The reason this leaching test was conducted was because a secondary precipitation of solution components was observed during one of the sulfate leaching tests (Figure 2.10). Since during L-F processing the same phenomenon can occur, it was of interest to determine the composition of the nonflotable fraction. Results of the sulfuric acid leaching are presented in Figure 2.28 together with results of the chloride leaching that followed.

In consequence, 88% of the solid sample was dissolved during two leachings; 75.5% during sulfate leaching and 12.5% during chloride leaching. Analysis of the results indicate that the "white" nonflotable fraction (Figure 2.28) was composed of basic sulfates of iron(III), zinc and copper, arsenates of calcium, iron(II) and iron(III), lead sulfate, calcium sulfate hydrate (gypsum) and nonsoluble gangue minerals. Zinc, copper and lead were totally extracted into solution. 87% of the iron and 10% of the arsenic were extracted. During the calcium chloride leaching about 50% of silver was extracted to solution too (Figure 2.28).

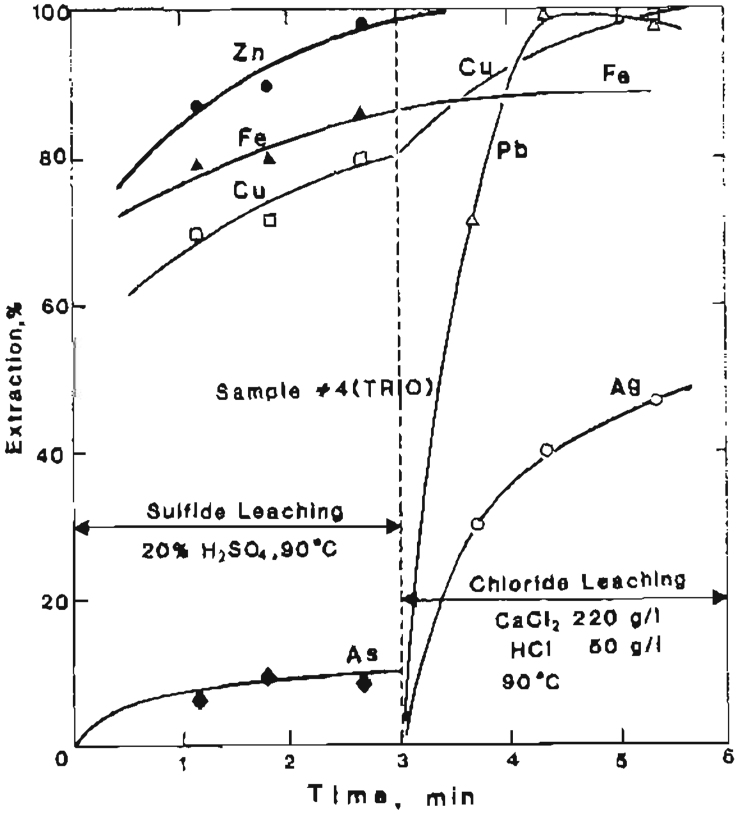

Figure 2.28. Metal extraction from "white" non-flotable fraction during sulfate and chloride leaching tests. Ore sample #4 (TRIO) after 4th L-F experiment. Solid/liquid = 40g/0.7L. Initial contents of metals in solid: Zn 0.4%, Pb 9.7%, Cu 0.1%, Fe 22.4%, As 6.3%, Ca 5.7%, Ag 28 ppm, Au 2.9 ppm.

2.6 Chloride Leaching of Flotation Products

Non-Flotable Fractions

Nonoxidative chloride leaching was applied for lead extraction from the nonflotable fractions produced in L-F process. Lead sulfate is easily dissolved in concentrated solution of soluble chlorides ($AlCl_3$, $CaCl_2$, $MgCl_2$, NaCl, KCl). Dissolution of galena PbS requires acidic or oxidative conditions. Where a calcium chloride is applied the concentration of sulfate ions in the solution is controlled by crystallization of scarcely soluble gypsum $CaSO_4 \cdot 2H_2O$:

$$PbSO_{4(s)} + Ca^{2+} + 4Cl^- + 2H_2O = PbCl_4^{2-} + CaSO_4 \cdot 2H_2O_{(s)} \qquad (2.4)$$

Lead extraction, by calcium chloride solution, from the "white" and the "heavy" nonflotable fractions is presented in Figure 2.29. Both fractions were separated from the bulk nonflotable fraction obtained from sample #1 during the 3rd L-F experiment (Table 2.8 and Figure 2.25). Reaction (2.4) is very fast and after a few minutes more than 99% of the lead was extracted from the "white" fraction. Extraction of lead from the "heavy" fraction was slower. Finally, after 2 hours of leaching, it was completed with high recovery of lead.

The chloride leaching tests on the "white" fraction from sample #4, after the 4th L-F experiment (Table 2.9 and Figure 2.26), were carried out in four different solutions:

- sodium chloride (234 g/L NaCl)
- calcium chloride (220 g/L $CaCl_2$)
- calcium chloride with hydrochloric acid (166 g/L $CaCl_2$ and 37 g/L HCl)
- ferric chloride with hydrochloric acid (290 g/L $FeCl_3$ and 5 g/L HCl)

As described earlier, this "white" fraction was probably composed of the products of hydrolysis of the sulfate solution, whose solubility is strongly pH dependant, and from other scarcely soluble sulfates and arsenates. The results presented in Figure 2.30 indicate that only 20 to 40% of the lead is extracted to neutral calcium chloride or sodium chloride solutions. Total lead extraction is observed in acidified solutions of calcium chloride or ferric chloride. Zinc is dissolved only with ferric chloride solution, indicating that it was probably in sulfide form.

Results of ferric chloride leaching of the "heavy" nonflotable fraction of sample #4 after the 4th L-F experiment (Table 2.9 and Figure 2.26) are presented in Figure 2.31.

After 60-80 min of leaching more than 90% of the investigated nonferrous metals are extracted to the solution containing only 20.2 g/L of iron(III).

Flotable Fractions

Results of ferric chloride leaching of the flotable fraction of sample #1 are shown in Figures 2.32 and 2.33, and of sample #4 in Figure 2.34.

The rapid extraction of silver and lead reaches 80-96% for Ag and more than 96% for Pb after 2-4 hours of leaching. The extraction of zinc was higher than 98% after 3 hours of leaching. The kinetics of copper extraction have a near linear character. This is typical for reactions with a high energy of activation. Prolongation of the leaching time will undoubtedly increase the yield of copper extraction.

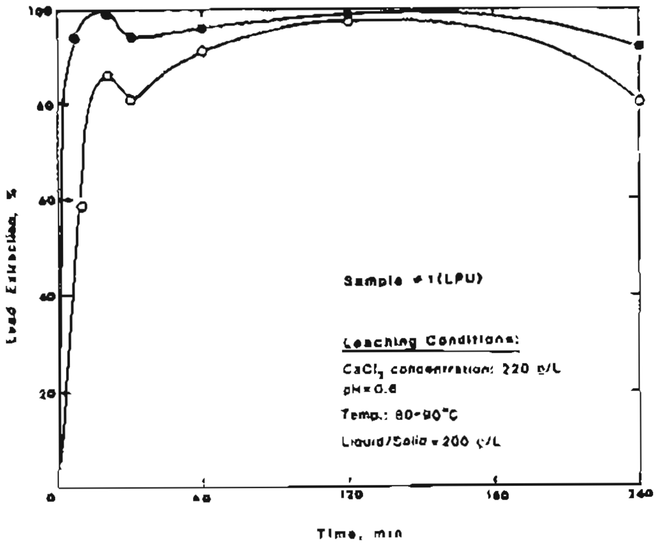

Figure 2.29. Lead extraction by calcium chloride solution from two non-flotable fractions: ● - "white" fraction, o - "heavy" fraction.

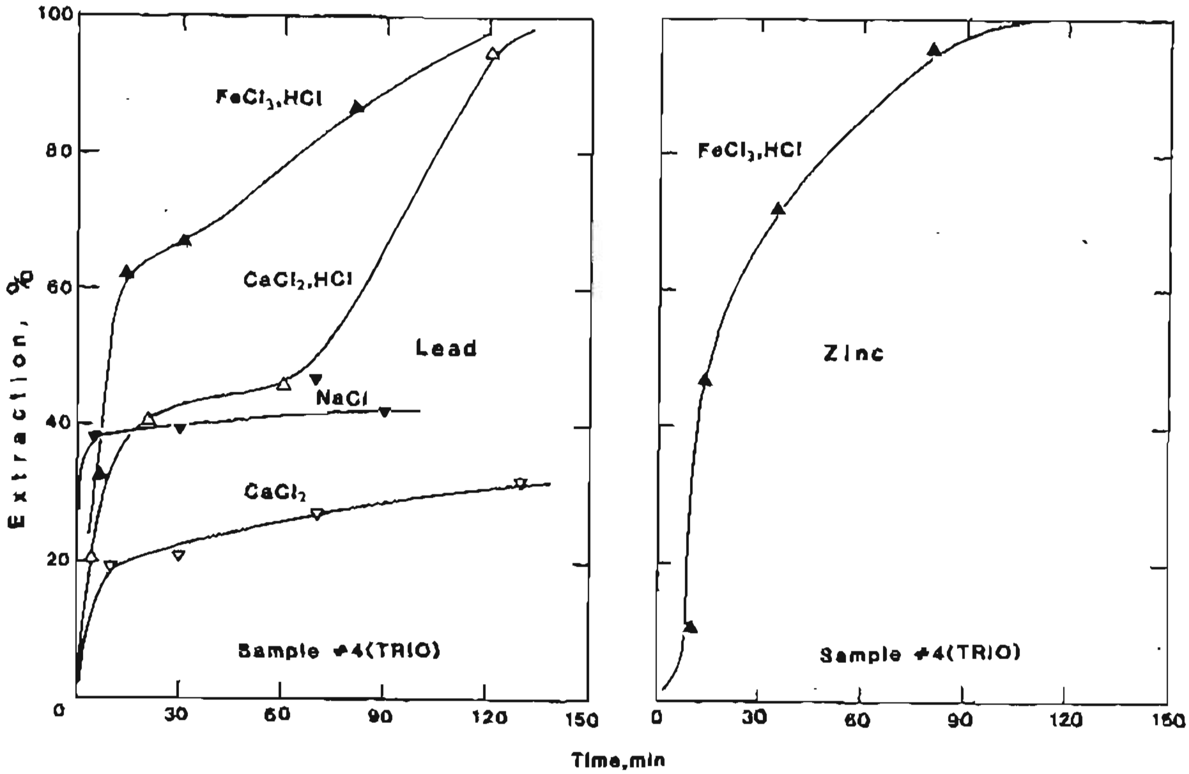

Figure 2.30. Lead and zinc extraction from "white" nonflotable fraction after 4th L-F experiment (Table 2.9 and Figure 2.26), during chloride leaching tests. Liquid/solid = 10g/0.3L. Temp. 90°C. a) lead extraction in: sodium chloride - 234g/L, calcium chloride - 220g/L, calcium chloride - 166g/L, with hydrochloric acid - 37g/L, ferric chloride - 290g/L, with hydrochloric acid - .5g/L; and b) zinc extraction with ferric chloride solution 290g/L and 5g/L HCl.

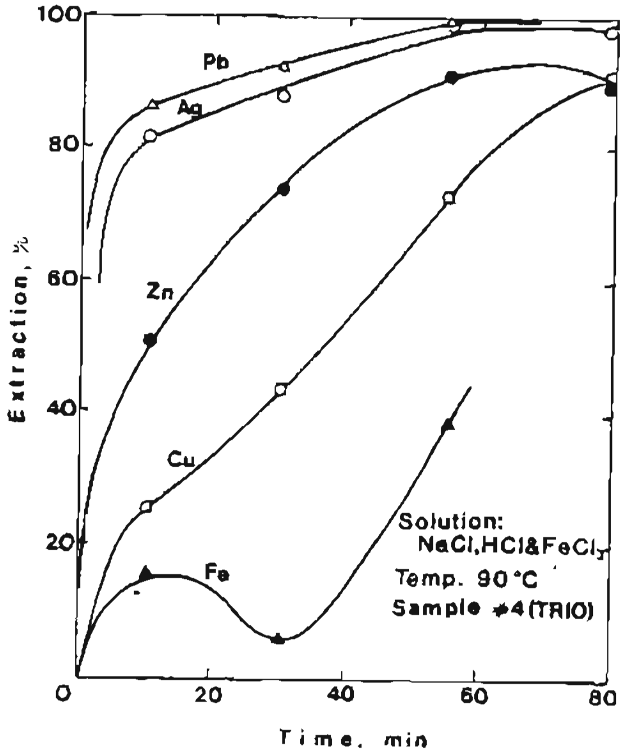

Figure 31. Ferric chloride leaching of "heavy" nonflotable fraction after 4th L-F experiment (Table 2.4). Initial metal concentration in solid fraction: Fe 31.76%, Zn 7.35%, Pb 5.84%, Cu 1.29%, As 6.72%, Ag 91.4 ppm, Au 3.26 ppm. S/L = 30g/0.7L. Initial composition of solution: NaCl 164g/L, HCl 9g/L, Fe^{3+} 20.2g/L. Temp. 90°C.

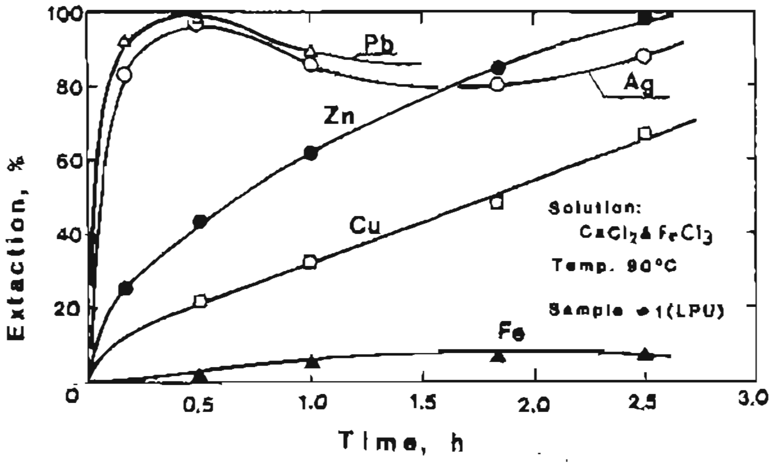

Figure 2.32. Ferric chloride leaching of flotable fraction after 3rd L-F experiment (Table 2.8). Initial metals concentration in solid: Fe 35.7%, Zn 0.38%, Pb 1.15%, Cu 0.19%, Ag 96 ppm. S/L=300g/1L. Initial composition of solution: $CaCl_2$ 220g/L, HCl 44g/L, Fe 48g/L, Zn 2.8g/L, Pb 4g/L, Cu 340mg/L, Ag 96mg/L.

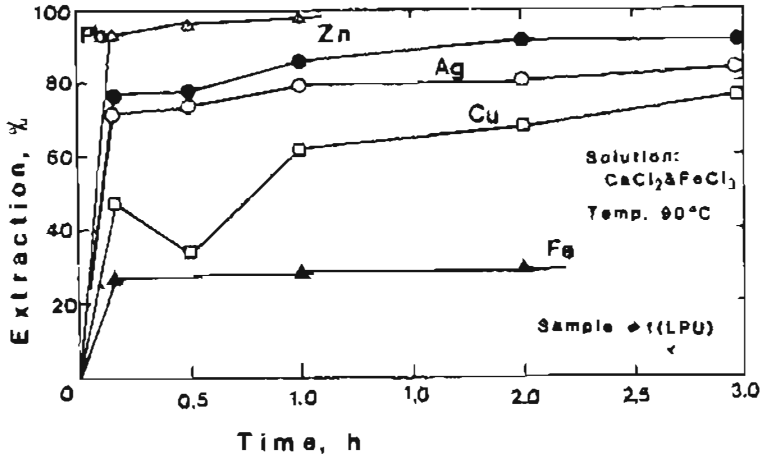

Figure 2.33. Ferric chloride leaching of flotable fraction after 2nd L-F experiment (Table 2.8). Initial metals and sulfur concentration in solid: Fe 43.2%, Zn 2.45%, Pb 1.33%, Cu 0.33%, Ag 176ppm, S^0 7.2%. S/L = 250g/L. Initial composition of solution: $CaCl_2$ 220g/L, Fe^{3+} 74g/L, pH 0.7.

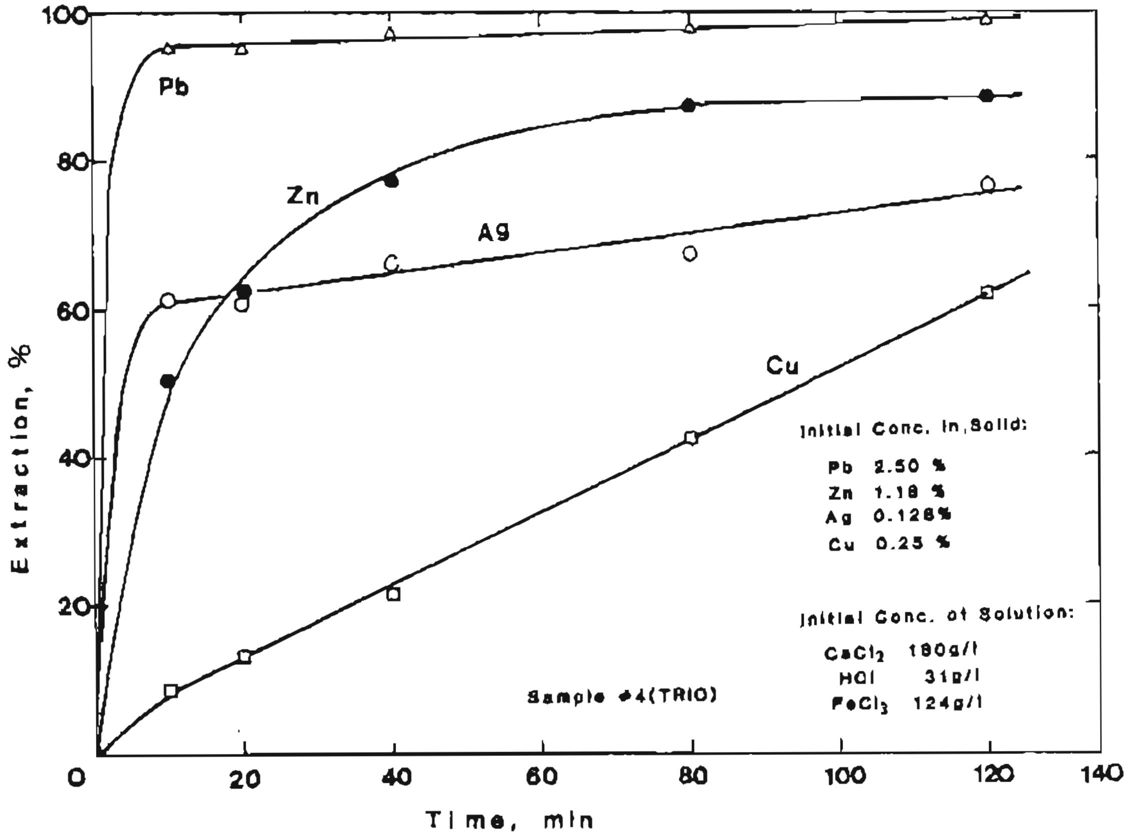

Figure 2.34. Ferric chloride leaching of the flotable fraction after 5th L-F experiment (Table 2.9). S/L = 50g/0.7L. pH 0.2. Temp. 90°C.

2.7 Sulfur Recovery

Only a small portion of the total sulfidic sulfur is transformed to its elemental form during leaching. The maximum amount of elemental sulfur that can be generated corresponds to the total concentration of decomposed sulfides in oxidative conditions applied in our tests. Theoretical amounts of elemental sulfur that can be formed, calculated from the compositions of the ore samples, are compared in Table 2.10 to actual sulfur yield from sulfate leaching and leaching-flotation tests (Tables 2.8 and 2.9). As indicated in Table 2.10, the concentration of elemental sulfur in the solid residues after ferric chloride leaching is only slightly higher than the elemental sulfur generated during sulfate leaching and leaching-flotation steps.

Elemental sulfur was extracted by xylene from the solid residue after ferric chloride leaching of the flotable fraction from the 2nd L-F experiment. The yield of extraction was about 96%. The remaining solid residue, after sulfur extraction, was then directed to gold leaching by cyanide or thiourea solution.

2.8 Gold Extraction

Gold extraction tests were performed using cyanide and thiourea solutions on ore sample #1 and on three solid residues after different steps of treatment. The leaching conditions were as follows:

- Thiourea leaching: [Th] = 50 g/L, [Fe2(SO$_4$)3] = 25 g/L, [H$_2$SO$_4$] = 40 g/L, pH = 1.15, temp. 25°C, solid/liquid = 70 to 100 g/0.2L, time of leaching - 20 h;
- Cyanide leaching: [NaCN] = 1 g/L, [NaOH] = 2 g/L, temp. 25°C, solid/liquid = 70 to 90 g/0.3L, time of leaching = 48 h.

Results of the tests are summarized in Table 2.11.

Table 2.10. Maximum of elemental sulfur that can be generated during ferric sulfate and ferric chloride leaching in experimental conditions and amounts of elemental sulfur found in solids after sulfate leaching and leaching-flotation tests.

Ore Sample	Maximum S° generated during leaching*)		S° found after L-S step (%) Experiments**)				
	after sulfate leaching	after chloride leaching	1	2	3	4	5
#1 LPU	4.94	14.22	12.79	14.17	8.06		
#2 LPL	5.56	15.63					
#3 DDS	5.25	12.62					
#4 TRIO	10.01	36.8				nd	34.70
#5 DDN	11.71	28.1					
#6 DDN	24.90	80.1					

* Calculated

** According Table 2.8 and 2.9; only for ore samples #1 and #4

nd not determined

Table 2.11. Gold concentration at different stages of tested flowsheet.

Solid Samples	Concentration of gold in sample (ppm)	Leaching Agent	Extraction (%)
Ore	3.48	Aqua Regia	Total
Residue after sulfate leaching	3.72	Thiourea	70.7%
Residue after ferric chloride leaching	4.48	Thiourea	71.4%
Residue after sulfur extraction	4.52	Cyanide	88.7%

2.9 Iron Oxidation by Oxygen

Iron oxidation of spent leach solutions accomplishes three goals:

- regeneration of the leach solution:

$$2Fe^{2+} + 1/2\ O_2 + 2H^+ = 2Fe^{3+} + H_2O \qquad (2.5)$$

- precipitation of excess iron accumulated in the solution during leaching, i.e.

$$2FeCl_3 + 3CaO + H_2O = 2FeOOH + 3CaCl_2 \qquad (2.6)$$

- purification of zinc sulfate solution prior to electrolysis:

$$2FeSO_4 + 1/2\ O_2 + 3H_2O = 2FeOOH + 2H_2SO_4 \qquad (2.7)$$

Such oxidation is very fast when oxygen is dispersed in solution under elevated pressure. Oxidation of ferrous chloride solution is easier than that of ferrous sulfate and can be conducted at lower pressure and temperature. The high corrosivity of chloride solutions presents engineering problems and at this stage of research only the oxidation of ferrous sulfate could be conducted at MIRL.

Oxidation of ferrous sulfate solution under a pressure of 40-140 psi was carried out in a 2-liter stainless-steel Parr-autoclave equipped with the following: a pyrex liner, a stirrer, a system for continuous feeding and dispersion of oxygen under pressure, a heating system, a temperature and a pressure control, and regulation systems.

Regeneration of the leaching agent can be coupled with precipitation of excess iron in one operation carried out under relatively low oxygen pressure 40-140 psi and at low temperature 70-90°C.

$$6Fe^{++} + 3/2\ O_2 + H_2O = 2FeOOH + 4Fe^{3+} \qquad (2.8)$$

The kinetics of such an oxidation are shown in Figure 2.35 and typical conditions are described briefly in Table 2.12. For the most part, solutions applied in the sulfate leaching and leaching-flotation experiments were regenerated using this technique.

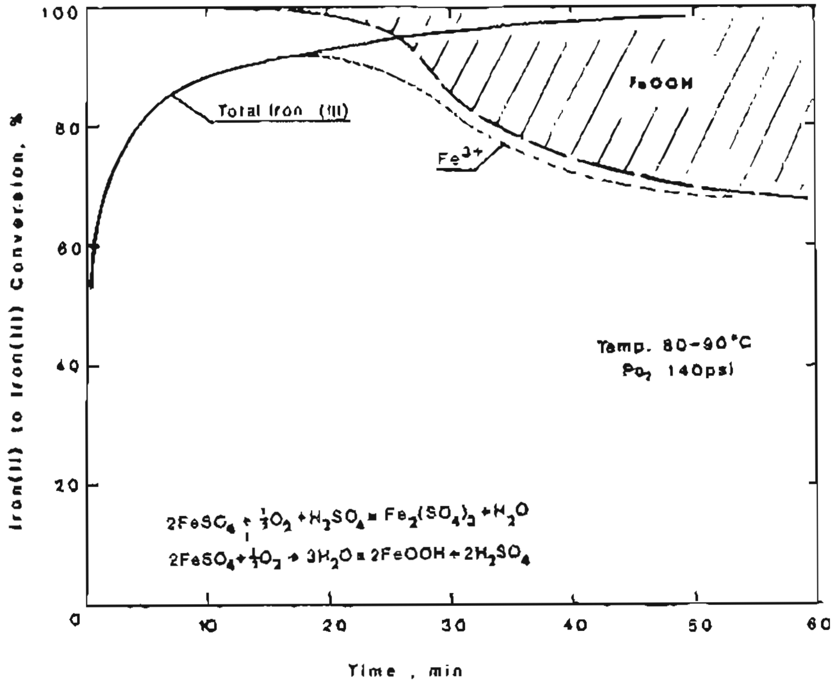

Figure 2.35. Typical characteristics of ferrous sulfate oxidation by oxygen with partial precipitation of iron as FeOOH.

Table 2.12. Regeneration of the leach solution by oxygen with partial precipitation of iron. Conditions: temperature 80-90°C; oxygen pressure 140 psi, double stirrer rotation 30 sec^{-1}. Total time of experiment: 30 min.

	Concentration, mol/L	
	Before regeneration[1]	After regeneration[2]
$Fe_2(SO_4)_3$	0.52	0.67[3]
$FeSO_4$	0.72	0.26
$ZnSO_4$	0.53	0.50
$CuSO_4$	0.02	0.02

1) After leaching-flotation step
2) Directed to the sulfate leaching step
3) 11% of iron (III) was precipitated after 20 min of oxidation when pH reached 2.2

2.10. Summary Results

The results of metals extraction from ore sample #1 (LPU) and #4 (TRIO) are summarized below. Metals extractions from the other ore samples during routine leaching tests were presented in Tables 2.3, 2.5 and 2.6.

Zinc	**Extraction**
- Direct nonoxidative leaching with HCl solution:	81%[1]
- Direct oxidative leaching with $FeCl_3$ solution (2-step):	95-97%[2]
- Direct oxidative leaching with $Fe_2(SO_4)_3$ solution (2-step):	89%
with a subsequent leaching-flotation step:	96.9%
- Direct leaching-flotation processing:	79%
with subsequent leaching by $Fe_2(SO_4)_3$ (1 step,4h):	96%
or with subsequent leaching by $Fe_2(SO_4)_3$ (2 steps,8h):	99%
or with subsequent oxygen pressure leaching (2 h):	98.5%

Copper	**Extraction**
- Direct oxidative leaching with $FeCl_3$ solution(2 steps):	61%[1,2]
- Direct oxidative leaching with $Fe_2(SO_4)_3$ solution(1 step, 4h):	51-75%
or (2 steps, 2 x 4h): 81.4%	
or with subsequent leaching-flotation step:	84.1%
- Direct leaching-flotation processing:	33.5-45%
with subsequent leaching by $Fe_2(SO_4)_3$ (1 step, 4h):	57%
or with subsequent leaching by $Fe_2(SO_4)_3$ (2 step,8h):	65%
or with subsequent oxygen pressure leaching (2h):	64%
and with subsequent $FeCl_3$ leaching of the flotable fraction:	72-92%
and with additional recovery of copper from the nonflotable fractions (simultaneous with lead extraction):	74-96%

Lead	Extraction
- Direct nonoxidative leaching with HCl solution:	96.8-99.9%
- Direct oxidative leaching with $FeCl_3$ solution:	96-97%[2]
- Leaching of the nonflotable fractions with $CaCl_2$ + HCl solution:	52-79%
with additional recovery of lead from the flotable fraction during $FeCl_3$ leaching (simultaneous with copper and silver recovery:	96-99%

Silver	Extraction
- Direct oxidative leaching with $FeCl_3$ solution:	85%[1,2]
- Leaching of the flotable fraction with $FeCl_3$ solution:	70-86%[3]
with additional silver recovery from the nonflotable fractions during $CaCl_2$ - HCl leaching (simultaneous with lead extraction):	84-91%
and with additional recovery during cyanide or thiourea leaching for gold recovery:	86-96%[3]

Gold	Extraction
- Cyanide or thiourea leaching of the solid residue after $FeCl_3$ leaching of flotable fractions:	71.4%[3,4]
- Cyanide or thiourea leaching of the solid residue after sulfur extraction:	88.7%[3,4]
with additional gold recovery from the selected "heavy" nonflotable fraction:	~90-92%[3,5]

Sulfur	Extraction
- Extraction with xylene from solid residue of the flotable fraction after $FeCl_3$ leaching: 14%[6]	

Notes: 1) From sample #1 only; 2) From the 140-170 mesh size fraction. All other cases: 325-400 mesh size fraction; 3) With experimental accuracy about ± 14%; 4) Without gold recovery from nonflotable fractions; 5) Theoretical estimation, no experimental confirmation; 6)Percent of total sulfidic sulfur in sample #1, including FeS_2.

2.11 General Recommendations for Future Research

The general recommendations for future research are comprised in 3 following tasks:

1. It is necessary to continue laboratory research to define a better separation of lead in the leaching-flotation step. A more distinct concentration of precious metals in the ore flotation fraction should also be researched.

2. A study on precious metals association with other sulfides in terms of their hydrometallurgical properties, must be continued on samples representative for economic part of the Delta deposit.

3. The very low concentrations of gold and silver in the ore and the multiple transformation of the solid material during successive processing, up to the point of precious metals extractions, makes their accurate determination extremely difficult at the present small laboratory scale. Research must be continued at larger, several-pound scale which will allow for accumulation of the solid semi-products directed to precious metals recovery.

2.12 Conception of Hydrometallurgical Processing of Delta-Ores

The mass balances for the three flowsheets of a direct ore processing are calculated on the basis of laboratory results:

- direct ore leaching with ferric chloride solution followed by a leaching-flotation step, with subsequent zinc separation in a solvent extraction step and electrolysis in chloride solution;
- direct ore leaching with ferric sulfate solution followed by a leaching-flotation step, with zinc sulfate electrolysis and other metals recovery in chloride leaching steps;
- direct ore treatment by leaching-flotation steps coupled with leaching with ferric sulfate solution, followed by with zinc sulfate electrolysis and other metals recovery in chloride leaching steps.

In all flowsheets silver is recovered during the chloride leaching steps and gold from flotation products during the cyanide leaching.

In the first flowsheet (Figure 2.36) ore is leached with concentrate solution of calcium and magnesium chlorides, containing ferric chloride. The principal objective of this operation is to supply a solution with minimum concentration of ferric chloride to solution treatment steps. Only about 30% of total "soluble" sulfides are decomposed in the 1st leaching

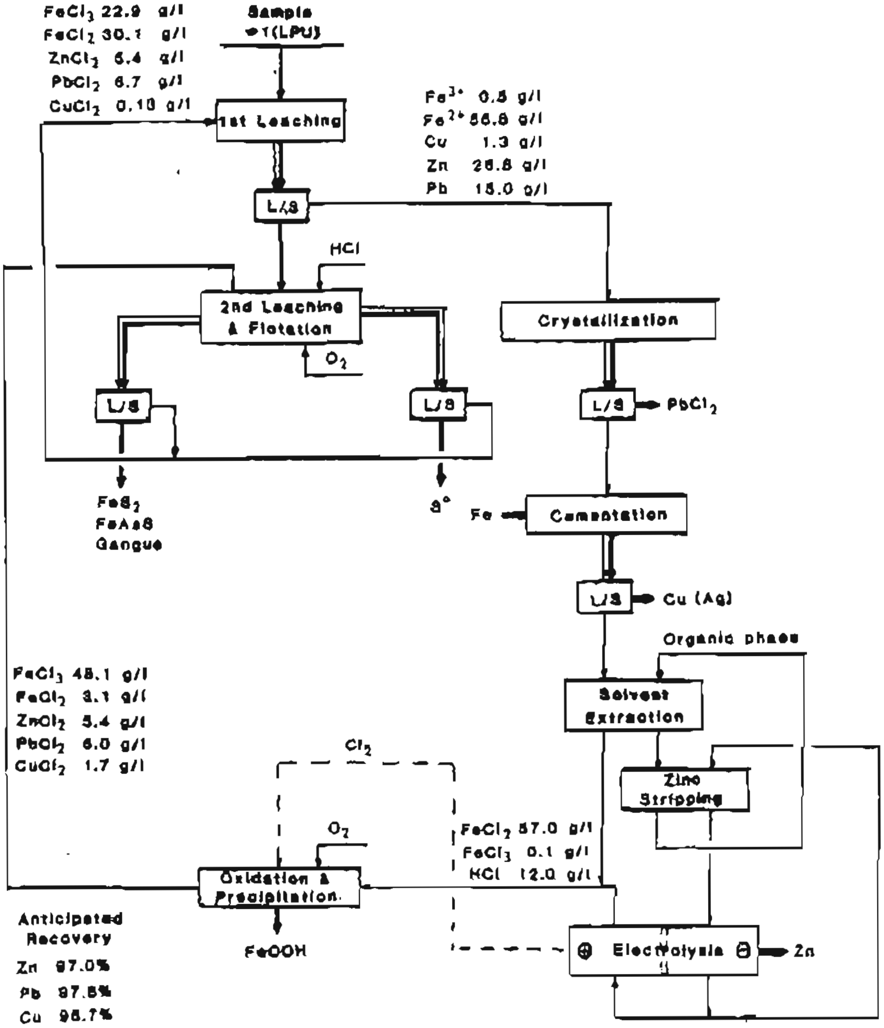

Figure 2.36. Flowsheet of the ore treatment with direct ferric chloride leaching. Only the main components of solution are indicated.

step during nearly total transformation of ferric chloride to ferrous chloride. Then about 60% of the dissolved lead is crystallized as crystalline lead chloride $PbCl_2$ from the solution which is subsequently directed to copper cementation by iron followed by zinc separation in the solvent extraction steps and electrolysis in diaphragm-electrolyzers. The stripped solution, enriched in hydrochloric acid after solvent extraction and electrolysis, is oxidized by chlorine gas from electrolysis and by oxygen under elevated pressure. In this manner 30% of the iron is precipitated from solution as goethite FeOOH, while 70% of the ferrous ions are oxidized to ferric ions. This strong oxidative solution containing $FeCl_3$ is for the second time contacted with the partially leached ore in a leaching-flotation step. The general task of this step is the maximum extraction of metals from the ore, and solution leaving this step has enough of nonreduced ferric chloride to dissolve about 30% of the "soluble" sulfides in the first leaching step. The best conditions for total metal extraction during L-F processing will probably be better when oxygen necessary to regenerate iron(III), will be supplied under an elevated pressure. Two solid flotation products are separated during the L-F step: the nonflotable fraction containing gangue minerals, depressed pyrite and other oxidized solid phases, and the flotable fraction containing sulfur and the incompletely decomposed "soluble" sulfides. Nor the secondary flotation of the nonflotable fraction producing the "heavy" pyritic fraction and the gangue minerals fraction, nor the cyanide leaching of gold from the "heavy" pyritic fraction are shown in flowsheet in Figure 2.36. These possibilities are evident in the light of laboratory results. Consumption of reagents and other anticipated data for the treatment of 1 t of the ore are presented briefly in Table 2.13.

In the remaining two flowsheets the general base of processing is the same. Leaching steps are coupled with leaching-flotation steps according to the different path of liquid and solid (Figures 2.37 and 2.38). The same processes are applied for purification of the zinc sulfate solution directed to electrolysis and the same leaching processes are applied to lead recovery from the nonflotable fractions, copper and silver from the flotable fractions, and gold with residual silver from the "heavy"

Table 2.13. Consumption of chemical reagents and electricity in electrolysis, amounts of winning products per 1 t of ore and composition of solid residue after treatment. Ore Sample #1 (LPU), according to flowsheet presented in Figure 2.36

Reagents	kg/t ore
O_2	17.95
HCl	18.45
Iron	2.29
Electricity*)	149.86 kWh/t
Products	**kg/t ore**
$PbCl_2$	36.98
Cu	3.68
Zn	64.32
S°	46.32
Solid Residue	**Composition, %**
FeS_2	68.0
FeAsS	1.0
Gangue	16.5
Other Sulfides	0.5
Water (humidity)	14.0

*) for electrolysis only, 2.33 kWh/kg Zn [2.21]

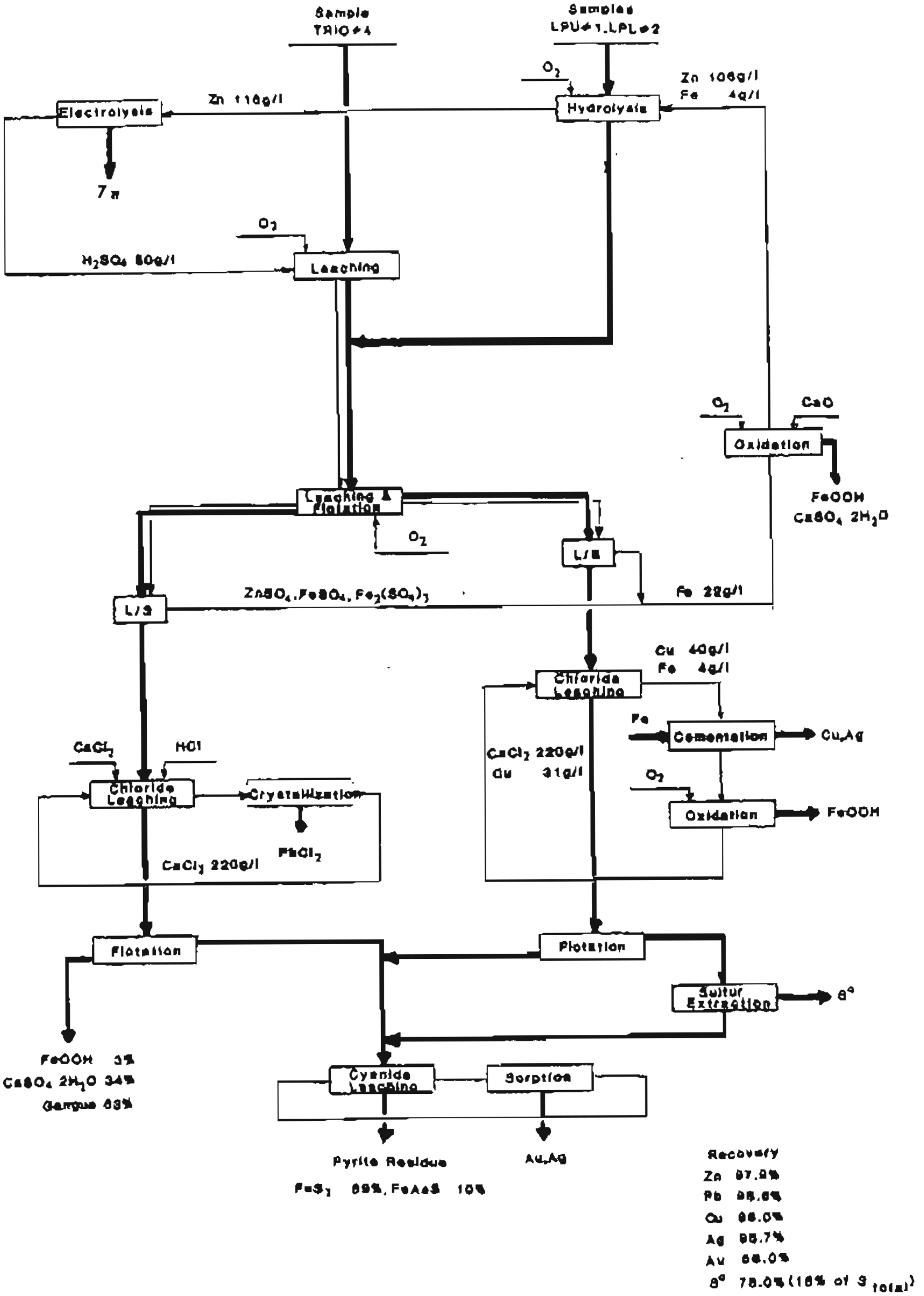

Figure 2.37. Flowsheet of the 1st variant of the ore treatment with leaching-flotation step in ferric sulfate solution. Only the main components of solution are indicated.

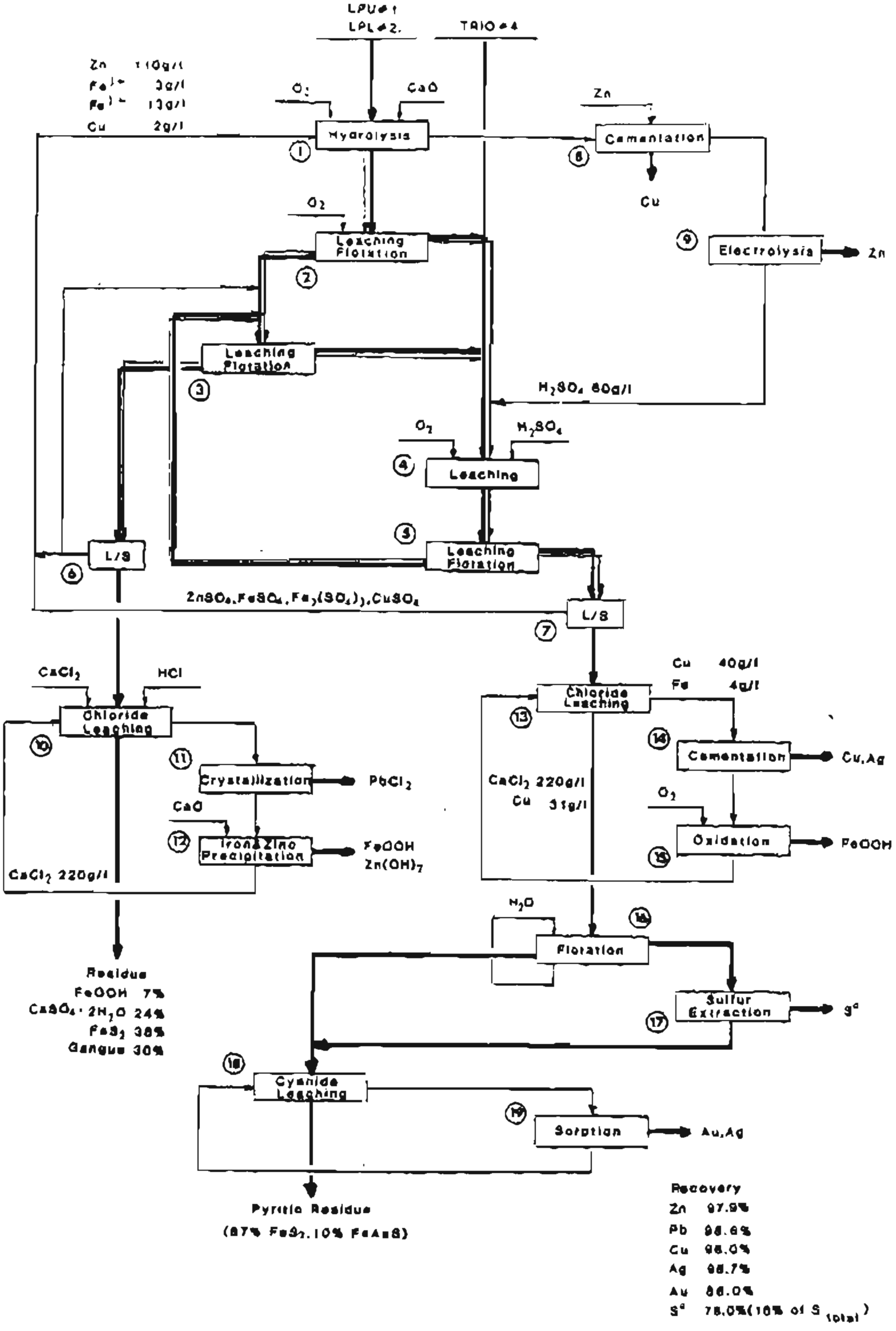

Figure 2.38. Flowsheet of the 2nd variant of the ore treatment with leaching-flotation steps in ferric sulfate solution. Only the main components of solution are indicated. Numbers in circle correspond to the unit processes numbers in Table 2.16.

pyritic fractions. The process presented in Figure 2.37 is easier to carry out and to control, especially during the leaching and leaching-flotation steps. However, the dissemination of pyrite into both the nonflotable and flotable fractions requires an additional separation of pyrite in the "heavy" fraction prior to the gold recovery step. The flowsheet presented in Figure 2.38 has a more complicated path of solid and liquid during leaching and leaching-flotation steps, but it is expected that this configuration will allow for the total accumulation of pyrite in the flotable fraction.

Both flowsheets are calculated for a hypothetical feed material containing 25% of ore sample #1 (LPU), 25% of sample #2 (LPL) and 50% of sample #4 (TRIO). All three ore samples have high concentration of precious metals and other nonferrous metals. Ore #4 contains a larger percentage of readily decomposable iron sulfide FeS and cannot be used for iron hydrolytic precipitation from the zinc sulfate solution.

As shown in Figure 2.37 two raw material paths are joined into one flow following two different initial operations. Ore #4 is directed to initial sulfate leaching conducted under low oxygen pressure. In this stage all easily "soluble" sulfides (PbS, FeS and partially ZnS) are decomposed. Fast dissolution of FeS supplies iron to solution. This iron is oxidized by oxygen and plays a principal role in leaching:

$$FeS + 1/2\ O_2 + H_2SO_4 = FeSO_4 + H_2O + S^\circ \qquad (2.9)$$

$$2FeSO_4 + 1/2\ O_2 + H_2SO_4 = Fe_2(SO_4)_3 + H_2O \qquad (2.10)$$

The sulfuric acid consumed in these reactions is supplied by spent electrolyte after zinc electrolysis (Figure 2.37).

The second portion of the ore is used as a neutralizer for iron precipitation from zinc sulfate solution. In this reaction oxygen under elevated pressure participates in reaction of precipitation of goethite FeOOH:

$$FeSO_4 + 1/2\ O_2 + 3H_2O = 2FeOOH + 2H_2SO_4 \qquad (2.7)$$

Total precipitation of iron requires neutralization or other removal of the sulfuric acid produced in this reaction. The excess acid is here consumed in the reaction of sulfides dissolution:

$$\begin{bmatrix} ZnS \\ PbS \end{bmatrix}_{(s)} + 1/2\ O_2 + H_2SO_4 = \begin{bmatrix} ZnSO_{4(aq)} \\ PbSO_{4(s)} \end{bmatrix} + S + H_2O \qquad (2.11)$$

A part of iron precipitated in the hydrolysis step is afterwards dissolved during the leaching-flotation processing. The undissolved part of iron accumulates as FeOOH in the nonflotable fraction which is directed to the lead extraction step by the calcium chloride solution. In an additional flotation step the "heavy" pyritic fraction is separated from the "white" nonflotable fraction containing goethite FeOOH, gypsum $CaSO_4 \cdot 2H_2O$ and insoluble gangue minerals. The flotable fraction, after leaching-flotation in sulfate solution, is directed to the ferric chloride leaching step where nearly total copper and silver are recovered. Then, during a routine flotation step sulfur is separated from a depressed pyritic fraction and is recovered by one of the known processes. The remaining pyritic fraction and a portion of other nonreacted sulfides after the sulfur extraction step, join with the "heavy" pyritic fraction and are together directed to gold recovery in the cyanide leaching step.

Returning to the middle of Figure 2.37, the sulfate solution (filtrate after the solid flotation product separating), can be oxidized prior to the hydrolysis step to induce a partial iron precipitation, if the iron concentration in solution is too high to be neutralized by the raw sulfides in the hydrolysis step. Supplementary operation of copper cementation with zinc can be considered too if the copper concentration in sulfate solution is too high. This is shown in the second "sulfate" flowsheet (Figure 2.38). The removal of excess iron and other components contaminating chloride solutions is also shown in Figure 2.38. Consumption of reagents and other anticipated data for the treatment of 1 t of mixte ore are presented in Table 2.14.

The mass balances calculated for these simplified flowsheets considers only chemical reactions and does not take into account many technical operations such as liquid/solid separation, washing, liquid evaporation etc. Moreover the mass balance calculated for the "sulfate" flowsheets are used for an initial evaluation of proposed flowsheets.

Table 2.14. Some anticipated data for ore treatment according to the 1st and 2nd simplified "sulfate" flowsheets:

a) consumption of chemical reagents and electricity for zinc electrolysis per 1 ton of raw material containing 25% of the ore sample #1, 25% #2 and 50% #4

Reagent	Consumption tons per 1 t of ore		Unit price $/t	Chemicals cost $/t of ore	
	1st 1) flowsheet	2nd 2) flowsheet		1st 1)	2nd 2)
Oxygen	0.054	0.044	180	9.72	7.92
Sulfuric Acid (96%)	0.098	0.085	80	7.84	6.80
Hydrochloric Acid (36%)	0.025	0.038	100	2.5	3.80
Zinc	–	0.007	880	–	6.16
Iron	0.011	0.004	120	1.32	0.48
Calcium Chloride	0.010	0.014	80	0.8	1.12
Cyanide	0.001	0.001	120	0.12	0.12
NaOH	0.004	0.004	500	2.0	2.0
CaO	0.030	0.027	50	1.5	1.35
Organic (Xylene)	0.005	0.005	600	3.0	3.0
Gold sorption approximative cost 3)				0.7	0.7
Electricity 4)	227.2 kWh	227.2 kWh	0.04	9.1	9.1
Chemicals & electricity total cost				38.6	42.55

b) Metal and sulfur production from 1 t of the same raw material

Products	Tons per 1 t of ore 5)	Unit price $/t	Value $ from 1 t of ore
Zn (electrolytic)	0.071	849	60.28
Pb	0.048	428	20.54
So	0.046	142	6.53
Cu	0.0085	1448	12.31
Ag	0.1048 kg	159/kg	16.66
Au	0.003015 kg	10824/kg	32.63
Winning metals & sulfur total value			148.95

1) After Fig. 2.37
2) After Fig. 2.38
3) Assumed cost, about 2% of recovered gold value
4) Average 3.2 kWh/kg Zn, in electrolysis only
5) The same recovery for 1st and 2nd flowsheet

2.13 Preliminary Economic Evaluation

The cost of the reagents and electricity consumed according to the 1st sulfate flowsheet (Figure 2.37) is 38.60 $/t of the ore, and 42.55 $/t for the 2nd flowsheet (Figure 2.38). The value of the recovered metals is for both flowsheets the same and at this time amounts 148.95 $/t of the ore. 26% to 28% of this sum is making cost of the reagents and electricity (in electrolysis, only). The engineering design of the plant cannot be determined on the actual results of research and no precise economic estimation can be made. Only a comparison of value of metals and sulfur in the investigated ore samples is presented in Table 2.15.

Sample #4 (TRIO) has the highest metals and sulfur values (192.74$/t). Values of sample #1, #2 and #6 are nearly equal. Samples #3 and #5 have the lowest value.

2.14 Technical Conception of the Delta Ore Treatment

The economic success of all new processes is a function of both the technical possibilities and the engineering concepts for industrial plants. For this reason, a trial of the technical characteristics of the proposed "sulfate" process flowsheets was made, based upon present levels of knowledge.

This analysis is presented in the form of a table (Table 2.16) in which the unit processes are characterized by specific conditions and parameters and by the type of apparatus desirable or required. Further information about these unit processes may be obtained from the references and by undertaking other studies recommended by the authors.

An illustration of the authors' idea, a simplified flowsheet of a plant corresponding to flowsheet presented in Figure 2.38 is shown in Figure 2.39. The ore (14t/h) is fed simultaneously into a 3-phase reactor (1) and a leaching-flotation multi-

Table 2.15. Values of metals and sulfur in 1 t of the investigated ore samples.

Metal	Price $/t (June 1986)	Values of metals and sulfur ($/t ore) #1 LPU	#2 LPL	#3 DDS	#4 TRIO	#5 DDN	#6 DDN
Au	10824/kg	37.67	28.25	8.12	43.08	20.89	6.71
Ag	159/kg	14.74	16.36	1.29	18.89	5.49	1.24
Zn	849	56.29	62.32	1.36	63.67	22.75	73.27
Pb	428	12.11	12.75	0.26	31.24	5.14	0.34
Cu	1448	5.50	5.79	11.58	19.55	21.72	17.09
S° 1)	142	6.60	7.0	6.30	11.42	14.71	34.08
(a) Total2)		132.9	132.5	28.91	187.85	90.70	132.74
(b) Sulfur as $H_2SO_4$3)	80	7.4	7.5	9.1	4.8	7.7	1.7
Total (a) + (b)		140.3	140.0	38.0	192.6	98.4	134.4

1) Only elemental sulfur generated during leaching
2) Theoretical value, to recovery on the hydrometallurgical way
3) Sulfur as H_2SO_4 from pyritic residue

Table 2.16. Level of knowledge and some specific conditions, parameters and the most important apparatus for the processing of 100,000 tons of ore per year. Flowsheet with direct leaching-flotation processing in ferric sulfate solution (Fig. 2.38 and 2.39).

Operation No.	Unit Process	Principal Reaction No.	Conditions and Parameters	Rate of Process[1)]	Apparatus type, Materials, Equipment	Study[2)] Required	Reference to the Knowledge Level[3)]			
							Lab.	Pilot	Industry	Other Rmks
1	Hydrolysis	2.8, 2.9, 2.11	Precipitation of total iron; Fe final conc. below 200 mg/L; Temp. 80-90°C; pH~2;P_{O_2}=50-100psi	Fast	Continuous gas/liquid/solid pressure reactor, mixing by injecting oxygen; initial S/L separation with cyclone	Lab. Study Eng. Study	(2.21) 2.22, 2.23	2.24 (2.25)		
2,3	Leaching-Flotation	2.1, 2.2, 2.3, 2.5, 2.7, 2.8	Two steps of L-F process in ferric sulfate solution; Temp. 80-90°C, P_{O_2}=50-100 psi, pH = 1-2	Moderate	Continuous,gas/liquid/solid pressure flotation column,with centrifugal separation of liquid/solid/oxygen suspension; minimum 4 mixing/flotation units in one column	Lab. Study Eng. Study	2.15	(2.26) 2.27		
4,5	Leaching-Flotation	2.1, 2.2, 2.3, 2.10	Two steps of L-F process in ferric sulfate solution; Temp. 80-90°C P_{O_2}=50-100 psi pH = 0-1	Slow	Continuous,gas/liquid/solid pressure flotation column,with centrifugal separation of suspension with higher capacity than for operation 2 & 3, Min. 6 mixing/flotation units in one column	Lab. Study Eng Study		(2.26) 2.27		
6	Filtration	–	Fine particles of goethite, gypsum and insoluble gangue mineral; Pressure 40-90psi temp. 70-80°C	Very Slow	High surface pressure filter with water washing	Ind. Proj.			2.26	known
7	Filtration	–	Coarse flotable fraction of sulfur and not reacted sulfides; pressure 40-90 psi temp. 70-80°C; Separation of oxygen necessary	Moderate	Pressure filter; good filtration; water washing necessary,oxygen collected must be compressed of about 20 psi and under pressure 60-120 psi turned back to process	Eng. Study Constr. Proj.			2.26	known
8	Cementation	2.12[4)]	Cementation of copper by zinc from purified zinc sulfate solution with solid particles sedimentation	Fast	Standard thickener	Ind. Proj.			2.27	known

Table 16. (cont.)

Operation No.	Unit Process	Principal Reaction No.	Conditions and Parameters	Rate of Process[1]	Apparatus type, Materials, Equipment	Study[2] Required	Reference to the Knowledge Level[3]			
							Lab.	Pilot	Industry	Other Rmks
9	Electrolysis	2.13[5]	Zinc electrolysis: [Zn] from 110 g/L to 60 g/L	Slow	Standard electrolyzers	Ind. Proj.			2.27	known
10	Calcium chloride leaching	2.4	Concentrate solution of $CaCl_2$ (200-220 g/L);pH=0; lead conc. 10-18g/L; Temp. 80-90°C	Fast	Typical vessel-reactor with mechanical mixing moderate chloride corrosion	Test Lab.		(2.11)		
11	Crystallization		Crystallization about 30% of Pb in form of $PbCl_2$ crystals, by cooling from 80-90 to 50-60°C	Moderate	Crystallizer with continuous separations of crystals by cyclone or centrifuge; moderate corrosion by chlorides	Test Lab.			2.30	
12	Precipitation	2.6	Precipitation of iron excess by CaO; Temp 60-70°C Probably with slow oxidation by oxygen under atmospheric pressure	Slow	Typical, not defined	Test Lab.	(2.21) 2.24 2.22,(2.25) 2.23			
13	Ferric chloride leaching	2.14[6]	$FeCl_3$ and HCl in concentrate $CaCl_2$ and $MgCl_2$ soln. [Fe(III)]=30-70g/L [HCl]=2-20g/L; [$CaCl_2$]=60-80g/L; [$MgCl_2$]=60-80g/L; Temp. 80-90°C	Moderate	Typical vessel reactors, thickener and belt-filter, strong corrosion by chlorides	Constr. Proj.	2.7- 2.11 2.9			
14	Cementation	2.12[4]	Cementation of copper and silver by iron or scrap	Fast	Column system with fixed bed of iron pellets	Lab. and Eng. Study	2.27			
15	Oxidation	2.8	Precipitation of 33% of iron from solution under elevated oxygen pressure.50-100psi Temp 70-80°C	Fast	Gas/Liquid/Solid low pressure reactor with injector.Initial cyclone separation and final with pressure filter; Strong corrosion by chlorides	Test Lab Constr. Proj.	(2.21) 2.24 2.22,(2.25) 2.23			

---

1) Very fast, fast, moderate, slow
2) TEST LAB. - Process is known, needs control tests on the representative ore sample only.
LAB. STUDY - Study on the kinetics reactions required
ENG. STUDY - Study on the engineering aspects and process conception required.
CONSTR. PROJ. - Process is sufficiently known to undertake construction projects
IND. PROJ. - Standard technology and apparatus construction needs only project on the industrial plant.
3) Items in paranthesis concern other similar processes or unit operation
4) $Zn + CuSO_4 = ZnSO_4 + Cu$ (2.12)
5) $ZnSO_4 + H2O = H_2SO_4 + Zn$ (2.13)
6) $CuFeS_2 + 4FeCl_3 = CuCl_2 + 5FeCl_2 + 2S$ (2.14)

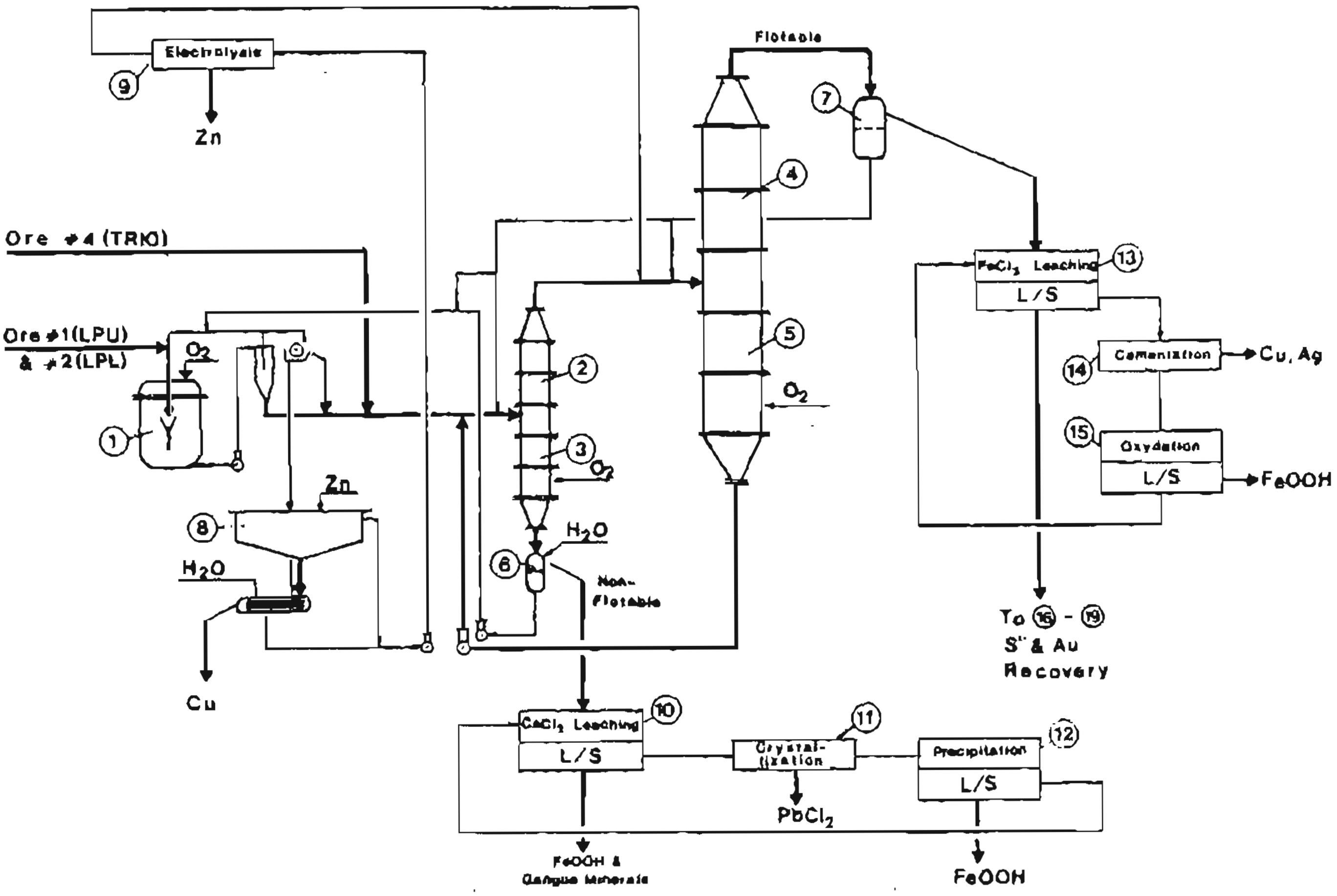

Figure 2.39. Concept of the ore treatment plant according to the 2nd variant with leaching-flotation steps in ferric sulfate solution. Numbers in circle correspond to the unit process numbers in Table 2.16.

step reactor (2)/(3). In reactor (1) nearly total iron is precipitated from zinc sulfate solution by reaction with easy to dissolve sulfides other than FeS, (ore sample #1 & 2) under elevated pressure of oxygen. In the L-F reactor (2)/(3) the nonflotable fraction of the reacted pulp of ore #4 and the solid from reactor (1) is separated from a "bulk" flotable fraction and directed to the calcium chloride leaching step (10). The "bulk" flotable fraction is directed to a second leaching-flotation multi-step reactor (4)/(5). From here the separated flotable fraction is directed after filtration in (7) to the ferric chloride leaching step (13). The "sulfate" solution from the leaching-flotation reactors is supplied from filters (6) and (7) to the reactor (1). The solution from (1), after reacting with ore #1 and 2 and separating from solids, is directed to final purification (8) and zinc sulfate electrolysis (9).

The total volume of L-F reactors will probably be below 80 m^3, for processing 100,000 tons of ore per year. This figure is based on the kinetics of zinc extraction from the investigated ore samples.

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Chapter 3

HYDROMETALLURGY OF THE DELTA SULFIDE ORES

Second Stage Research

F. Letowski and P.D. Rao

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ABSTRACT

This report contains results of the Fluidized-Bed Leaching (FBL) initially adapted to improve Leaching-Flotation (LF) processing of Delta ores in sulfate solution. The research carried out in the continuous laboratory installation show, however, that the new, 3-phase (solid-liquid-gaseous) reactor also performs satisfactorily in other leaching systems. A new process of pyritic matrix destruction for precious metals recovery in the FBL reactor, and a new process for recovery of zinc and other metals in a chloride system are proposed on the basis of laboratory results.

3.1 Introduction

The general research program on hydrometallurgy of Delta ores conducted for the Nerco Minerals Company in 1986/87 was divided into two parallel investigations:

1st - research on ferric chloride leaching, conducted by Dr. Hsing Kuang Lin, and
2nd - supplementary research on the Leaching-Flotation (LF) process in sulfate solution under elevated pressure of oxygen, conducted by Dr. F. Letowski.

This report contains results of the supplementary research but they are not necessarily limited to sulfate leaching. The Fluidized-Bed Leaching (FBL) system initially adapted only for improving the LF process in sulfate solution was tested for mixed sulfate/chloride and different chloride systems also.

Results of the following research are described:

1. Experiments on Leaching-Flotation processing of the old (1985) LPU ore-sample. The tests were carried out to confirm results described in Chapter 2.

2. Fluidized-Bed Leaching and Flotation tests conducted on the new (1986) LP ore-sample, under elevated oxygen pressure in sulfate solution. The tests, carried out in a continuous laboratory installation were extended by chloride leaching of lead and silver immediately following sulfate leaching in the same installation.

3. Fluidized-Bed Leaching tests on the LP-86 new ore-sample in ferric chloride and cupric chloride solutions under oxygen pressure.

4. Supplementary investigation of Delta ore processing with mixed sulfate/chloride and other chloride systems. This investigation was done as a consequence of features of the Fluidized-Bed Leaching system that allow considerably improved recovery of metals from ore.

5. Gold and sulfur extraction from residues after FBL processing.

6. Study of FBL adaptation to existing and new processes.

The research described in this report was performed with active participation from Mrs. Wendy Atencio. Her contribution, apart from the routine chemical analysis, was as follows:

- Carrying out the non-pressure experiments on the leaching and leaching-flotation processes, including calculations and graphical representation of the results, and participating in the final analyses of experimental data and final preparation of the report.

3.2 Supplementary Tests on the LPU Ore

The supplementary tests of ferric sulfate leaching were performed in the same general conditions as the test described in the 1st stage report (1986) but with concentration of ferric sulfate halved. Initial iron concentration was diminished from about 60 g Fe/l in previous tests, to 34 g Fe/l in this test.

Two LPU ore-samples were leached according to the 2-step flowsheet presented in Figure 3.1. The first sample was leached by new solution in steps LS-93 and LS-95. The second sample was leached in the first step LS-94 by the spent solution after LS-93, and in the second step LS-96 by the new solution. Solid residues from flows (4) and (7) were directed to the three-step Leaching-Flotation processing LF-97-99 in the spent solution from the previous leaching.

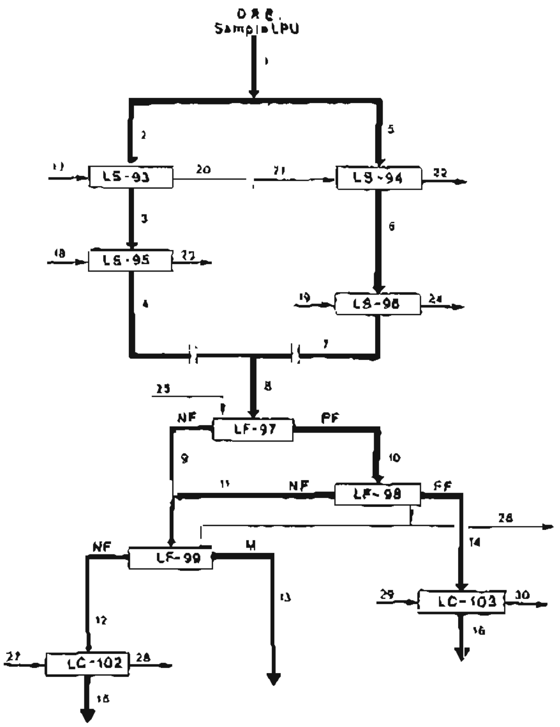

Figure 3.1 Experiments flowsheet carried out with the old ore sample LPU (1985). LS-93 to LS-96: ferric sulfate leaching under atmospheric pressure; LF-97 to LF-99: 3-step flotation under atmospheric pressure in the ferric sulfate solution; LC-102: calcium chloride leaching; LC-103: ferric chloride leaching; NF - nonflotable fraction; FF - flotable fraction, M - mixed fraction. The numbers identify flows according to Table 3.1 and 3.2.

Three fractions were collected after LF processing: non-flotable (NF), mixed (M) and flotable fraction (FF). Fraction NF was leached in calcium chloride solution (LC-102) and fraction FF in ferric chloride solution (LC-103). The mass balance for the experiments, calculated from metal concentration in solids, is presented in Table 3.1. Metal concentration in solutions are shown in Table 3.2.

Metals extraction at different stages of processing, calculated from the mass balance in solids, is presented in Table 3.3 and extraction progress during the leaching steps is shown in Figure 3.2. Kinetic characteristic of the Leaching-Flotation step was not controlled. The time required for this step was not longer than 30 minutes. The metals partition among the solution and the different solid fractions after the LF step are presented in Table 3.4.

General results of these tests confirm the data presented earlier in the 1st stage report (1986). Even with only half the iron(III) concentration in the leaching solution, the final copper extraction (after ferric sulfate and subsequent chloride leaching) exceeds 90%. The silver extraction exceeds 85% (Table 3.3). However, for zinc leaching in ferric sulfate solution only, the yield strongly depends on the leaching solution properties. The best zinc recovery was observed during leaching LS-93 and LS-96 (Figure 3.3). The 2nd steps of leaching LS-95 and LS-96 produce relatively high ferric ion concentrations. During LS-95 about 45% of the total iron in solution is in ferric form; during LS-96 about 30% is in ferric form. During 1 step-leaching (LS-93), the ferric ion concentration drops from an initial concentration of 0.46 mol/l to 0.12 mol/l after the first hour. This corresponds to about 20% of the total iron concentration remaining in the oxidized form, Fe^{3+}.

During 1st step leaching (LS-94), LPU ore is contacted with the solution from LS-93 which contains only 20% of total iron in oxidized form, (6.7 g Fe^{3+}/l). After some minutes of leaching, inspite of drastic diminishing of the oxidation potential,

Table 3.1. Leaching-Flotation processing of the LPU-ore sample (325-400 mesh). Mass balance of the experiments in sulfate and chloride solution according to flowsheet in Figure 3.1.

Specifications			ID No*)	Weight Grams	Grams in Solids (Ag: milligrams)					
					Cu	Fe	Zn	Pb	Ag	Ca
Ferric Sulfate Solution	1st Steps of Leaching	Total Inlet	1	400	1.52	129	26.52	11.32	37.08	
		Inlet to LS-93	2	200	0.76	64.5	13.26	5.66	18.54	
		After LS-93 to LS-95	3	180.29	0.33	59.3	4.79	n.a.	n.a.	
		After LS-95	4	169.68	0.117	56.1	0.51	5.08	19.59	
	2nd Steps of Leaching	Inlet to LS-94	5	200	0.76	64.5	13.26	5.66	18.54	
		After LS-94 to LS-96	6	194.84	1.58	60.3	11.46	n.a.	n.a.	
		After LS-96	7	177.76	0.322	49.8	4.27	5.15	20.06	
	Leaching-Flotation Steps	Inlet to LF-97	8	347.44	0.449	108.3	4.89	10.48	40.58	
		Non-Flotable fraction from LF-99	12	60.63	0.007	1.07	0.058	7.35	4.37	13.60
		Mixed Fraction from LF-99	13	26.05	0.031	8.22	0.33	0.42	3.31	
		Flotable Fraction from LF-98	14	240.90	0.270	83.06	3.26	2.17	30.36	0.02
Chloride Solutions		Final residue after LC-102	15	47.50	0.006	0.83	0.035	0.144	0.75	0.50
		Final residue after LC-103	16	225.82	0.126	103.2	0.0988	1.03	4.23	35.80

*) Identification numbers of the flows according to the flowsheet (Figure 3.1).
Metals concentrations in LPU-ore sample: Cu - 0.36%, Fe - 32.25%, Zn - 6.63%, Pb - 2.83%, Ag - 92.7 ppm, Ca - 0.35%.

Table 3.2. Leaching-Flotation processing of the LPU ore sample. Concentration and volumes of solutions used in experiments according to flowsheet in Figure 3.1.

Specifications		ID No*)	Volume (liters)1)	Concentration, g/l (Ag: mg/l)						
				Cu	Fe	Zn	Pb	Ag	Ca	pH
In Sulfate Solutions	Leaching solution inleting to LS-93	17	1.60	0.5	33.8	8.2	–	–	–	0.63
	Leaching solution inleting to LS-95	18	1.28	0.5	33.8	8.2	–	–	–	0.63
	Leaching solution inleting to LS-96	19	1.28	0.5	33.8	8.2	–	–	–	0.63
	Solution from LS-93	20	1.54	0.8	35.5	17.1	–	–	–	0.91
	Leaching solution to LS-94	21	1.51	0.8	35.5	17.1	–	–	–	0.91
	Solution from LS-94	22	1.57	–	37.2	17.5	–	–	–	0.89
	Solution from LS-95	23	1.23	0.7	33.9	13.5	–	–	–	0.77
	Solution from LS-96	24	1.21	1.7	35.0	18.4	–	–	–	0.66
	Solution inleting to LF-97	25	1.0	0.52	35.7	8.3	–	–	–	0.72
	Solution from LF-97-992)	26	(1.5)	(0.44)	(34.7)	(6.4)	–	–	–	n.a.
In Chloride Solutions	Solution inleting to LC-1023)	27	1.05	–	–	–	0.90	0.62	28.2	n.a.
	Solution from LC-102	28	0.99	0.004	0.06	0.017	6.96	3.68	30.1	n.a.
	Solution inleting to LC-103	29	1.14	–	30.8	0.003	0.001	–	32.6	n.a.
	Solution from LC-103	30	1.23	0.068	32.8	1.47	1.036	13.20	31.8	n.a.

* Identification numbers of the flows in Figure 3.1.
n.a. - not analyzed
1) Volumes of wash waters are not included.
2) Lack of data; volume and concentrations estimated from the balance in the solids (Table 3.1).
3) Recalculated from experiment carried out on 37.35g NF99 sample to the real weight of flow 12, i.e. 60.63g.

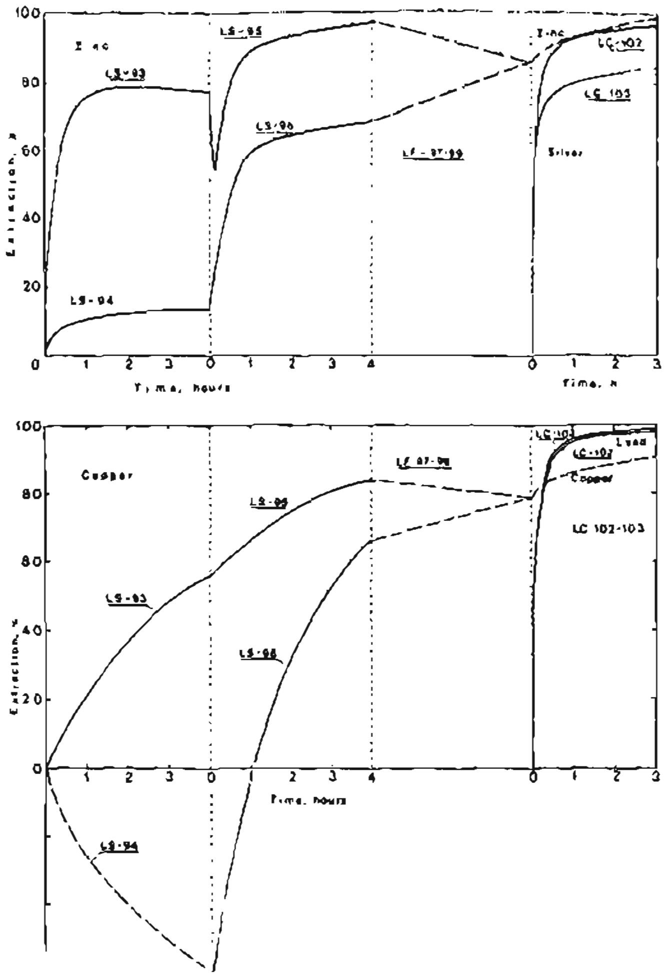

Figure 3.2 Progress of zinc, copper, lead and silver extraction during experiments carried out according to the flowsheet presented in Figure 3.1. Temperature 90-95°C.

both sulfides - PbS and ZnS, decomposed and H_2S evolved. During this period of leaching, total copper was precipitated from the solution in the form of CuS (Figure 3.2).

Such behavior of the reactive medias during these experiments is clear in light of basic bibliographical data, and indicates the chemically-controlled rate of the zinc sulfide decomposition. A temporary precipitation of zinc from the solution observed during the first 30 minutes of LS-95 leaching did not seem to have any importance during this kind of leaching.

Extraction of lead and silver from the non-flotable fraction by calcium chloride leaching, and from the flotable fraction by ferric chloride leaching, is fast and easy (Figure 3.4). However, both cases confirmed secondary precipitation of lead and silver that would probably also occur during prolonged leaching.

The general conclusions after supplementary research on the LPU ore leaching are as follows:

1. Effective leaching with lower concentration ferric sulfate solution can be conducted with simultaneous reoxidation of ferrous ions to ferric ions.
2. Zinc extraction from LPU ore-sample using the above solution is about 96% after 5 to 8 hours of leaching. Short-time (1 hour) leaching in chloride solution increases the total zinc extraction to 99%.

Table 3.3. Metals extraction during Leaching-Flotation processing of the LPU ore sample (325-400 mesh) calculated from metals content in solids, according to the flowsheet in Figure 3.1.

Specification		Extraction %				
		Cu	Fe	Zn	Pb	Ag
Sulfate Leaching 1st Step	After leaching LS-93	56.57	8.56	76.92	-	-
	After leaching LS-94	-60.5$^{1)}$	6.20	13.57	-	-
Sulfate Leaching 2nd Step	Cumulative after LS-93 and LS-95	84.6	12.96	96.15	-	-
	Cumulative after LS-94 and LS-96	70.46	16.01	81.56	-	-
Sulfate Leaching and Flotation	Cumulative after leaching LS-93-LS-95 and LF-97-99	79.74	28.40	86.23	-	-
Chloride Leaching	From non-floatable (NF) fraction after $CaCl_2$ leaching LC-102	14.3	22.4	39.6	98.04	96.32
	From flotable fraction (FF) after $FeCl_3$ leaching LC-103	58.16	-13.3*)	97.24	89.18	87.43
Sulfate and Chloride Leaching	Total cummulative extraction after chloride leaching	91.3	19.14	99.54	89.96	85.25

*) Precipitation from solution expressed as excess to total initial concentration in solids.

**) Calculated as 1-(15+16)/(1-13) where (1), (13), (15), and (16) are silver amount in flows 1, 13, 15, and 16

Table 3.4. Leaching-Flotation processing of LPU (old) ore sample. Metals partition among flotation fractions and solution (in weight percent).

		Per cent				
	Weight grams	Cu	Fe	Zn	Pb	Ag
Sulfate solution	18.12*)	79.74	28.40	86.25	-	-
Non-flotable fraction	15.15	0.46	0.83	0.22	73.95	11.49
Mixed fraction	6.51	2.04	6.37	1.24	4.22	8.70
Flotable Fraction	60.22	17.76	64.39	12.29	21.83	79.81

*) Loss of sample weight during leaching.

3. The degree of silver extraction from solid residues after "sulfate treatment" by leaching with chloride solution is about 85%.

4. The degree of copper extraction from the same residues in the same conditions is about 90%.

5. From the metals remaining in solid residues 90% of iron, 88% of zinc, 88% of copper, 80% of silver and 70% of gold are accumulated in the flotable fraction, while 74% of lead is collected in the non-flotable fraction.

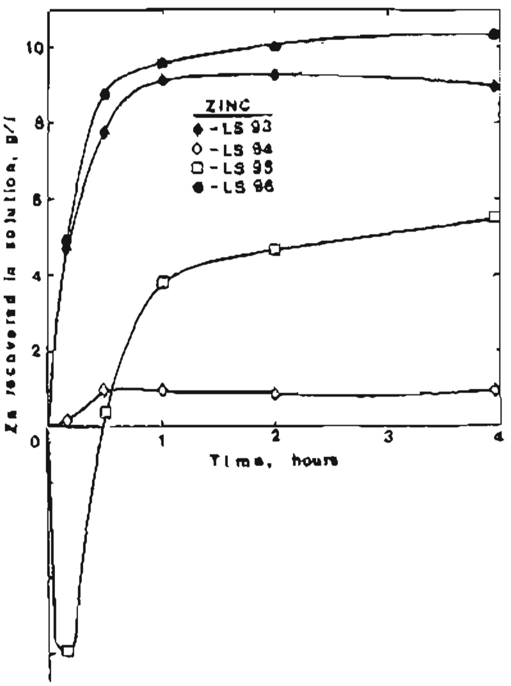

Figure 3.3. **Zinc behavior during the leaching tests LS-93 to LS-96.**

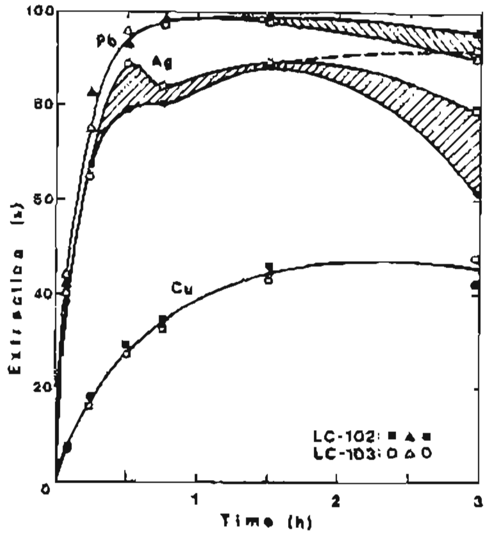

Figure 3.4. **Behavior of silver leaching during the leaching tests LC-101 (CaCl2 soln.) and LC-103 ($FeCl_3$ soln.). Temp. 90-95°C, other conditions and results: Table 3.1 and 3.2.**

3.3 Sulfate Leaching Under Oxygen Pressure

Process description

The laboratory installation built from Corning glass elements and schematically shown in Figure 3.5 is a mini-copy of the leaching section of the ore treatment plant suggested earlier (Chapter 2).

The scale of this mini-pilot installation is 1:63,000 and the retention time of ore in the leaching reactor (R_1) is about 4 hours. Unfortunately, this glass-built installation while excellent for direct visual observation did not allow for experimentation under pressure higher than 50 psi. The oxygen pressure, necessary for rapid ferrous ion reoxidation in sulfate solution with low cupric ion concentration is about 150 psi.

One conclusion was that the initial concept of the Leaching-Flotation process needs modification. The acceptable zinc extraction (96%) requires several hours of leaching. Meanwhile, the continuous, simultaneous, much faster flotation causes too early removal of non-reacted sulfides from the leaching solution. Of course the possibility of zinc extraction from the ore particles suspended in the flotation froth is evident, especially under elevated oxygen pressure, but initial investigations carried out during fall,1986 were not sufficient for any quantitative conclusion.

In spite of these difficulties, the following operational modifications were carried out:

- The oxygen supply to the 1st leaching reactor (R_1) had to be stopped for a time sufficient for nearly total zinc extraction from the ore.
- Ore pulp had to be fed from the pulp preparation beaker (B) to the 1st reactor (R_1) while the solution is recirculated upward through the reactor at a rate allowing for the ore particles suspended in the leaching solution to have the retention time necessary for zinc extraction. Such a process was named Fluidized-Bed Leaching (FBL).
- Solution from the 1st reactor had to be transported to the second reactor (R_2) while oxygen, dispersed by porous

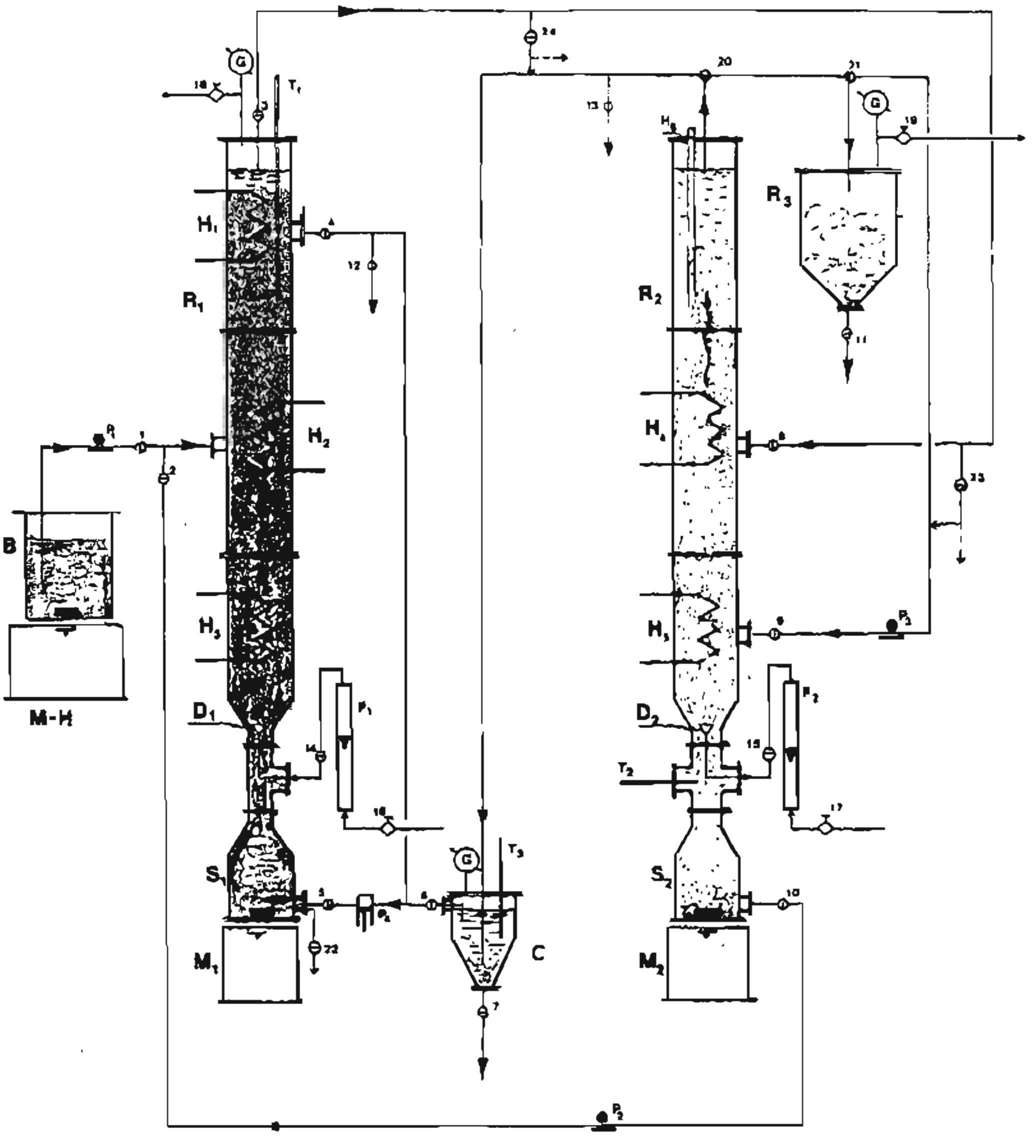

Figure 3.5. Laboratory Corning-glass installation for the continuous leaching and flotation under elevated pressure of oxygen:

R_1 and R_2 - Column reactors (dia. 4 inch, height 48 inch, max. pressure 50 psi)
R_3 - Pressure liquid/solid separator (150 psi)
S_1 and S_2 - Separators for sedimented fraction of suspension (50 psi)
B - Pulp preparation beaker
C - Pressure crystallizer (100 psi)
D_1 and D_2 - Fritted-glass discs for oxygen dispersion in reactors (60 psi)
F_1 and F_2 - Oxygen flow-meters (150 psi)
G-G_3 - Gauges (oxygen, 150 psi)
H_1-H_5 - Heating tapes
H_6 - Immersion heater (in fused quartz tube)
M_1 and M_2 - Magnetic stirrers
M-H - Hot plate with magnetic stirrer
P_1-P_3 - Tubing pumps Masterflex with Norprene tube, adapted to pulp transportation under 50 psi pressure
P_4 - Piston metering pump for solution (150 psi)
T1-T_3 - Thermometers
1-13 and 22-24 - Teflon plug valves joint with teflon pipes (100 psi)
14-19 - Teflon needle valves for oxygen flows regulation (100 psi)
20 and 21 - 3-way valves for pulp or foam direction (50 psi)

glass disc (D_2) under elevated pressure, oxidized ferrous ions to ferric ions. The solution then went through the crystallizer (C) and had to be directed to the bottom of the reactor (R_1).

- When the zinc extraction is nearly completed, oxygen can be injected into the 1st reactor (R_1) and the Leaching-Flotation (LF) process is begun. During the 2-step LF process carried out in both reactors (R_1 and R_2), the flotable fraction from the 2nd reactor (R_2) is collected in the separator (R_3). The mixed fraction from the bottom part of the second reactor is recycled through a separator S_2 to the 1st reactor (R_1). The non-flotable fraction sedimented in the 1st reactor (R_1) is recovered from the separator (S_1).

During the Fluidized-Bed Leaching process a segregation of solid particles as a function of their specific gravity takes place. The "heavy" fraction is suspended in the fluidized-bed in the 1st reactor. It contains the particles of sulfides, lead sulfate and other minerals with a specific gravity higher than 3.5. The "light" fraction, containing particles of gangue minerals and gypsum having a specific gravity lower than 3, is accumulated in the separator (S_2) and the crystallizer (C). In the crystallizer, additional crystallization of gypsum is going on from the solution.

A simplified flowsheet of the sulfate process carried out in the installation is shown in Figure 3.6.

The fluidized-bed sulfate leaching conducted under oxygen pressure does not necessarily have to be ended by the leaching-flotation process. It can be continued by chloride leaching, also carried out in the fluidized-bed system, but under atmospheric pressure. Such an exchange of the leaching agent can be done immediately by a simple introduction of the new chloride solution to the 1st reactor (for example, through the sampling tube, valve 12, pump P4 and valve 5) or with intermediate washing by water to diminish the zinc sulfate transfer to chloride solution. During these operations sulfate solution is collected in the separator (R_3). Because of very fast lead and silver leaching, a single pass of the chloride solution through the 1st reactor is sufficient to complete extraction of these metals. This solution was recovered during experimentation from the sampling tube and valve 24.

Fifteen different experiments were carried out to find the best treatment method.

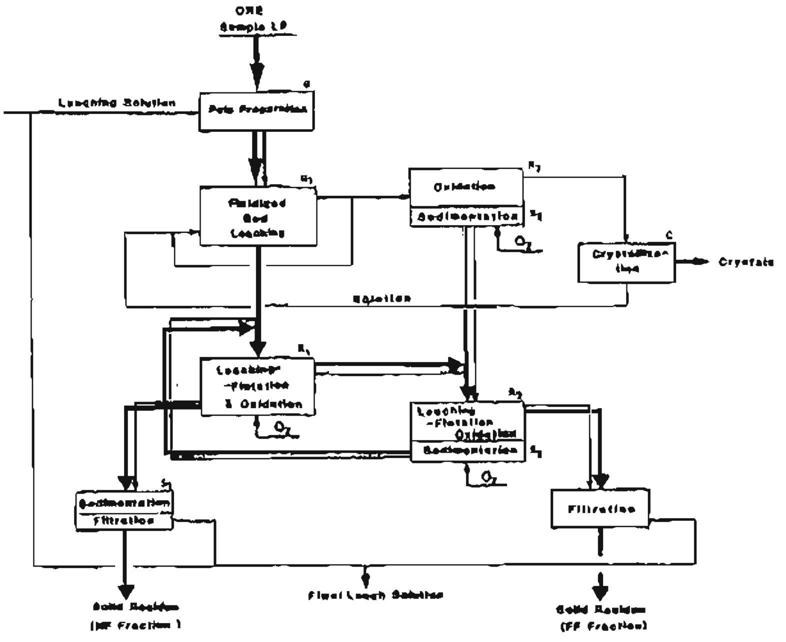

Figure 3.6. General flowsheets of experiments carried out in pressure installation presented in Figure 3.5.

A schematic flowsheet is presented in Figure 3.7. Generally, the left branch of the flowsheet, beginning with flow #2, joins the fluidized-bed leaching with the leaching-flotation processes. The right branch, beginning with flow #37, is composed of the fluidized-bed leaching process without flotation. Both groups of processes started from direct leaching-flotation steps (LF 203-208 left side, and LF 221 right side) to withdraw the non-flotable fractions from the multistage processing. The non-flotable fractions were further leached together in a calcium chloride solution in the fluidized-bed system (FBL 225).

The flows of the flotable or "heavy" fractions are shown in Figure 3.7 by coarse lines and the non-flotable, "mixed" or "light" fractions by fine lines. The following symbols are used for the tests identification:

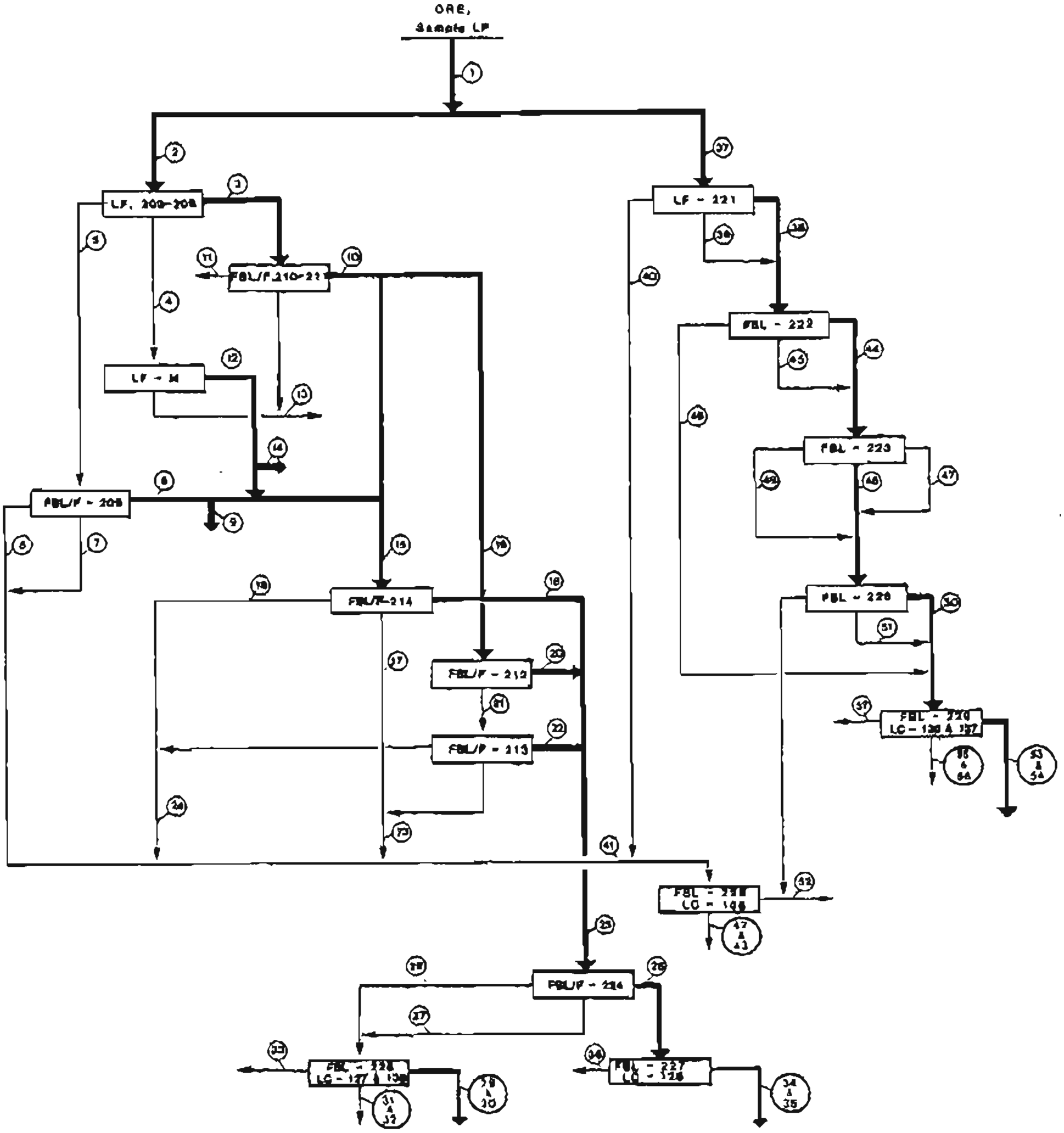

Figure 3.7. Flowsheet of experiments on Fluidized-Bed Leaching and Flotation in sulfate solution in the laboratory installation (Figure 3.5). Circled numbers of flows correspond to the identification numbers in Table 3.6.

LF	Direct ore leaching-flotation process
FBL	Fluidized-bed leaching
FBL/F	Fluidized-bed leaching followed by flotation
LF-M	Supplementary leaching-flotation of the "mixed" fractions carried out in a separate non-pressure installation
LC	Supplementary ferric chloride leaching of final residues after treatment in the continuous installation, carried out in a typical laboratory glass-reactor under atmospheric pressure.

General experimental conditions of the continuous tests are presented in Table 3.5. The runs of experiments performed on the ore-sample-flow #2, and on the flotable fractions of the left branch of flowsheet (Figure 3.7) are shown in Figures 3.8 and 3.9. The feeding time was different and was a function of the quantity of sample and the testing conditions. However, the rate of solution transportation, using the pump P_6, was relatively stable. It was varied from 80 ml to 160 ml per minute. The rate of transportation was adjusted to stabilize the fluidized-bed of solid particles suspended inside the reactor for different liquid/solid ratios. The average rate was about 114 ml/min. The liquid/solid ratio varied from 2.38 l/kg to 1.18 l/kg with an average value of 1.65 l/kg.

During the first experiment LF 203-208, the total sample (2,500 g) was supplied to the reactor as pulp in 5 equal portions. Each portion of pulp was introduced with sulfuric acid (H_2SO_4) (marked by arrows in the graph in Figure 3.8,a). H_2SO_4 was added to stop observed iron precipitation from the leaching solution. During the entire time of the experiment, the 2-step leaching flotation, including recycling of mixed fractions from the 2nd and 1st reactor, was carried out. Technical

Table 3.5. Run of the continuous tests in pressure installation.

	Weight of feeding solid[1] (g)	Time of feeding (min)	Retention time FBL time (min)	Flotation time FL time (min)	Remarks
LF 203-208	2,500.0	102	~25 [2]	124	See Figure 3.8a)
FBL/F 209	n.d.[3]	~100 [4]	105	15	~85°C 30 psi
LF-M	n.d.[3]	n.d.	–	60	95°C, LF in another non pressure reactor
FBL/F 210-211	907.1	66	30	15	See Figure 3.8b)
FBL/F 212	700.0	212	98	12	80-100°C; 20 psi
FBL/F 213	n.d.	26 [5]	–	–	90°C, 30 psi, L-F step in another non pressure reactor
FBL/F 214	800.0	15	86	–	See Figure 3.8c)
FBL/F 224	1,102.5	146	70	15	See Figure 3.9
FBL 227	615.3	50 [6]	90 [7]	–	Single passing of $CaCl_2$ leach solution through fluidized bed (see Figure 3.9)
FBL 228	545.6	20 [6]	60 [7]	–	90°C, atm. pressure, single passing of $CaCl_2$ leach solution
FBL 221	1,050	45	40	10	75-80°, 20-36 psi
FBL 222	802.4	~60	160	–	80-85°, 18-24 psi
FBL/F-223	536.1	15	60	–	90-95°, ~10 psi
FBL 226	513.5	–	50	–	80-107°, 5-10 psi $CaCl_2$
FBL 229	583.7	40	110	–	92-95°, 18-24 psi
FBL 225	398.5	30 [6]	60[7]	–	90°C, atm. pressure; single passing of $CaCl_2$ leach solution

1) This real weight of solid can be different from mass of the same flows indicated in Table 3.6. Values in Table 3.6 are recalculated from real values to the correct theoretical mass balance.
2) This is an average time from 5 feeding operations during L-F processing.
3) Not determined and not analyzed; weight of products from FBL/F209 in Table 3.6 is determined.
4) Not precise because some interruption during feeding.
5) Experiment stopped after feeding because of technical problems. LF-step in another non-pressure reactor.
6) Corresponds to the time of washing with water.
7) Corresponds to the time of chloride leaching.

problems in transporting pulp to the reactor caused a one-day interruption of processing just after feeding the 1st beaker of ore.

Temperature and pressure were controlled during experiments in the points indicated in Figure 3.5. Concentration of ferrous ions, and total iron were analyzed from the samples of solutions. The mass balance in the experiments is presented in Table 3.6. It is based on the analyses of metals in solid samples. Analyses of solutions could not be applied to these calculations because of imprecise measurement of their total volumes. The degrees of metals extraction from LP ore-sample during fluidized-bed leaching and flotation in sulfate and chloride solution at the different stages of the ore treatment are shown in Table 3.7. They are calculated from the mass balance in Table 3.6.

Because of relatively low extraction of zinc (84.4%) from ore in sulfate solution, and lead (91.9%) in calcium chloride solution, additional leaching of solid residues with ferric chloride solution were carried out after FBL and FL processing. The following solid samples were submitted to this leaching:

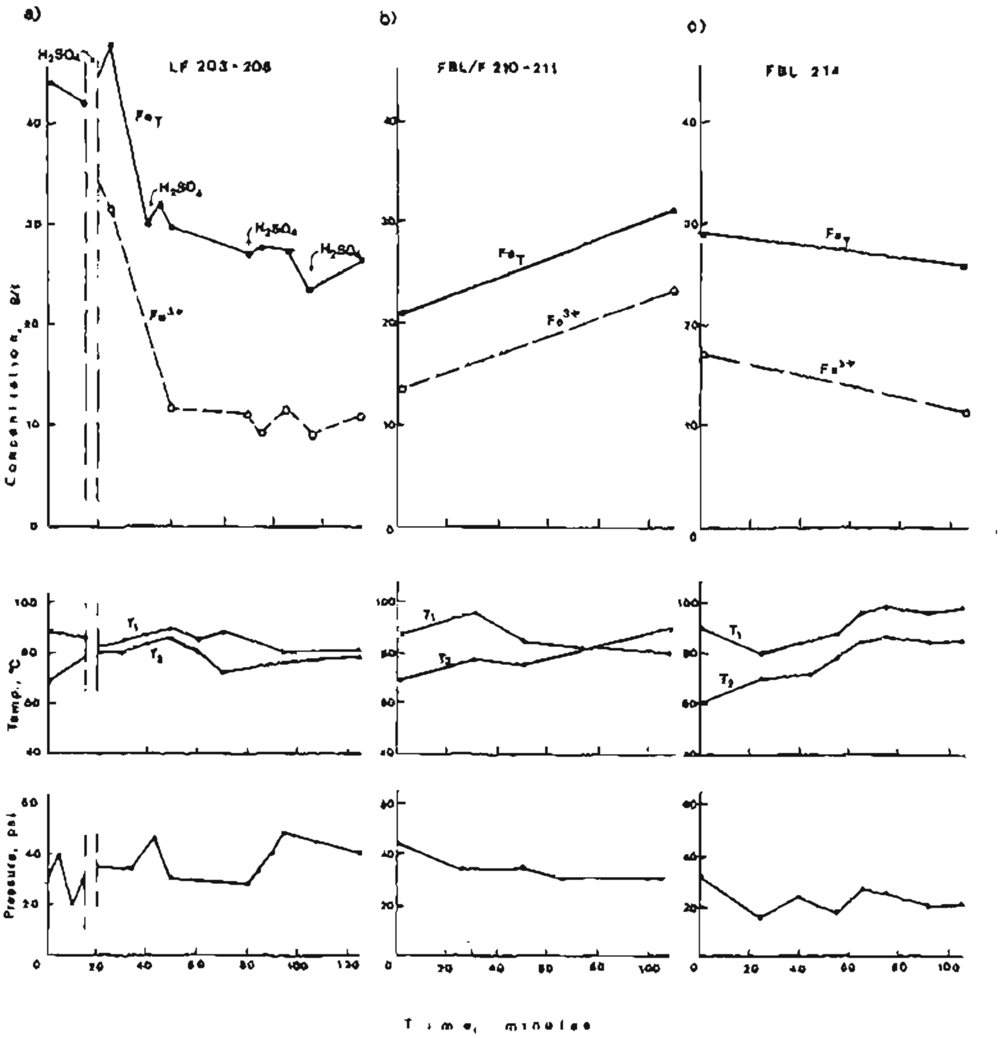

Figure 3.8. Characteristics of the continuous fluidized-bed sulfate leaching tests described as LF 203-209, FBL/F-210, 211 and FBL-214 (Figure 3.7 and Table 3.6). Description in the text.

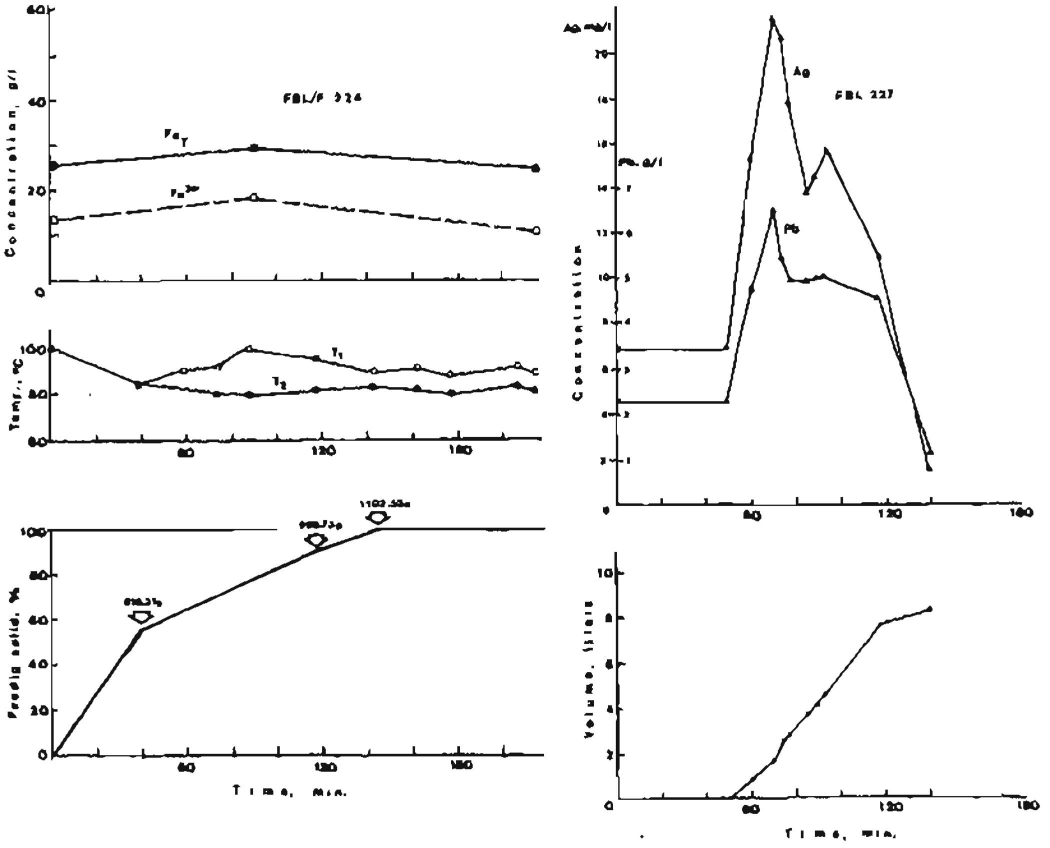

Figure 3.9. Characteristic of the continuous tests FBL/F-224 in sulfate solution and followed FBL-227 in calcium chloride solution carried out with the flotable fraction from FBL/224.

Total residue after FBL 225
Total residue after FBL 227
Heavy fraction after FBL 228
Light fraction after FBL 228
Heavy fraction after FBL 229
Light fraction after FBL 229

About 30 g samples of these residues were leached with 0.7 l of chloride solution containing:

Fe^{3+} from 21 to 22 g/l as $FeCl_3$
Ca^{2+} from 16 to 22 g/l as $CaCl_2$
Mg^{2+} from 14 to 18 g/l as $MgCl_2$

and 100 ml of 36% HCl per liter. The solution used for leaching samples FBL 228 also contained 6.4 g/l Zn as $ZnCl_2$ and 3.3 g/l Pb as $PbCl_2$.

Each leaching was carried out at a temperature of 90-95° C for 4 hours in a glass reactor with stirrer. Results of these supplementary leachings are presented in Tables 3.6 and 3.7.

The behavior of silver, lead and antimony during sulfate treatment, and especially the possibility of their earlier extraction from solid products are important. The silver content in solid residues drops from one step of sulfate treatment

Table 3.6. Fluidized-bed leaching and flotation. Mass balance of the experiments in sulfate and chloride solution according to the flowsheet in Figure 3.7. Sample LP, fraction 400 mesh x 20μm.*)

	Specifications	ID No**)	Sample Weight (grams)	Content in Solids, grams (Ag, Au: mg)									
				Cu	Fe	Zn	Pb	Ag	Sb	As	Au	Ca	S
Leaching Flotation (LF) in sulfate solution: 203-208	Total ore sample	1	3,550	10.0	1,090.6	241.4	125.0	309.15	2.244	34.36	7.45		
	Ore inlet to LF-203-208	2	2,500	7.05	768.	170.0	88.0	217.71	1.580	24.20	5.25		
	Flotable Fraction (FF) from 203-208	3	907.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.			
	Mixed Fraction (M) from 203-208	4	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.			
	Non-Flotable Fraction (NF) from 203-208	5	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.			
FLUIDIZED BED LEACHING & FLOTATION (FBL/F) in ferric sulfate solution: 209-214 and 224	FF from FBL/F 209	6	546.3	1.147	18.8	18.57	11.36	63.81	0.131	6.01	0.981		
	M from FBL/F 209	7	95.2	0.094	19.9	1.51	8.77	9.78	0.047	0.53	0.077		
	NF from FBL/F 209	8	192.5	0.068	14.5	1.15	37.31	13.07	0.108	0.38	0.117		
	Sample excluded from processing	9	18.8	0.039		0.64	0.39	2.27	0.004	0.21			
	FF from FBL/F 210-211	10	843.7	2.19	329.9	29.70	10.79	89.94	0.194	10.21	1.305		
	M from FBL/F 210-211; excluded from processing	11	51.0	0.018	11.3	0.82	3.88	4.05	0.005	0.10			
	FF from LF-M	12	260.9	0.57	104.6	8.19	4.96	27.58					
	ΣNF from FBL/F 210-211 and LF-M	13	12.37	0.069	1.6	0.09	2.38	1.83	0.024	0.044			
	Sample excluded from processing	14	50.0	0.127	20.0	1.37	1.04	3.29	0.008	0.63			
	Inlet to FBL/F-214	15	843.7	1.85	144.8	28.26	16.46	97.07					
	FF from FBL/F-214	16	685.9	1.372	247.6	15.02	10.35	77.50	0.315	8.44			
	M from FBL/F-214	17	122.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.			
	NF from FBL/F-214	18	40.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.			
	Inlet to FBL/F-212	19	738.2	2.09	288.6	25.99	16.46*	77.5					
	FF from FBL/F-212	20	145.9	0.262	53.0	2.64	2.65	19.98	0.073	1.71			
	Agglomerated portion from FBL/F 212 to FBL/F 213	21	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.			
	FF from FBL/F-213	22	436.1	0.480	163.9	7.50	2.83	46.10	0.174	5.36			
	ΣM from FBL/F 213 and FBL/F 214	23	149.21	0.164	61.6	2.64	3.75	19.99	0.069	1.52			
	ΣNF from FBL/F 213 and FBL/F 214	24	46.83	0.077	15.5	1.07	3.39	6.62	0.047	0.04			
	Inlet to FBL/F 224	25	1267.9	2.114	464.6	25.16	15.81	143.58	0.562	15.31			
	FF from FBL/F 224	26	707.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.			
	M from FBL/F 224	27	234.5	0.523	70.6	2.74	4.32	21.79	0.123	1.94			
	NF from FBL/F 224	28	399.9	1.066	125.0	4.44	7.44	57.84	0.222	5.68			
Calcium chloride fluidized bed leaching: 227 and 228 Ferric chloride leaching: LC-127, 128 and 138	Heavy (H) fraction from FBL-228	29	596.3	0.735	181.7	6.18	0.49	22.65	0.126	4.69	1.324		
	H-fraction after FBL-228 from LC-127	30	572.1	0.430	226.3	0.81	0.33	17.66					
	Light fraction from FBL-228	31	80.5	0.094	28.2	0.59	0.41	3.36	0.022	0.64			
	L-fraction after FBL-228 from LC-138	32	75.9	0.045	23.3	0.03	0.03	2.23					
	Crystals from cooling system FBL-228	33	35.4	0.001	0.06	0.006	14.40	0.04				2.12	
	H-fraction from FBL-227	34	621.5	1.112	201.4	10.01	1.53	54.49	0.193	7.39	1.560		33.00
	H-fraction after FBL-227 from LC-128	35	594.7	0.578	188.3	1.12	0.37	21.65					
	Crystals from cooling system FBL-227	36	3.4	-					-	-			
FBL-221 in sulfate solution	Ore inlet to LF-221	37	1,050.0	2.961	322.6	71.40	37.0	91.44	0.664	10.16	2.205		
	FF from LF-221	38	507.5	1.265	150.3	24.80	12.88	56.30	0.184	5.61			
	M from LF-221	39	305.3	0.518	83.5	13.27	9.57	35.19	0.102	2.47			
	NF from LF-221	40	84.3	0.022	2.7	1.36	4.03	6.20	0.101	0.10			
FBL-225 in CaCl$_2$, LC-135 in FeCl$_3$	ΣNF from 209 and 212-214	41	483.7	0.402	111.3	6.37	46.19	49.46	0.271	2.49			
	Total from FBL-225	42	550.9	0.424	104.0	6.32	5.83	14.94	0.172	n.a.	0.800	2	
	Total after FBL-225, from LC-135	43	448.4	0.207	90.7	0.26	0.14	6.42					
FBL-222 and 223 in ferric sulfate solution	H-fraction from FBL-222	44	443.5	0.953	148.16	12.74	11.01	50.36	0.128	5.47	1.001		
	Mixed (M) fraction from FBL-222	45	104.0	0.125	29.9	1.44	5.38	11.85			0.197		
	Crystals from cooling system FBL-222	46	75.2	0.126	23.4	1.30	2.71	8.49	0.031	0.54			
	H-fraction from FBL-223	47	489.9	0.965	165.4	11.23	10.16	48.81	0.157	5.02	1.019		
	M-fraction from FBL-223	48	45.7	0.079	13.7	0.96	2.06	4.88	0.017	0.42	0.133		
	Crystals from cooling system from FBL-223	49	5.7	0.006	1.2	0.08	0.33	3.96			0.012		
FBL-226 in CaCl$_2$	H-fraction from FBL-226	50	506.5	0.954	150.7	9.10	0.76	22.32	0.123	5.13			
	M-fraction from FBL-226	51	47.2		15.7	0.53	0.04	1.35					
	Σ crystals from FBL-225 & 226	52	42.3	0.0004	0.02	0.003	0.19	0.04	0.002	-		1.90	
FBL-229 in CaSO$_4$, LC-131 in FeCl$_3$	H-fraction from FBL-229	53	460.5	1.019	148.3	10.23	2.27	73.31	0.092	3.82	1.082		22.38
	H-fraction after FBL-229 from LC-136	54	505.1	0.232	96.9	0.45	0.27	11.37					
	L-fraction from FBL-229	55	68.5	0.070	22.1	0.90	0.55	2.68	0.013	0.45	0.177		
	L-fraction after FBL-229 from LC-137	56	60.9	0.036	21.7	0.03	0.04	1.43					
	Crystals from FBL-229	57	5.9	-	n.a.	-	0.07	0.45	-	-			

LF: Leaching-Flotation
FBL: Fluidized Bed Leaching
FBL/F: Fluidized Bed Leaching and Flotation
LC: Chloride Leaching
n.d.: not determined
n.a.: not analyzed

* Metals concentration in the LP ore sample: Cu - 0.282%, Fe - 30.74%, Zn - 6.80%, Pb - 3.52%, Ag - 87.09 ppm, Sb - 630 ppm, As - 0.97%, Au - 2.1 ppm, Ca - 0.146%

** Identification flow-numbers according to the flowsheet in Figure 3.7.

Initial concentrations of the solutions:

a) Sulfate solution: Zn 21-35 g/l, Cu 1-2 g/l, Fe$_T$ 23.8-28.1 g/l, H_2SO_4 5% w.t.
b) Calcium chloride solution: $CaCl_2$ 200 g/l, HCl 1.2% w.t.
c) Ferric chloride solution: Fe^{3+} 20-22.2 g/l, $CaCl_2$ 47 g/l, $MgCl_2$ 68 g/l, HCl 2% w.t.

Table 3.7. Metals extraction during fluidized-bed leaching and flotation in sulfate and chloride solutions; calculated from metals content in solids (see Table 3.6 and Figure 3.7).

	Specifications	Processing Time (min)	Extraction (%) Cu	Fe	Zn	Pb	Ag	Sb	As	Au
Branch LF 203... (Flow 2)	Extraction after steps 203-211 and LF-M	av 30	47.37	n.d.	64.69	--	--	44.3	6.1	--
	Cummulative extraction from 203-214	av 135 $^{1)}$	59.02$^{8)}$	n.d.	78.59	--	--			
	Extraction after 203-214, 224 227 and 228	443 $^{2)}$	66.68	n.d.	84.42	90.97$^{9)}$	56.07$^{9)}$	n.d.	n.d.	--
	Total extraction from flow (2) (after LC-127,128 and 138)	503 $^{3)}$	84.14	n.d.	93.65	95.39$^{9)}$	71.01$^{9)}$	n.d.	n.d.	--
Branch LF 221... (Flow 37)	Extraction after LF 221		39.01	26.69	44.78	--	--	41.72	19.49	
	Extraction after FBL 222	220 $^{1)}$	58.93	36.90	77.61	--	--			--
	Extraction after steps 221-223, 226 and 229	430 $^{4)}$	64.3$^{12)}$	43.6$^{12)}$	84.11	93.62	58.94$^{10)}$	n.d.	n.d.	--
	Total extraction from flow (37) (after LC-136 and 137)	490 $^{5)}$	62.9	62.9$^{1)}$	99.27	97.68	60.12$^{11)}$	n.d.	n.d.	--
Total Flowsheet from flow 1 to 56	Total extraction from flow (1) after "wash-leaching" in FBL 225 and FBL 227-229 with $CaCl_2$ solution	av 436 $^{6)}$	64.28 59.05$^{8)}$	37.15	84.4	91.94	58.97 71.8$^{8)}$	72.46 32 $^{8)}$	n.d.	--
	Total extraction from flow (1) after final $FeCl_3$ leaching (LC-127, 128, 135-138)	av 506 $^{7)}$	83.9	40.65	98.88	99.06	79.44	n.d.	n.d.	--

av: average; n.d.: not determined

1) Time of processing in sulfate solution
2) 353 min in sulfate solution and 90 min in $CaCl_2$ solution
3) As above with additional 60 min in $FeCl_3$ solution
4) 370 min in sulfate solution and 60 min in $CaCl_2$ solution
5) As above with additional 60 min in $FeCl_3$ solution
6) Average from 2) and 4)
7) Average from 3), 5), and simultaneous leaching of NF fractions in: $CaCl_2$ solution (FBL-225) - 60 min, and in $FeCl_3$ solution (LC-135) ~60 min
8) Calculated from metals balance in solutions
9) As yield from flow (25)
10) As yield in FBL 226 from flows (47) to (49)
11) Extraction from flow (37) after FBL 226 excluding silver in flow (40)
12) Extraction from flow (37) after FBL 223.

to another. One probable reason of such a silver behavior is its slow dissolution in the sulfate solution as silver sulfate (Ag_2SO_4).

For this reason, the leachability of silver, lead and antimony by a non-oxidative calcium chloride solution was investigated in ten samples taken from different solid residues from the left branch of the flowsheet. The leaching tests were carried out on 20-30 g of samples in 0.7 l of solution containing 52 to 66 g Ca/l and 10 ml of HCl (36%) during 4 hours at 90-95°C in a standard laboratory installation. The results are presented in Table 3.8. The kinetics of leaching for more typical samples is shown in Figures 3.10 and 3.11. General conclusions after sulfate leaching are:

1. Sulfate leaching in fluidized-bed coupled with flotation or not, allows for relatively selective zinc extraction from complex sulfide ores. Simultaneous extraction of copper depends on its concentration and its sulfidic form in the ore.

Table 3.8. Results of control chloride leaching of lead, silver and antimony (see text for experimental conditions)

No. of Test	Solid Sample	I.D. No. of flow[1]	Extraction % from sample[2] Pb	Ag	Sb
LC-113	NF fraction from FBL/L 209	8	>99.9	92.5	>99
LC-114	M fraction from FBL/L 209	7	85	62	>80
LC-115	NF from FBL/F 210-211	11	93.5	87	n.d.
LC-116	FF fraction from LF-M	12	99	70.3	n.d.
LC-117	FF from FBL/F 210-211	10	97.8	75.1	n.d.
LC-118	FF from FBL/F 212	20	>99.9	74	62-68
LC-119	FF from FBL/F 213	22	>99.9	70	52-93
LC-120	Heavy fraction from FBL 214	16	>99.9	78	48
LC-121	M from FBL/F 213 and FBL 214	23	98._	72	85-92
LC-122	NF from FBL/F 213 and light fraction from FBL 214	24	96.8	75.7	n.d.
LC-123	M from LF-M and FBL/F 210-211	13	99	97.9	n.d.

NF - non-flotable fraction
M - mixed fraction
FF - flotable fraction
n.d. not determined
1) Numbers of flows from Figure 3.7
2) Yield in the carried out test (not cumulative extraction degree)

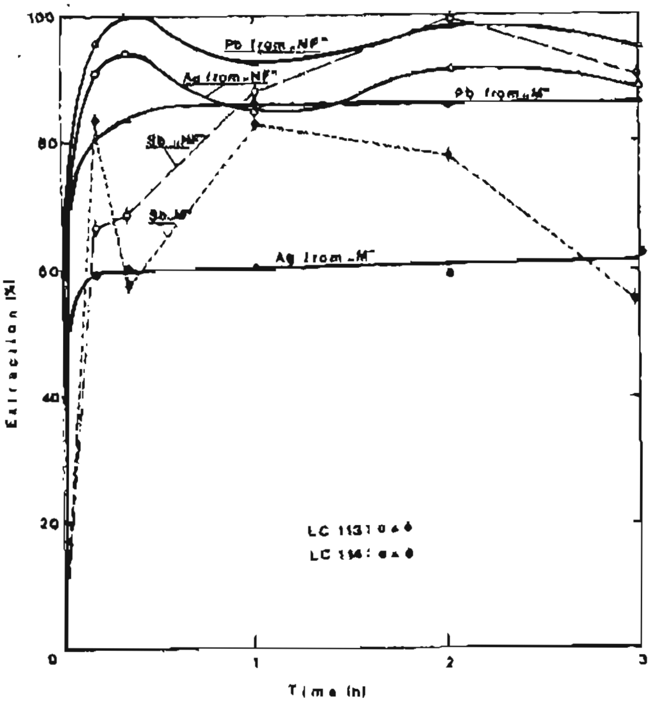

Figure 3.10. Leachability of lead, silver and antimony from nonflotable (LC-113) and mixed (LC-114) fractions after FBL/F-209 in calcium chloride solution. For other conditions see text.

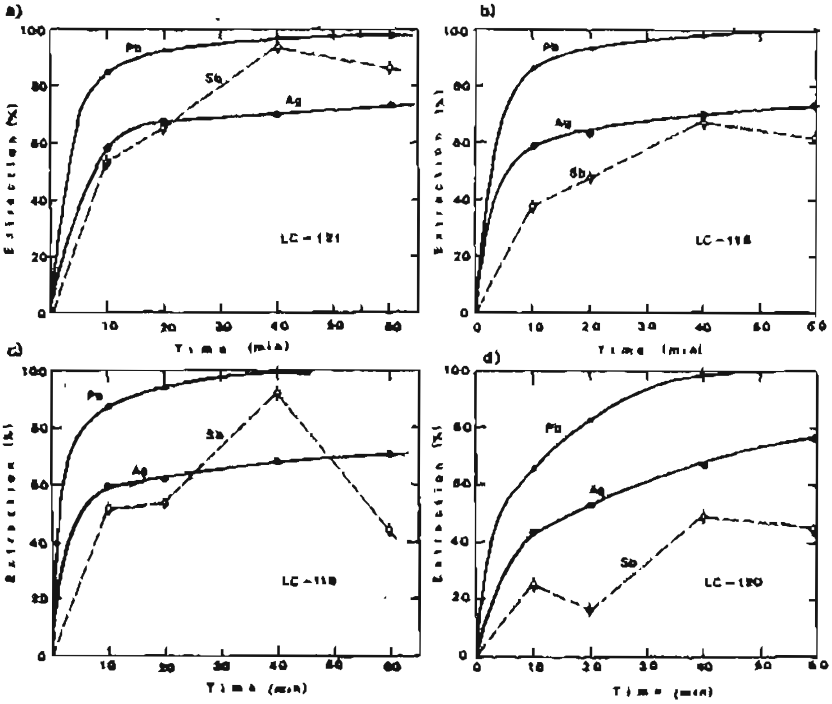

Figure 3.11. Leachability of lead, silver and antimony from different fractions after FBL 212 to 214 in calcium chloride solution:
a) from mixed fractions after FBL 213 and 214 (LC-121)
b) from flotable fraction after FBL 212 (LC-120)
c) from flotable fraction after FBL 213 (LC-119)
d) from flotable fraction after FBL 214 (LC-120)

2. Slow reoxidation of ferrous ions under oxygen pressure of 20-30 psi and low temperature (80-85° C) caused poor zinc extraction. After 7 hours of treatment only 84% of the zinc was extracted. This degree of extraction was lower than in previous classical experiments described in Chapter 2 and in Section 3.2. After an additional hour of ferric chloride leaching the cumulative zinc extraction augmented to an acceptable level of 94-99%. The classical experiments were performed on the LPU sample without iron reoxidation by oxygen. The amount of ferric ions was high enough to protect good kinetics of leaching because there were high liquid/solid (L/S) ratios from 8 to 11 l/kg. (The exception was one 3-step experiment where L/S was about 3.6 l/kg but final ferric ions concentration was high enough: 40.7 g/l in 1st step, 77 in 2nd and 126 g/l in 3rd.) During FBL processing the liquid/solid ratio was from 1.18 to 2.38 l/kg and final ferric ion concentration was often only 7 to 9 g Fe^{3}/l. Leaching with low L/S ratio is important because of diminished reactor volume and higher zinc concentration in solution. However, the rate of leaching in these conditions must be protected by higher oxygen pressure (from 100 to 150 psi) and higher temperature from 90 to 95°C.

3. Lead extraction to the calcium chloride solution during the non-oxidative, fluidized-bed leaching that follows sulfate-FBL processing, achieves 92%. Lead extraction increase to 99% after one hour of oxidative leaching in ferric chloride solution (Table 3.7). Non-oxidative chloride leaching easily shifts into oxidative leaching by increasing the ferric chloride concentration in the leaching solution.

4. Simultaneous with lead, silver extraction achieves 59% in the non-oxidative conditions and 79.4% in oxidative conditions (Table 3.7).

5. About 96% of total lead and 71% of total silver contained in LP ore-samples are transformed into soluble compounds in the chloride-non-oxidative solution, during the initial stage of sulfate treatment (Table 3.8). The extraction of lead, silver and in some cases, antimony from different samples is schematically shown in Figure 3.12. It is evident that not more than about 30% of the total silver is dispersed in the non-soluble pyritic matrix.

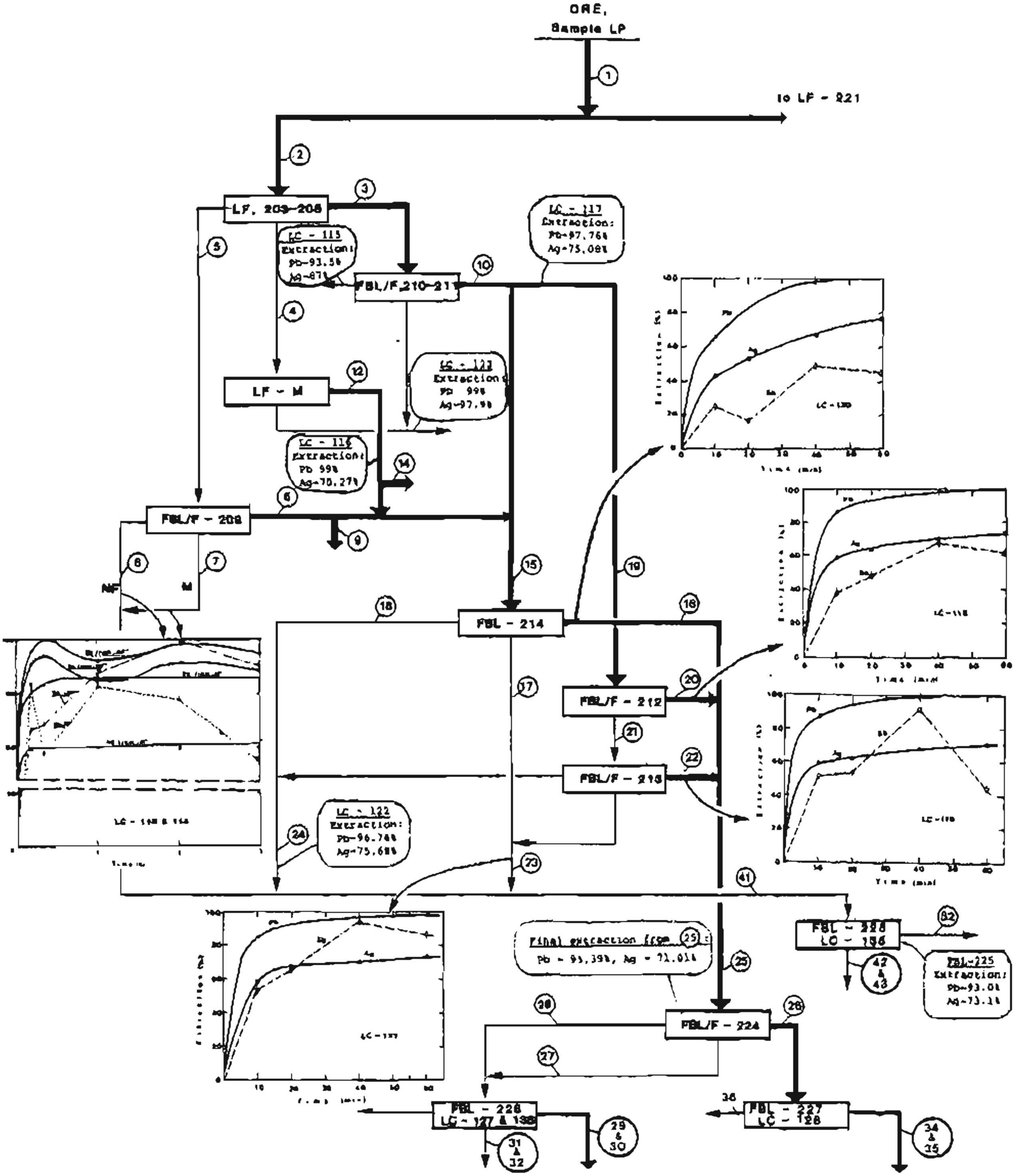

Figure 3.12. Leachability of lead, silver and antimony from solid semi-products at different steps of treatment of the flow (2) (left branch of the flowsheet in Figure 3.9).

3.4 Fluidized-Bed Leaching in Chloride Solutions

Oxidation of ferrous ions in chloride solution is considerably faster under 40-50 psi of oxygen pressure than in sulfate solution and oxidation of cuprous ions in chloride solution is even faster under atmospheric pressure. For this reason leaching by $FeCl_3$ and $CuCl_2$ solution was chosen as the best attainable at MIRL. Such a demonstration of the Fluidized-Bed Leaching features contributes the 1st "chloride" sub-program conducted in MIRL and another Nerco's engagement in hydrometallurgical chloride technologies.

The tests were carried out according to a flowsheet presented in Figure 3.13 in the mini-pilot laboratory installation shown in Figure 3.5. When the ore suspension was introduced to the 1st reactor (R_1), the leaching solution circulated from the reactor (R_1) to the oxidation reactor (R_2); through valve 20 to the crystallizer (C_1); then through the pump (P_4) to the bottom part of the reactor (R_1). The particles with specific gravity above 4.5, generally the pyrite fraction of the ore, were retained in the fluidized-bed. Particles with specific gravity below 4, and all very fine particles were transported with the solution to the second reactor (R_2), where the heavier fraction with specific gravity 3-4 (FeOOH, jarosite, gangue minerals) sedimented in the separator (S_2), and lighter fraction particles below 3 (gypsum, quartz) sedimented in the crystallizer (C).

It was expected that some part of the lead would crystallize in the form of lead chloride and sediment in the crystallizer also. The continuous reoxidation of the used leaching reagent was carried out by oxygen dispersed under pressure in the

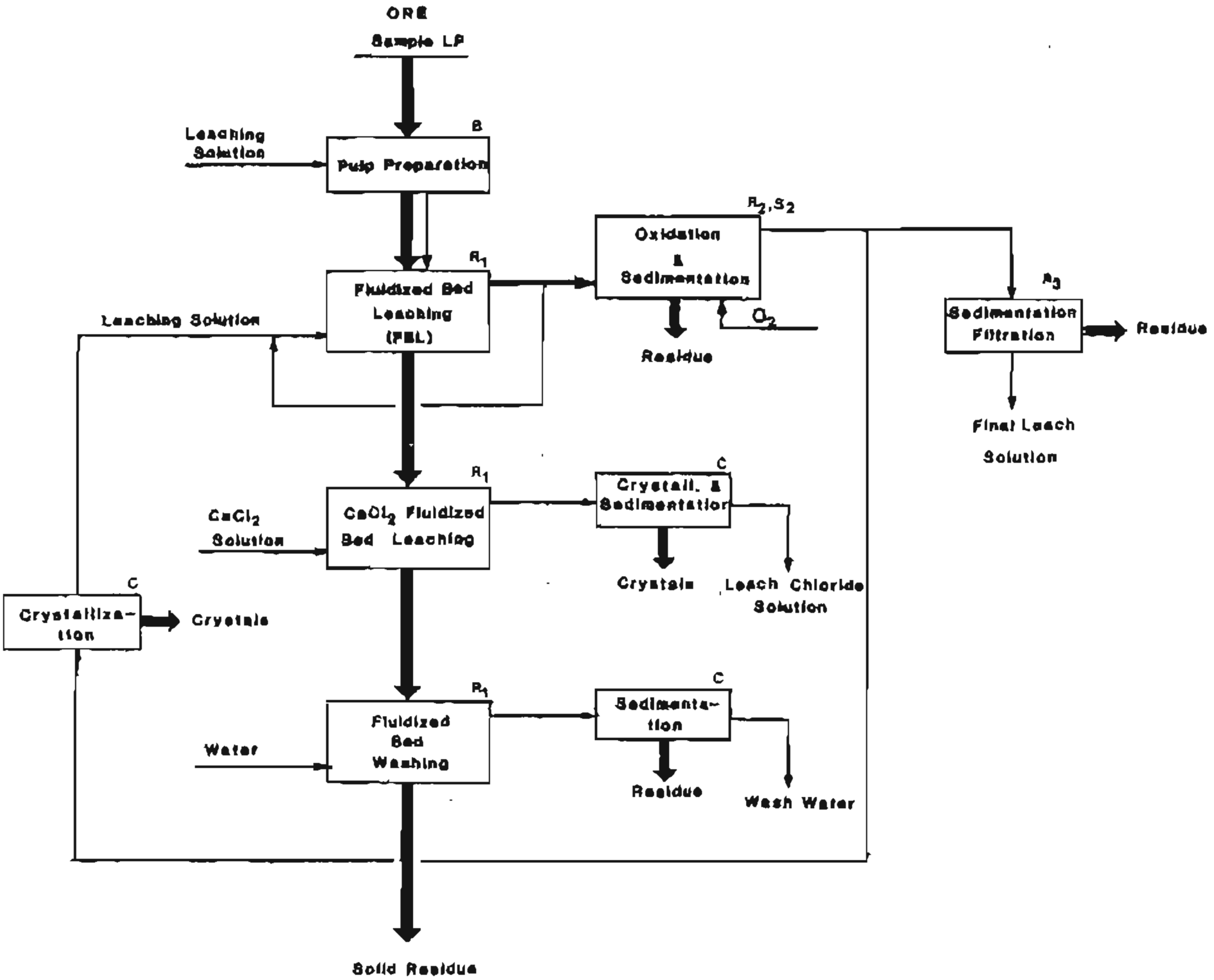

Figure 3.13. General flowsheet of experiments carried out in chloride solutions in the pressure installation presented in Figure 3.5.

second reactor (R_2). When leaching was finished the calcium chloride solution had been fed continuously to the 1st reactor, through the valve (12) and the pump (P_4) in a volume necessary to dissolve insoluble-in-water metals compounds. At the same time the spent solution previously filling the 1st and 2nd reactors was directed to the collector (R_3) and then outside the installation. The spent $CaCl_2$ wash solution was transported, bypassing the 2nd reactor, directly to the crystallizer and then outside the installation.

Fluidized-bed calcium chloride ($CaCl_2$) washing was conducted under atmospheric pressure but at elevated temperatures (80-90°), and some solution components had crystallized after cooling in the crystallizer. Of course, the spent wash solution could be mixed with the spent leaching solution, but this was not done during the tests.

The final fluidized-bed washing with pure water was conducted in the same manner as the first $CaCl_2$ washing. A schematic flowsheet of the two experiments is presented in Figure 3.14. Two steps of leaching were carried out with the same solution. The left branch of the flowsheet, beginning from the flow #2 corresponds to the 2-step cupric chloride leaching, the right branch, beginning from the flow #10 corresponds to the 2-step ferric chloride leaching. Two LP ore-samples, 700 g each of the fraction 400 mesh x 20 μm, were leached according to the above procedure (Figures 3.13 and 3.14). The tests were carried out in the following steady state conditions:

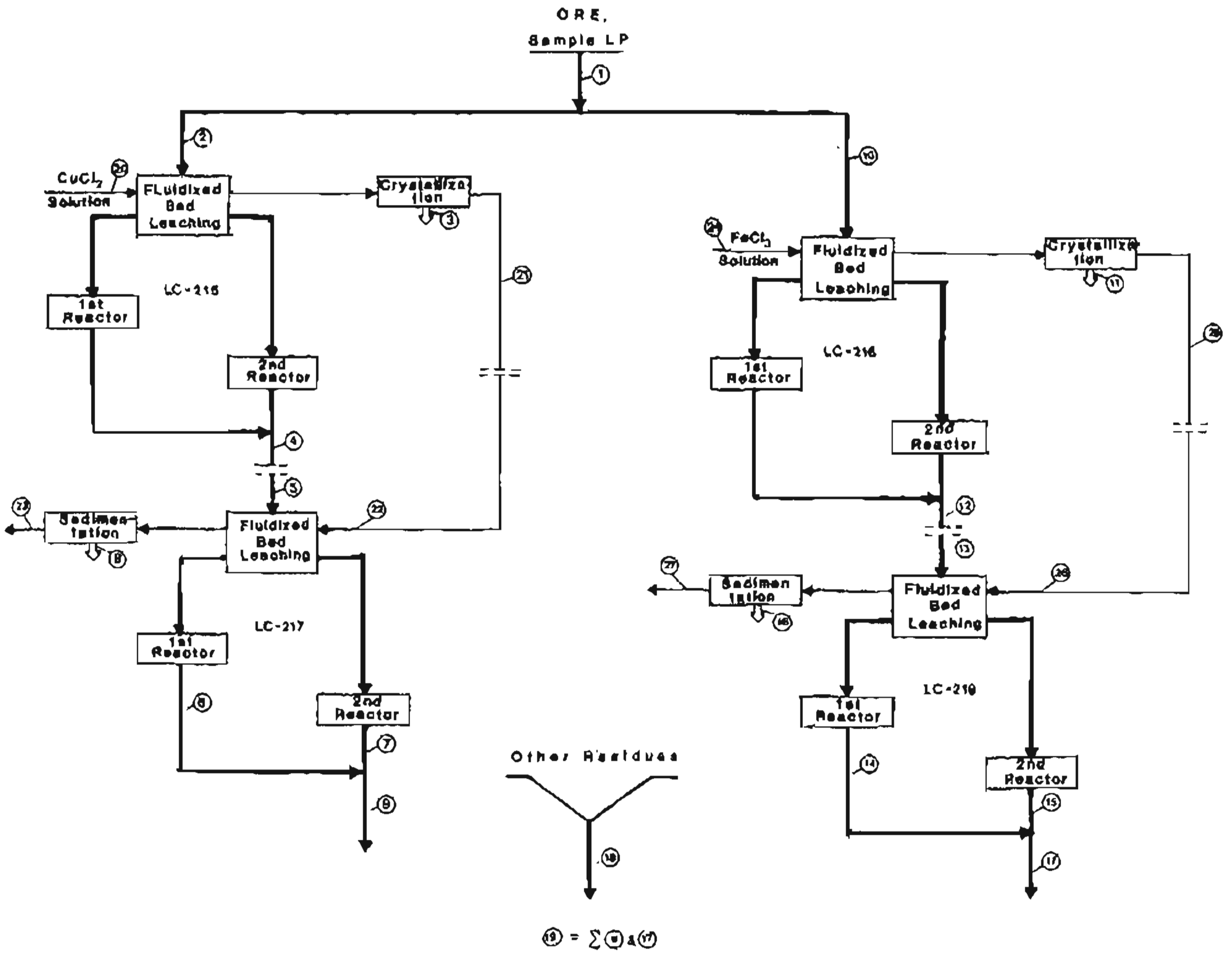

Figure 3.14. Flowsheet of experiments on the Fluidized-Bed Leaching in cupric and ferric chloride solutions in the laboratory installation (Figure 3.5). Circled numbers of flows correspond to the identification numbers in the Tables 3.9 and 3.10.

Temperature:90-95°C in the 1st, FBL-reactor, and
75-90°C in the 2nd, oxidation-reactor

Pressure: 16 psi during $CuCl_2$ leaching test, and
17-20 psi during $FeCl_3$ leaching test

Time of heating the ore pulp to 90°C in the beaker (pulp preparation in B, Figure 3.13): 30-40 min

Time of pulp feeding to the 1st reactor:

$CuCl_2$ leaching: 1 step (LC-215) 40 minutes
2 step (LC-217) 34 minutes

$FeCl_3$ leaching: 1 step (LC-216) 20 minutes
2 step (LC-219) 25 minutes

Time of ore retention in the fluidized-bed state (after feeding):

$CuCl_2$ leaching: 1 step 83 minutes
2 step 116 minutes

$FeCl_3$ leaching: 1 step 100 minutes

2 step 117 minutes

Rate of transportation of the circulating solution during leaching period:

$CuCl_2$ leaching: 1st step: 100-150 ml/minutes
2nd step: 100-175 ml/minutes

$FeCl_3$ leaching: 1st step: 120-160 ml/minutes
2nd step: 85-125 ml/minutes

Initial composition of the leaching solution:

$CuCl_2$ leaching: Cu 35.48 g/l
Fe 9.96 g/l
Ca 63.7 g/l

$FeCl_3$ leaching: Cu 8 mg/l
Fe 27.28 g/l
Ca 76.3 g/l

Calcium chloride washing solution composition:

$CuCl_2$ leaching: Ca 46.4 g/l
Fe 4.53 g/l
Pb 1.86 g/l
Cu 1.26 g/l
Zn 0.32 g/l
Ag 2.15 ppm

$FeCl_3$ leaching: Ca 14.27 g/l
Fe 0.02 g/l
Pb 2.89 g/l
Cu —
Zn 0.06 g/l
Ag 7.18 ppm

Hydrochloric acid (36% HCl) added to the leaching solution:

$CuCl_2$ leaching: 1st step: 150 ml
2nd step: 70 ml

$FeCl_3$ leaching: 1st step: 150 ml
2nd step: 100 ml

Liquid/solid ratio in the 1st reactor:

$CuCl_2$ leaching: 1st step: 1.75 l/kg
2nd step: 2.08 l/kg

$FeCl_3$ leaching: 1st step: 2.00 l/kg
2nd step: 2.70 l/kg

Other conditions and data are presented in Tables 3.9 and 3.10 - the mass balances of metals in solid and in solution. Results of the leaching tests are presented in Table 3.11.

Table 3.9. Fluidized-bed leaching. Mass balance of metals content in solids during cupric- and ferric-chloride leaching according to the flowsheet in Figure 3.13.

		Specifications	ID No*)		Content in Solids, grams (Ag. Au: mg)								
				weight	Cu	Fe	Zn	Pb	Ag	Sb	As	Au	Ca
		Total Inlet	1	1,400	3.948	430.4	95.2	49.28	121.92	0.882	13.55	2.814	0.2
Cupric Chloride Leaching	LC-215	Inlet to LC-215	2	700	1.974	215.2	47.6	24.64	60.96	0.441	6.78	1.407	0.1
		Crystals from cooling system	3	68.1	0.021	4.85	0.29	0.01	0.48	0.005	0.13	n.a.	14.2
		Outlet from LC-215	4	680.3	1.425	271.3	17.03	0.45	24.96	0.18	8.38	n.a.	10.8
	LC-217	Inlet to LC-217	5	672.9	1.416	270.4	17.05	0.45	24.92	0.18	8.29	n.a.	10.6
		After Leaching - 1st reactor	6	285.3	0.213	117.7	1.07	0.183	4.89	0.055	2.57	0.544	0.01
		After Leaching - 2nd reactor	7	171.8	0.171	57.3	0.84	0.097	3.92	0.039	1.45	0.390	1.40
		Crystals from Cooling System	8	18.7	0.098	3.9	0.002	--	0.24	--	0.06	0.012	1.9
		Outlet From 217	9	457.1	0.384	175.0	1.91	0.28	8.81	0.094	4.02	0.934	1.4
Ferric Chloride Leaching	LC-216	Inlet to LC-216	10	700	1.974	215.2	47.6	24.64	60.96	0.441	6.78	1.407	0.1
		Crystals from cooling system	11	47.1	0.007	1.02	0.02	0.061	0.21	0.004	0.04	n.a.	3.75
		Outlet from LC-216	12	524.2	1.327	224.8	12.89	0.635	35.09	0.323	6.43	n.a.	n.a.
	LC-219	Inlet to LC-219	13	521.5	1.320	223.6	12.82	0.632	34.91	0.321	6.40	n.a.	n.a.
		After Leaching - 1st reactor	14	358.1	0.895	132.9	2.15	0.37	21.11	0.166	4.82	n.a.	0.02
		After Leaching - 2nd reactor	15	49.9	0.074	16.9	0.14	0.04	1.91	0.018	0.58	n.a.	0.003
		Crystals from cooling system	16	47.05	0.070	16.1	0.08	0.05	1.76	0.015	0.44	n.a.	0.05
		Outlet from LC-219	17	408.0	0.969	149.8	2.29	0.41	23.02	0.184	5.40	n.a.	0.02
Solid residues from reactors cleaning after LC-217 and 219			18	194.6	0.228	69.78	0.85	0.19	5.33	0.047	1.89	n.a.	0.95
Total in solid residues after leaching LC-217 and LC-219			19	865.0	1.353	324.8	4.20	0.69	23.02	0.278	9.42		1.43

* Identification numbers correspond to the flow numbers in Figure 3.14.

Table 3.10. Fluidized-bed leaching. Mass balance of metals content in solutions during cupric- and ferric-chloride leaching according to the flowsheet in Figure 3.13.

Specifications		ID No*)	Volume (liters)	Content in Solution, grams (Ag, Au: mg)								
				Cu	Fe	Zn	Pb	Ag	Sb	As	Au	Ca
Cupric Chloride Leaching	Inlet to LC-215	20	8.38	147.47	59.70	6.32	12.35	27.44	0.145	n.a.	-	451.8
	Outlet from LC-215	21	10.70**)	149.35	56.04	44.56	35.59	72.14	0.564	n.a.	-	617.4
	Inlet to LC-217	22	5.59	133.12	49.01	31.35	24.10	56.95	0.488	n.a.	-	513.2
	Outlet from LC-217	23	6.48**)	117.06	47.61	41.20	21.26	63.19	0.482	1.34	-	235.8
Ferric Chloride Leaching	Inlet to LC-216	24	8.74	0.038	122.9	0.26	12.32	30.89	0.16	n.a.	-	403.8
	Outlet from LC-216	25	9.02**)	1.991	122.5	37.39	30.60	52.58	0.389	0.57	-	613.3
	Inlet to LC-219	26	4.50	1.500	116.8	26.98	17.40	26.38	0.165	n.a.	-	n.a.
	Outlet to LC-219	27	7.06**)	2.228	114.4	35.95	17.65	34.05	0.255	1.17	-	n.a.

* Identification numbers correspond to the flow numbers in Figure 3.14.

** Including wash-waters.

Table 3.11. Metals extraction during fluidized bed leaching in chloride solutions, calculated from metals content in solids (see Table 3.9 and Figure 3.13).

Specifications		Leaching Time (min)	Extraction, %						
			Cu	Fe	Zn	Pb	Ag	Sb	As
$CuCl_2$ Leaching	Conditioned at 60°C1)	15	-13.72)	1.8	2.6	40.2	30.7	1.8	n.a.
	Conditioned at 95°C3)	37	-2.42)	2.7	11.3	73.0	40.3	25.9	n.a.
	After LC-2154)	123	27.8	-26.12)	64.2	98.2	59.0	59.2	n.a.
	After LC-2175)	273	76.9	1.7	95.5	97.6	82.8	75.2	28.2
$FeCl_3$ Leaching	After LC-2166)	120	32.8	- 4.52)	72.9	97.4	42.4	26.8	5.1
	After LC-2197)	262	46.7	16.5	94.7	98.1	59.4	54.7	7.6

1) During 1st beaker feeding to the 1st reactor (LC-215); 350 g of solid (LP) in 700 ml of the solution; flow (20).

2) Precipitation from solution. Expressed as excess in solid residue after leaching (-13.7 means 13.7% of copper in solid after leaching).

3) During 2nd beaker feeding to the 1st reactor (LC-215); 350 g of solid (LP) in 700 ml of the solution; flow (20).

4) Temp: 1st reactor 85.--> 96°C; 2nd reactor 78 --> 83°C; average O_2 pressure: 16 psi; solid/liquid ratio (S/L) in 1st reactor: 0.57 kg/L.

5) Temp: 1st reactor 95°C; 2nd reactor 80°C; O_2 pressure: 16±2 psi; S/L (1st reactor): 0.48 kg/L.

6) Temp: 1st reactor 95°C; 2nd reactor 75°C; average O_2 pressure 20 psi; S/L (1st reactor): 0.50 kg/L.

7) Temp: 1st reactor 92°C; 2nd reactor 90°C; average O_2 pressure 17 psi; S/L (1st reactor): 0.37 kg/L.

Extraction of metals after 4 1/2 hours leaching in both cases attains 94% for zinc and 98% for lead. Extractions of copper and silver are higher in the cupric than in the ferric chloride solution. Copper extraction attains 76.9% and 46.7% in $CuCl_2$ and $FeCl_3$ solution, respectively; and silver extraction 82.8% and 59.4%, respectively, in the same solutions. The better extraction in the cupric chloride solution probably results from the following advantages of copper over iron in chloride solution:

- higher oxidative potential Cu^{2+}/Cu^{+} than Fe^{3+}/Fe^{2+};
- faster reoxidation of cuprous than ferrous ions by oxygen;
- catalytic properties of cupric ion;
- more favorable mechanisms of secondary chemical reactions of copper in solution.

Moreover, in our case, the oxidative capacity of the cupric chloride solution was higher than the ferric chloride solution because of higher concentration of oxidant in the cupric solution. The results of the fluidized-bed chloride leaching generally confirm the advantages of this system.

Probably the most important advantage of the fluidized-bed chloride leaching is the possibility of producing a high concentration zinc chloride solution with minimal concentration of oxidant $CuCl_2$ or $FeCl_3$, that would be reoxidized continuously under elevated oxygen pressure.

For this reason, the tests were carried out on metals extraction from LP ore by a chloride solution in which a low concentration of oxidant and a high zinc concentration were used. The conditions of the leaching tests and some results are presented in Table 3.12. A kinetic characteristic of the leaching test LC-125 is shown in Figure 3.15. Excellent results, unexpected by the authors, were obtained. 97% of the zinc extraction after two hours of leaching should be confirmed in the fluidized-bed system with simultaneous reoxidation of the leaching agent under oxygen pressure.

Table 3.12. Delta ore leaching by low concentration ferric chloride solution with high concentration of zinc chloride. Sample LP, fraction -400 mesh, without cyclone cinders below 20μm typical laboratory glass reactor, temp 90-95°C, leaching time 4 h.

		Leaching test LC 124	Leaching test LC 125
Initial Concentration in leaching solution (g/l)	Zn	183	170
	Fe^{3+}	24	20.5
	HCl	36	30
Solid/liquid ratio		50g/700 ml	20g/700ml
Loss of weight during leaching (%)		20.3	22.8
Extraction to solution after 4 hours, (%)	Cu	44.37	57.89
	Fe	10.4	28.46
	Zn	97.38	99.35
	Pb	98.42	98.34
	Ag	71.14	73.0
	Sb	56.28	53.82
	As	n.d.	10

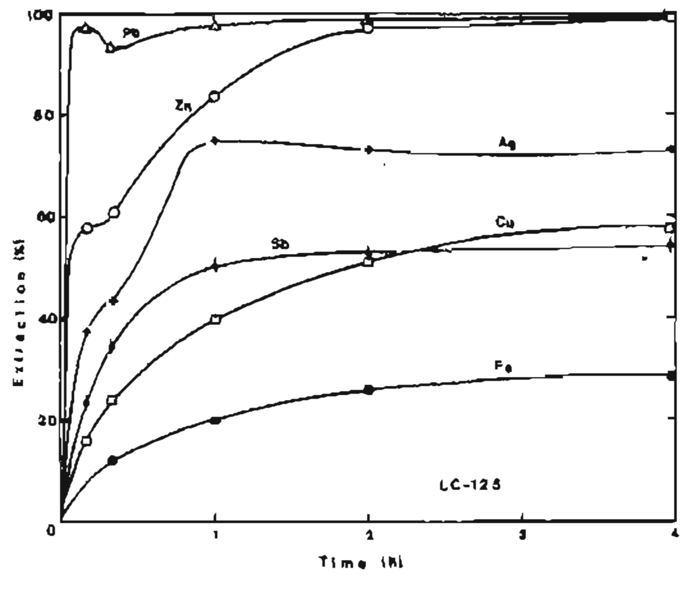

Figure 3.15. Extraction of metals during leaching of the LP ore sample with zinc chloride/ ferric chloride solution. Experimental conditions see Table 3.12.

3.5 Supplementary Tests on the Mixed Chloride/Sulfate Leaching

Two supplementary tests were performed with aluminium chloride solution. In the first test, ferric chloride, and in the second test, ferric sulfate, were used as oxidizing agents. By such a combination the influence of the high concentration of sulfate ions on chloride leaching, without gypsum precipitation occurring because of a calcium chloride solution, was investigated. Results presented in Figure 3.16 indicate good extraction of lead and zinc in chloride solution. At sulfate ion concentrations of about 1.6 mol/l, no negative impact was observed on the lead extraction (Figure 3.17). However, a retarding effect of sulfate ions on the zinc extraction is visible, although the extraction degree is higher than in pure ferric sulfate solution under the same leaching conditions.

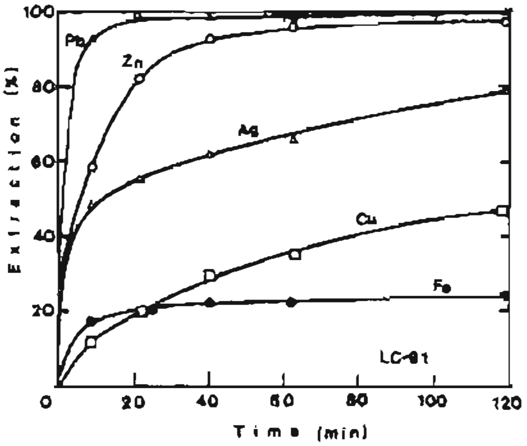

Figure 3.16. Kinetic of leaching in ferric chloride-aluminum chloride system. Sample LP, fraction 200-270 mesh. Solution concentration: [Fe] = 30 g/l; [Al] = 27 g/l, [Cl] = 5.6 mol/l; [HCl] = 18 g/l, liquid/solid ratio = 0.7 l/50 g, temp. 95°C.

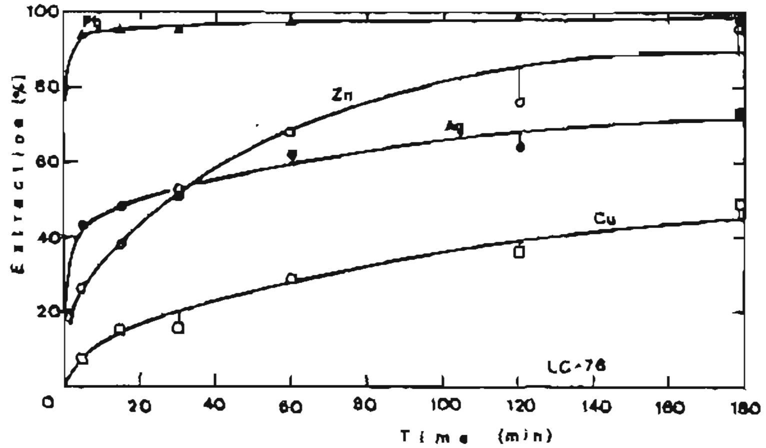

Figure 3.17. Kinetic of leaching in ferric sulfate-aluminum chloride system. Sample LPU (old) fraction 325-400 mesh. Solution concentration: [Fe] = 60 g/l, [Cu] = 1.7 g/l, [Al] = 40 g/l, [SO_4^{2-}] = 1.60 mol/l, [Cl^-] = 3.5 mol/l, temp. 95°C, liquid/solid ratio = 0.7 l/50 g.

3.6 Sulfur and Gold Extraction from Residues after FBL Processing

Gold extraction from the residues after Fluidized-Bed sulfate processing was investigated in a function of the pyritic matrix decomposition. For this purpose the solid residues were leached in ferric sulfate solution with continuous addition of small quantities of nitric acid. In this condition sulfidic sulfur can be oxidized to the elemental form:

$$3FeS_2 + 2NO_3^- + 8H^+ = 2NO + 4H_2O + 3Fe^{2+} + 6S^\circ$$

Competitive reaction in stronger oxidative conditions leads to partial oxidation of sulfides to the sulfates.

$$3FeS_2 + 6NO_3^- + 8H^+ = 6NO + 4H_2O + 3Fe^{2+} + 4S^\circ + 2SO_4^{2-}$$

In both cases the ferrous ions are nearly instantaneously oxidized to the ferric ions:

$$3Fe^{2+} + NO_3^- + 4H^+ = NO + 3Fe^{3+} + 2H_2O$$

Results of tests on the gold recovery as a function of the pyritic matrix destruction are presented in Table 3.13. The heavy flotable fraction of the sample LP, after sulfate processing and fluidized-bed calcium chloride washing FBL 227 (Figure 3.7, flow 34), was leached by ferric sulfate solution with continuous addition of nitric acid. In the experiments about 32%, and 54% to 72% of pyrite was decomposed, respectively, during 1st (LN-142) and 2nd (LN-230/231) "nitrate" leaching. The solid residues obtained after these leaching tests, as well as the sample from FBL 227 not treated by "nitrate" leaching, were leached with cyanide solution under conditions described in Table 3.13. Elemental sulfur generated during "nitrate" leaching was not extracted from the sample and remained in the solid residues during cyanide leaching. However, in an additional experiment sulfur was extracted by xylene from another portion of the solid residue after "nitrate" leaching LN-142; it was then directed to cyanide leaching under the same conditions as the other samples.

A relatively strong increase in the gold recovery with the pyritic matrix destruction (Table 3.13) is visible. Indeed, only about 80% of gold is extracted if two-thirds of pyrite is decomposed, but this result is not final. The sulfur extraction from the solid residue before cyanidation improves the gold recovery even when a third of pyrite is decomposed. This result confirms previous observations (Chapter 2).

Stronger oxidation conditions diminish elemental sulfur formation. The amount of elemental sulfur found in the residue after strong "nitrate" leaching (LN 231) corresponds only to 35.4% of total sulfidic sulfur that was oxidized in this leaching. The remaining amount is oxidized to sulfates.

Mild oxidizing conditions promote elemental sulfur formation. During "nitrate" leaching with controlled addition of nitric acid (LN-142 and LN 230) about 66 to 68% of total sulfur is oxidized to the elemental form, but it is difficult to forecast now if more, and how much more pyritic sulfur can be generated in elemental form in technically acceptable conditions.

Cyanide leaching seems to be suitable for gold recovery from residues after sulfate leaching. The degree of the gold extraction indicated in Table 3.13 is attainable after 16 to 26 hours. The fluidized-bed system should be tested for the cyanidation process also.

Table 3.13. Gold recovery from treated ore in function of the pyritic matrix destruction by "nitrate" leaching. Sample LP; heavy, flotable fraction after FBL227 (flow 34 in Figure 3.7). Gold concentration in the sample 2.51 ppm.

Solid Sample Specification	Loss of weight (%)	Concentration of metals and sulfur after leaching Cu (%)	Fe (%)	Zn (%)	Pb (ppm)	Ag (ppm)	S (%)	Degree of pyrite decompo-sition (%)	Cyanide Leaching Liquid/solid Ratio l/g	Change of pH during leaching (pH)	Gold extraction (%)$^{***)}$	Silver extraction (%)
Residue from FBL227	-	0.18	32.40	1.61	897	87.67	5.31	—	0.7/151	11.54/10.12	53.7/58.1	66.6
Residue from LN142	19.62	0.17	27.52	0.36	744	106.11	9.95	32	0.5/39	11.65/10.56	62.7/65.3	n.d.
Residue after sulfur extr. from LN142	12.07	0.19*	30.56*	0.40*	826*	117.85*	-	32	0.5/33	11.78/10.31	69.0/78.4	75.4
Residue from LN230/231	52.67	0.23	28**	0.61	1033	83.13	19.98	63±10	0.5/42	12.05/10.50	74.8/84.7	82.6

Leaching conditions - LN-142: [$Fe_2(SO_4)_3$] = 0.12 mol/L; [H_2SO_4] = 1.35 mol/L; Av. rate of HNO_3 (70%) feeding = 0.6 ml/min.; leaching time 205 min; Initial Liquid/solid (L/S) ratio 0.7L/101g.; Temperature: progressive increase from 68° to 93°C. LN-230/231: 1st step: [$Fe_2(SO_4)_3$] = 0.12 mol/L; [H_2SO_4] = 1/35 mol/L; Av. rate of HNO_3 (70%) feeding = 0.3 ml/min; Leaching time 140 min; Initial L/S - 0.35 L/100.4g; Temp. 82-92°C. 2nd step: [$Fe_2(SO_4)_3$] = 0.19 mol/L [HNO_3] = 2.8 mol/L; Leaching time - 18 min; Initial L/S ratio = 0.275 L/73.2g. Cyanide Leaching: [NaCN] = 1g/L [NaOH] = 1g/L; Leaching time = 48 h.

*) Calculate from balance
**) Low accuracy ±10%
***) Analytical results from two digested solid samples
n.d. - not determined

3.7 Summary and Conclusions

3.7.1 Leachability of LP Ore-samples

LPU ore-sample (old sample from 1985) represents better leachability than new LP (1986) sample. The comparison of some results is presented below:

		LPU (old, 1985 sample)	LP (new , 1986 sample)
Concentration in ore	Zn	6.63%	6.80%
	Pb	2.83%	3.52%
	Cu	0.38%	0.28%
	Ag	92.7 ppm	87.1 ppm
	Au	3.48 ppm	2.10 ppm
Extraction in comparative conditions (%)	Zn	89-96	~96
	Pb*	96-99	98-99
	Cu	60-84	~60
	Ag*	70-91	60-80
	Au	70-90**	60-80***

*) in chloride $FeCl_3$ leaching

**) in cyanide leaching followed sulfate/chloride and sulfur extraction steps

***) in cyanide leaching after "nitrate" leaching

The comparison of metals extraction from the LP ore-sample is presented for the different leaching processes in Table 3.14. These results should be analyzed carefully because of the different experimental systems that were used. Nevertheless,

Table 3.14. Metals extraction from Delta ore (sample LP) in the investigated leaching systems.

No.	Leaching System	Kind of Processing	Time of Processing (h)	Cu	Fe	Zn	Pb	Ag	Sb	As
				Cummulative Extraction, %						
1a	$Fe_2(SO_4)_3$, $CaCl_2$., O_2	FBL/F	7.3	61.7	37.15	84.4	91.94	58.97	72.46	32
1b	$Fe_2(SO_4)_3$, $CaCl_2$, $FeCl_3$, O_2	FBL/F	8.4	n.d.	40.6	98.99	99.06	79.44	n.d.	n.d.
1c	$Fe_2(SO_4)_3$ - O_2, $CaCl_2$, HNO_3	FBL/F-LC	n.d.	77.0	66	97.2	n.d.	81.56	n.d.	n.d.
1d	$Fe_2(SO_4)_3$ - O_2 , $CaCl_2$, HNO_3, NaCN	FBL/F-LC	n.d.	82.3	n.d.	n.d.	n.d.	96.8	n.d.	n.d.
2	$FeCl_3$ - $CaCl_2$, O_2	FBL	4.37	46.7	16.5	94.75	98.15	59.4	54.7	7.6
3	$CuCl_2$ - $CaCl_2$, O_2	FBL	4.55	76.9	n.d.	95.5	97.6	82.8	75.2	28.2
4	$FeCl_3$ - $ZnCl_2$	LC	4.0	57.9	28.5	99.35*	98.3	73.0	53.8	10.0
5	$FeCl_3$ - $AlCl_3$	LC	2.0	58.6	25.1	97.3	97.6	58.5	21.0	n.d.
6	$Fe_2(SO_4)_3$ - $AlCl_3$	LC	3.0	55.8	24.2	77.2**	97.7	57.66	n.d.	n.d.

FBL/F - Fluidized-Bed Leaching and Flotation
FBL - Fluidized-Bed Leaching
LC - Non-continuous experiment in classical glass reactor
n.d.- Not determined
1c - cummulative extraction after partial destruction (~63%) of pyritic matrix (see Table 3.13)
1d - cummulative extraction after cyanide leaching (see Table 3.13)
All experiments, except No. 6: Ore sample LP(1987); Experiment 6: Sample LPU (1986).
All experiments, except No. 5 and 6: Fraction -400 mesh, without cyclone cinders -20μm; No. 5: 200-270 mesh; No. 6: 325-400 mesh,
* After 2h of leaching; 97%
** Low accuracy ± 15%

visible superiority of the silver extraction in $CuCl_2$ solution, the total and fast zinc extraction in $ZnCl_2/FeCl_3$ solution, as well as relatively good results of the fluidized-bed, multistadial, sulfate/chloride leaching is evident.

A high degree of silver and gold recovery is confirmed by cyanide leaching carried out after partial destruction of the pyritic matrix. Probably the same silver recovery (96.8%) can be obtained in chloride leaching conducted after pyrite destruction. 80% of the gold extraction with cyanide solution, from residue left after decomposition of about 60% of the pyrite should be improved in the next experiments.

3.7.2 Fluidized-bed leaching (FBL) reactor

The Leaching-Flotation (LF) process was modified by coupling with the Fluidized-Bed leaching (FBL) process. This improvement is important because it combines adjustment of long leaching time with fast flotation, under elevated oxygen pressure. The tests on the fluidized-bed leaching accumulated evidence about advantages of this leaching system.

Low capital investment and low operating costs are expected due to the high capacity of the FBL reactor (liquid/solid ratio: 1:1.5); its simple construction and the applicability of the similar units to different leaching or precipitation processes; easy transport of reactive medias; and segregation of different solid components constrained by their physical and physico-chemical properties also under elevated pressure of gaseous reagents. The fluidized-bed leaching system creates conditions for producing solutions with high concentration of extracted metals. For production of very concentrated leach solutions the FBL process can be conducted on a semicontinuous cyclic base, like elution from loaded ion exchangers, where the solution only is transported through fluidized-bed, or solids only are transported through the same solution.

Fluidized-bed leaching segregates particles according to their specific gravity, shape and size:

		Specific Gravity			
Heavy Minerals		Medium Spec. Gravity Minerals		Light Mineral	
PbS	7.5-7.6	FeS_2	4.9-5.0	$FeSO_4{\cdot}H_2O$	2.97
Ag_2S	7.2-7.4	CuS	4.6-4.8	$ZnCl_2$	2.91
$PbSO_4$	6.2-6.35	$CuFeS_2$	4.1-4.3	SiO_2	2.65
FeAsS	6.1-6.8	ZnS	3.9-4.1	$CaSO_4{\cdot}2H_2O$	2.3-2.37
$PbCl_2$	5.8	FeOOH	3.3-4.3	S°	2.07
AgCl	5.55	Jarosites	2.9-3.3	$ZnSO_4$	1.98

For instance, during fluidized-bed sulfate leaching, non-reacted PbS, new formed $PbSO_4$ and arsenopyrite FeAsS, were collected in the bottom part of the reactor. Other sulfides were suspended in the fluidized-bed in the central part of the reactor. Elemental sulfur, that is non-agglomerated with sulfides, gypsum and silica were transported with solution outside the reactor and sedimented. The fluidized-bed leaching can be coupled with the flotation under oxygen pressure to segregate the leached particles according to their flotability.

The FBL process can work in any kind of leaching solution, including cyanide, and can be used for recovery of any metal from disintegrated material.

The fluidized-bed leaching conducted under oxygen pressure is thought to be a new process. No bibliographical references are known by the author. From an engineering point of view, the fluidized-bed leaching reactor belongs to a group of three phase (solid-liquid-gaseous) reactors.

3.7.3 FBL-Process application in the sulfate system.

The proposed flowsheet of processing is schematically shown in Figure 3.18. The principal elements are similar to the flowsheet for the second variant of ore treatment presented in Chapter 2. According to the current version, the sulfate leaching steps are conducted in three 3-phase (solid-liquid-gaseous) reactors (Figure 3.18). In the 1st reactor, production of the purified zinc sulfate solution with simultaneous separation of solid in two flows is resolved by coupling the fluidized-bed leaching (FBL) process with flotation (F). In the 2nd reactor, three flows of the solid suspensions in solution are separated: 1st, a flotable fraction with non-reacted sulfides and sulfur; 2nd, a light nonflotable fraction, generally with products of iron hydrolysis, gypsum and quartz; and 3rd, a heavy non-flotable fraction with lead sulfate, silver chloride, some gangue minerals. Probably total gold will also accumulate in the 3rd fraction. In the third reactor, destruction of the pyrite matrix is carried out in the presence of nitric oxides. In this reactor, the 3-phase froth (solid-liquid-gaseous) is the principal reactive medium. Elemental sulfur is separated from this reactor in the flotable fraction. The suspension of the non-flotable particles is directed to the 2nd reactor.

The major part of the solid products of iron hydrolysis is precipitated in the 3rd reactor. However, the final formation of easy-to-separate crystalline goethite and jarosite is formed in the 2nd reactor. This occurs in very favorable conditions because about 20 g/l of ferric ions remains in solution after precipitation.

The spontaneous decomposition of pyrite by leaching with nitric acid is known:

$$3FeS_2 + 6NO_3^- + 8H^+ = 6NO + 4H_2O + 3Fe^{2+} + 4S^\circ + 2SO_4^{2-}$$

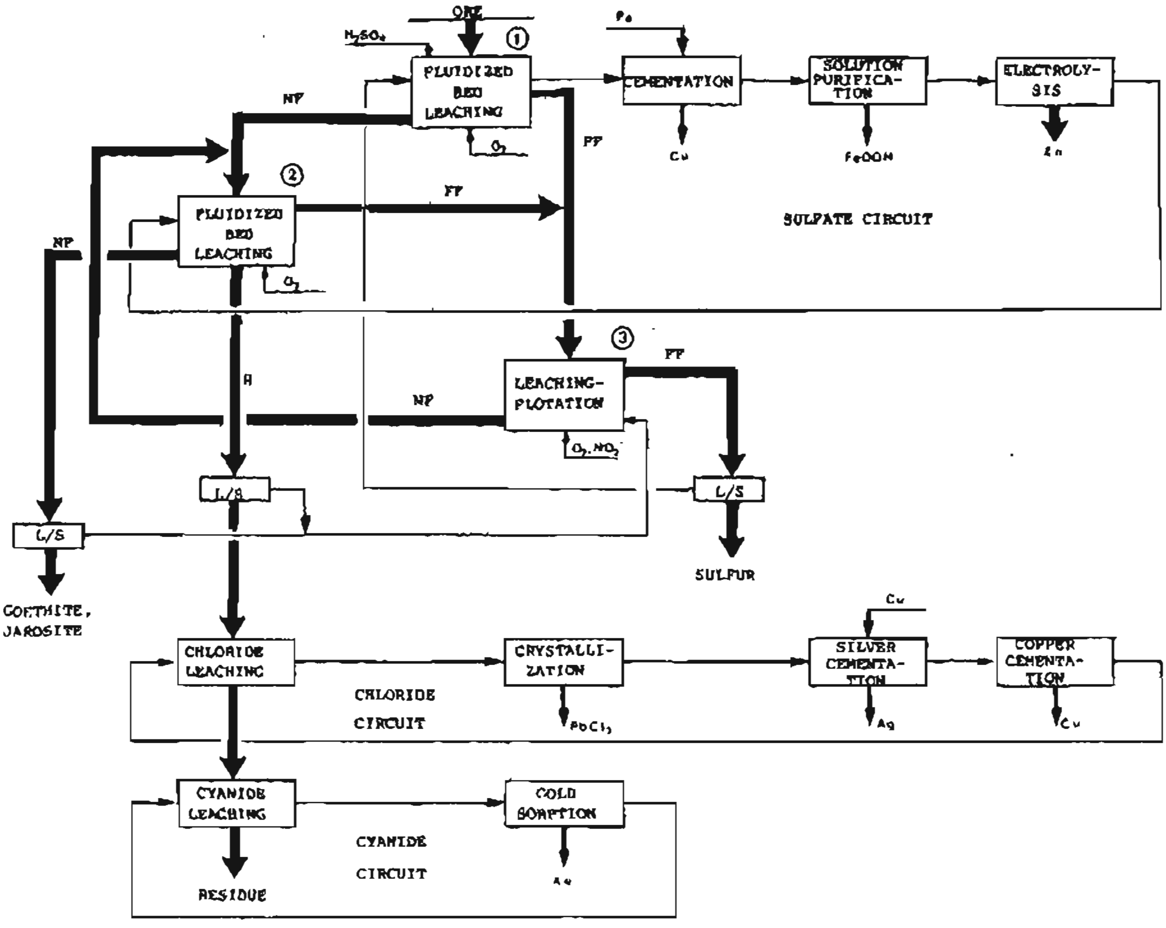

Figure 3.18. Simplified flowsheet of the Fluidized-Bed and Flotation Processing in the sulfate solution.

Processes based on this reaction were proposed as one way to recover metals from difficult-to-dissolve sulfides. A disadvantage of these strong oxidative processes is that a considerable portion of the generated sulfur is oxidized to sulfates. This spontaneous reaction can be changed into a controllable action of nitrous oxides with nitric acid generation under elevated oxygen pressure:

$$2NO(g) + O_2(g) = 2NO_2(g)$$
$$3NO_2(g) + H_2O(l) = 2HNO_3(aq)$$

This reaction is attainable in the proposed reactor during leaching-flotation (LF) processing, conducted in the 3rd reactor. At the same time, small quantities of nitric acid transported with the non-flotable fraction to the 2nd reactor, and with recycled solution to the 1st reactor, accelerate the relatively slow decomposition of sphalerite.

Lead sulfate and insoluble (in these conditions) gold and silver are accumulated in the heavy nonflotable fraction (2nd reactor). It is worth mentioning that the possible dissolution of silver can be lessened in the sulfate solution by the addition of small quantities of chloride ions.

Lead and silver are recoverable from the heavy nonflotable fraction by short, simple non-pressure fluidized-bed leaching in calcium chloride solution. Gold can be extracted by the classical cyanidation, taking no longer than 24 hrs, or in the fluidized-bed cyanide leaching under elevated oxygen pressure with an expected retention time from 1 to 2 hours. The gold concentration in the cyanide solution after fluidized-bed leaching is expected to be higher than 100 ppm.

3.7.4 FBL-Process in the chloride systems.

An application of fluidized-bed leaching to known chloride systems, does not change the general flowsheets of the chloride processing. The most important new features arising from this modification are:

- diminishing the concentration of the leaching agent, and increasing the concentration of the extracted metals under elevated oxygen pressure;
- continuous iron oxidation with partial precipitation of the iron hydrolysis products, under elevated oxygen pressure or by chlorine action;
- diminishing of the total volume of the leaching installation.

The activation of cupric chloride or ferric chloride leaching by nitric oxides accelerates leaching of the scarcely soluble sulfides ($CuFeS_2$, MoS_2), allows for decomposition of nearly insoluble pyrite, and dissolves precious metals which form complexes with chloride ions. This is economically sound if reoxidation of nitrous oxide (NO) to nitric oxide (NO_2) is carried out. The Fluidized bed leaching/Flotation (FBL/F) reactor is particularly useful for this kind of processing.

3.7.5 Zinc-chloride leaching process.

Chloride leaching of complex sulfide ores with a high concentration of zinc chloride solution containing ferric chloride is experimentally confirmed at MIRL as one of the best (Table 3.14). The following unexpected laboratory results were obtained:

- LP ore leaching by solution with initial concentrations: 170g/l Zn (354.6 g/l $ZnCl_2$), 20g/l Fe (58 g/l $FeCl_3$), and 30g/l HCl in the typical conditions (Table 3.12) give the following results:
  Lead - 96.5% extraction after 10 min.
  Silver - 75% extraction after 1 hour
  Zinc - 96% extraction after 2 hours

Maximum $ZnCl_2$ solubility is very high - 48 moles $ZnCl_2$ per liter of solution, at a temperature of 25-80°C. This solubility is similar to the value for the eutectic mixture in the fused salts systems. The solution containing 7.8 mol/l $ZnCl_2$ has a freezing point of -62°C. Viscosity of the $ZnCl_2$ concentrated solution is many times higher than that of water. Specific gravity of concentrated solutions attains 2.5. The solution with 6 mol/l $ZnCl_2$ has pH = 1.

The concentrated solution of $ZnCl_2$ is an excellent electrolyte for the electrolysis processes. Maximum conductivity at 25° C has the $ZnCl_2$ solution containing 170 g/l Zn. This value is two times higher than $ZnSO_4$ solution containing 120 g/l Zn. Also cathodic current efficiency is best at this zinc chloride concentration: 87% efficient for cathodic current density 1,100 A/m^2, and 75% efficient for 2,200 A/m^2.

Other electrolysis conditions in the $ZnCl_2$ concentrated solution are compared in Table 3.15 with actually known zinc chloride electrolytic cells in which compact, dendrite-free zinc cathodes are electrowon.

It is worth mentioning that at a temperature of 9.6°C (40°F), chlorine gas produced at the anode during electrolysis of chloride solution reacts with water and forms yellow crystalline chlorine hydrate. This solid product can be removed from electrolysis as a slurry in the spent electrolyte, diminishing the risk of environmental contamination by gaseous chlorine.

Zinc deposition from concentrated $ZnCl_2$ solution (Thomas & Fray) undoubtedly presents the highest advantages: it is simple, represents high yield from the same cathodic surface and operates in the best electrochemical concentration. Only a decrease of the cathodic current density, i.e. to value 1,100 A/m^2 (still higher than for comparative processes), increases the current efficiency to a level of 90%.

However, in spite of this obvious superiority, none of the known sulfide leaching processes was able to supply a concentrated solution of zinc chloride of suitable quality. Most frequently, the solvent extraction processes were aimed to purify diluted solution after leaching and to concentrate it, but not so strongly. At the same time, purification of the high concentration zinc chloride solution containing 170-200 g Zn/l can be carried out before zinc electrowinning, without the

Table 3.15. Comparison of zinc electrolysis conditions from zinc chloride solutions, for three known processes.

	Thomas and Fray - Cambridge Univ. England[1]	Tecnicas-Reunidas Process[2]	CANMET Process[3]
Zinc concentration in soln. fed to electrolysis (g/l)	150	60-70	30
Zinc solution concentration in cathodic compartment	142	30	15
Zinc concentration in spent anolyte	142	0.2	?
Inert chloride in catholyte	NH_4Cl (0-70g/L)	NaCl (166g/L)	NaCl (0-1 mol/L)
HCl in catholyte (g/L)	—	2-3	5
Cell voltage (V)	3.95	2.9	4.1-5.5
Cathodic current density (A/m^2)	2,500	700	325
Current efficiency (%)	76	92	96
Cathode/Anode compartment separator	none	cation-exchange NAFION	diaphragm type DYNEL

1) B.K. Thomas, D.J. Fray
2) E.D. Nogueira, J.M. Refige, and M.P. Viegas
3) D.J. MacKinnon, J.M. Brannen and R.M. Morrison
All from P.D. Parker (Editor), "Chloride Hydrometallurgy" The Metallurgical Society of AIME, New York, 1982.

solvent extraction step:

- iron is easy to precipitate in the form of crystalline goethite from a solution having such a zinc chloride concentration;
- lead is easy to precipitate by zinc by the method of the last patent of the Tecnicas-Reunidas, or by other known techniques.

The flowsheet of complex sulfide-ore processing based on leaching with a concentrated solution of zinc chloride will be described in the patent application.

Chapter 4

HYDROMETALLURGY OF THE DELTA SULFIDE ORES

Third Stage Report

F. Letowski and P.D. Rao

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ABSTRACT

This report contains the results of research on arsenic and antimony removal from chloride leach solutions prior to solvent extraction treatment and zinc electrowinning. The research, carried out in a continuous laboratory installation, shows that arsenic concentration in solution depends strongly on the oxidative conditions of leaching. Arsenic removal from solution is relatively fast under elevated oxygen pressure. Arsenic concentration can be reduced to near 100 ppm at pH 2; further reduction requires additional neutralization. Under the experimental conditions, arsenic precipitated with iron and lead and the elemental sulfur concentration in the final residues was 16.1%. Gold recovery from these residues by cyanidation was from 66 to 77%. A short description of supplementary research and designs and construction of a laboratory electrolyser are given.

The research described in this report was performed with active participation from the following persons:
Mr. Wang Zhao Fang

- Laboratory tests of leaching in high concentration zinc chloride solution;
- Zinc electrolyser set up;
- Analytical help in all experiments

Mr. Winghsiao Yuen

- Cyanide leaching tests.

Mrs. Jane Smith

- Analytical support in all research.

4.1 Introduction

The knowledge of arsenic and antimony behavior in hydrometallurgical processes is important because of the following reasons:

- Arsenic and antimony occur in nearly all complex sulfide ores.
- The presence of arsenic in aqueous solutions, directed to electrolysis, degrades properties of deposited metals (Cu, Zn, Ni, Pb, etc.) and diminishes current efficiency during electrolysis.
- Gold and silver are often intimately associated with refractory arsenic-sulfur or antimony-sulfur minerals. Recovery of these precious metals requires destruction of the mineral matrix.
- Arsenic and antimony are toxic and disposal of solid wastes containing even their relatively stable compounds can be hazardous and subject to environmental regulation.
- Arsenic forms many scarcely soluble compounds with several metals and disturbs hydrometallurgical processes.
- Both elements and their compounds have many technical applications and have high value.

In aqueous solutions arsenic occurs in third and fifth degree oxidation states as the arsenite anion AsO_3^{3-} and the more stable arsenate anion AsO_4^{3-}.

The relative dominant regions of these ions are presented in the E-pH diagram in Figure 4.1 [4.1]. The regions of thermodynamic stability of arsenopyrite FeAsS and ferric arsenate $FeAsO_4$ are presented in the E-pH diagram of the system Fe-As-H_2O (Figure 4.2)[4.2].

In solutions that do not contain sulfate, phosphate or carbonate ions, arsenic forms many stable solid phases with several metals. Stability of these compounds depends on electrochemical conditions (oxidative-reductive potential) concentration of dissolved species and pH of solutions [4.3, 4.4].

The regions of thermodynamic stability of iron, copper, zinc, lead, silver and calcium arsenates are shown in Figures 4.3-4.8. These regions can be diminished in chloride solutions because of strong complexation of metal ions by chloride ion.

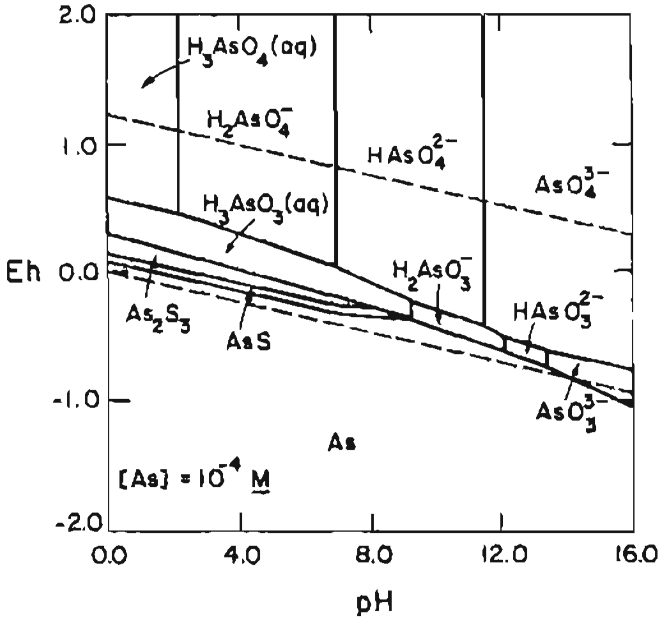


Figure 4.1. E-pH diagram for the As-S-H_2O system at 25°C [4.1].

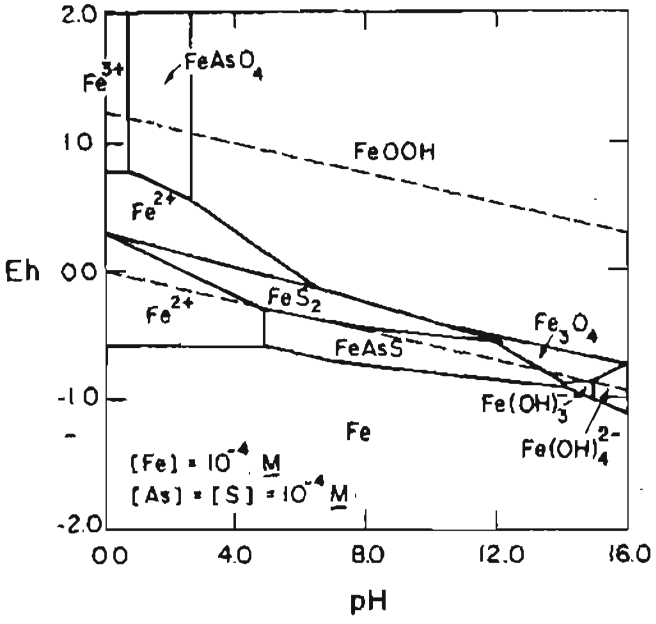


Figure 4.2. E-pH diagram for the Fe-As-S-H_2O system at 25°C.

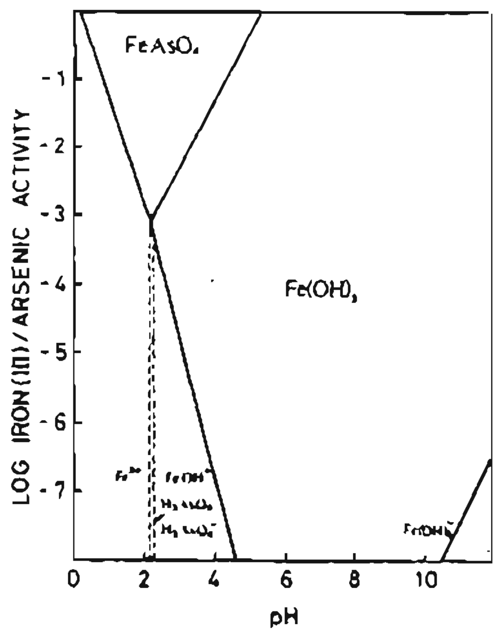


Figure 4.3. Stability diagram in the Fe(III)-As(V)-H_2O System at 25°C, for equal activities of iron and arsenic and p_{CO_2} = $10^{-1.5}$ kPa [4.2]

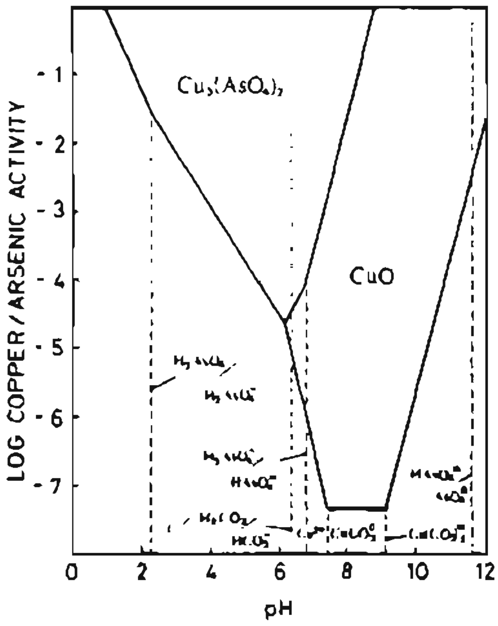


Figure 4.4. Stability diagram in the Cu(II)-As(V)-H_2O system at 25°C for equal activities of copper and arsenic and p_{CO_2}=$10^{-1.5}$ kPa [4.2].

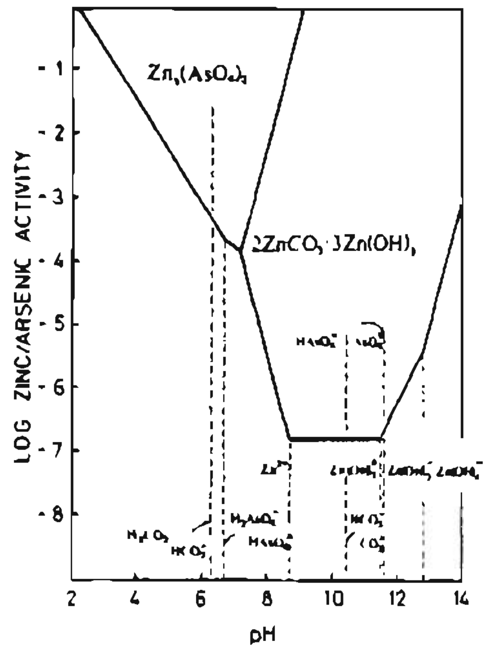


Figure 4.5. Stability diagram in the Zn-As(V)-H_2O system for equal activities of zinc and arsenic and p_{CO_2}=$10^{-1.5}$ kPa (25°C) [4.2].

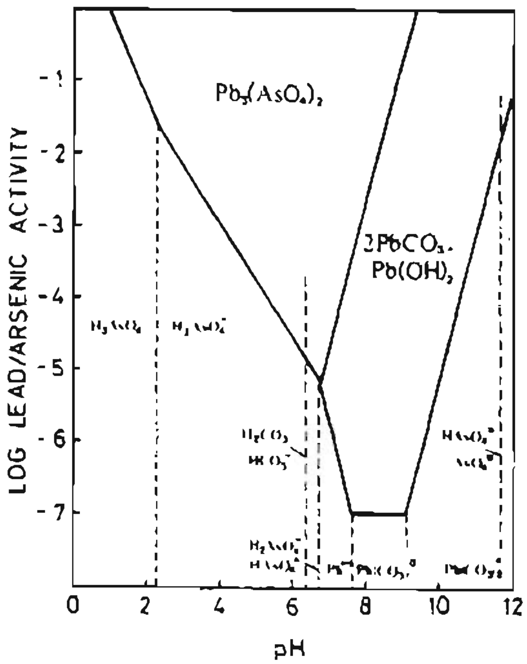


Figure 4.6. Stability diagram in the Pb-As(V)-H_2O system for equal activities of lead and arsenic and p_{CO_2}=$10^{-1.5}$ kPa (25°C) [4.2].

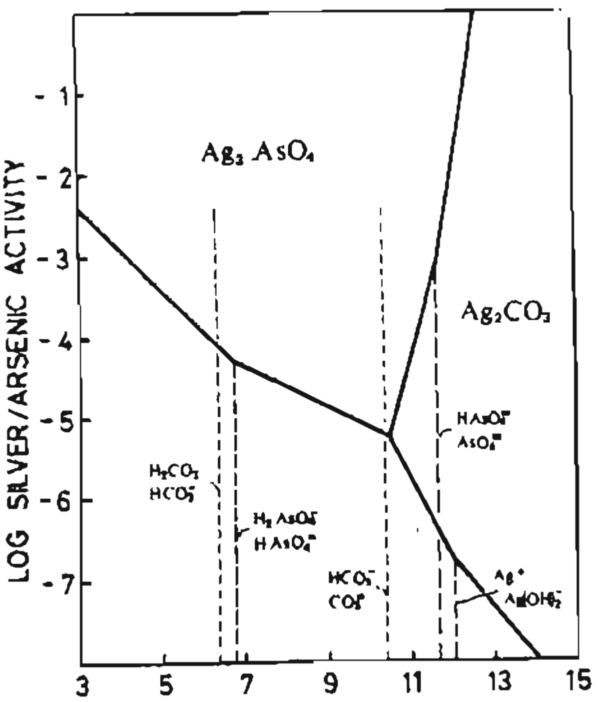


Figure 4.7. **Stability diagram in the Ag-As(V)-H_2O system for equal activities of silver and arsenic and $p_{CO_2}=10^{-15}$ kPa (25°C) [4.2].**

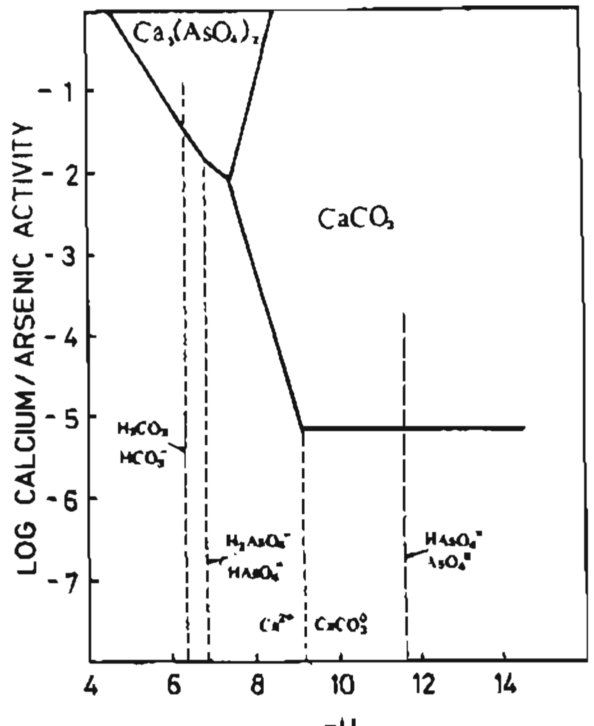


Figure 4.8. **Stability diagram in the Ca-As(V)-H_2O system for equal activities of calcium and arsenic and $p_{CO_2}=10^{-1.5}$ kPa (25°C) [4.2].**

Respective metals arsenites, As(III) compounds, are more soluble and generally cannot be precipitated from solutions of pH lower than 3 [4.3]. Arsenic (III) oxide (As_2O_3) is relatively stable in acidic solution. It can be precipitated from solution with concentration higher than 0.2 mol/L. The stability diagram of ferrous-arsenite compounds is shown in Figure 4.9. Introducing sulfates, phosphates or carbonates to solutions containing AsO_3^{3-} and AsO_4^{3-} ions causes formation of new solid phases generally associated with the formation of basic salts [4.5].

Even at low sulfate concentration, precipitation or crystallization of mixed arsenic-sulfate compounds can occur. These are:

- Beudantite, $PbFe_3(AsO_4)(SO_4)(OH)_6$ group compounds, in which lead can be replaced by calcium or hydronium ion (H_3O^+).
- Crandallite, $CaFe_3(AsO_4)_2(OH)_5H_2O$, group compounds in which calcium ion can be replaced by barium or lead.

Beudantite can be associated with scorodite $FeAsO_4 \cdot 2H_2O$ and anglesite-$PbSO_4$. From stoichiometric point of view beudantite corresponds to the following composition of compounds:

$$(PbSO_4)(FeAsO_4 \cdot 2H_2O)(2FeOOH)(2H_2O)$$

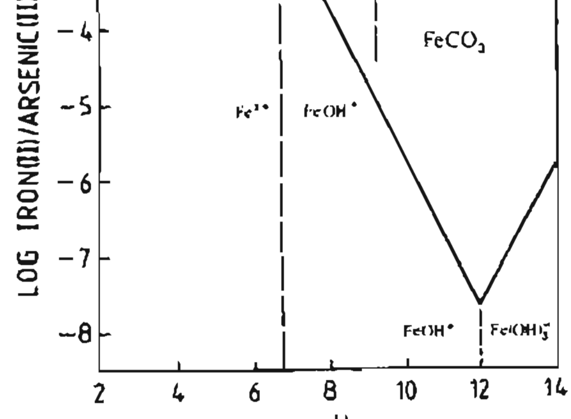


Figure 4.9. **Stability diagram in the Fe(II)-As(III)-H_2O system for equal activities of calcium and arsenic and $p_{CO_2}=10^{-1.5}$ kPa [4.2].**

Despite the similarity of beudantite to the above composition, beudantite has its own distinctive crystallographic symmetry.

The application of chloride leaching to metals recovery from Delta-ores has been investigated by MIRL since the fall of 1985. The leachability of sulfides occurring in the Delta ores in chloride solutions at moderate temperatures (90-104°C), depends on the oxidative conditions of leaching. Easily soluble under nonoxidative conditions, with the evolution of H_2S, are galena (PbS) and pyrrhotite (FeS). Under mildly oxidative conditions created by ferric ions, galena, pyrrhotite and sphalerite (ZnS) are decomposed with elemental sulfur generation. Decomposition of tetraheadrite ($(Cu, Zn, Fe)_{12} Sb_4S_{13}$), chalcopyrite ($CuFeS_2$), and other copper-iron sulfides requires stronger oxidative conditions created by $CuCl_2$, $FeCl_3$ and elevated oxygen pressure. Under such conditions, greater than 90% of sulfidic sulfur is oxidized to elemental sulfur and not more than 10% to sulfates. Strong oxidative conditions formed by catalytic action of nitric oxides or nitric acid are necessary to decompose pyrite (FeS_2), arsenopyrite (FeAsS) and probably tenantite ($(Cu, Fe)_{12} AsS_{13}$) in a period time comparable to those of easily soluble sulfides. At these conditions, more sulfidic sulfur is oxidized to sulfates, whose presence in the chloride solutions strongly affect solubilities of many metallic compounds including compounds of arsenic and antimony. However, only cursory attention was directed at arsenic and antimony behavior during chloride leaching [Chapters 2 and 3].

Results of some previous experiments indicate weak arsenic extraction in chloride or sulfate solutions and higher extraction of antimony. The highest extraction of both metals was observed in the $CuCl_2$ - $CaCl_2/MgCl_2$ leaching system. The extraction data collected in Table 4.1 corresponds to leaching conditions in which more than 94% of zinc, more than 98% of lead, 50% of silver and not more than 54% of copper were extracted.

In high concentration ferric chloride solutions where a portion of the arsenopyrite is decomposed, the arsenic concentration in solution is controlled by the precipitation of low solubility ferric aresenate ($FeAsO_4 \cdot 2H_2O$), or when the solution contains soluble sulfates, by precipitation of scarcely soluble hydroxo-sulfates and arsenates. Good leaching selectivity of nonferrous metals in contrast to arsenic and antimony was observed for the $FeCl_3$-$CaCl_2$ system. However, ferric arsenate can be dissolved under strongly acidic leaching conditions.

A second important observation was that the decomposition of pyritic, arsenopyritic, or other refractory sulfidic matrices causes an increase in the subsequent gold extraction by cyanidation.

Table 4.1. Approximate data of arsenic and antimony extraction in different chloride solutions [4.6, 4.7].

	Leaching System	Sample of the Delta Ore	Extraction (%)	
			As	Sb
1	$FeCl_3$ - $CaCl_2$	LPU	6.2 - 10.9	54.7
2	$FeCl_3$ - $ZnCl_2$	LPU and TRIO	6 - 10	52 - 54
3	$FeCl_3$ - $AlCl_3$	LPU	25	23
4	$CuCl_2$ - $CaCl_2$	LPU	28.2	75.2
5	$Fe_2(SO_4)_3$ - $AlCl_3$	LPU	10.7	n.a.
6	$Fe_2(SO_4)_3$	TRIO	12.3 - 26.9	n.a.

Time of Leaching:	4-6 hours
Temperature:	80-96°C
Size of Ore Sample:	from 200 to 400 mesh
Initial Iron Concentration:	20-30 g/L
Liquid/Solid Ratio:	0.7 L/50g - 0.7 L/20 g

The following four sections of this report discuss:

1. The identification of conditions controlling arsenic and antimony extraction during chloride leaching of complex sulfide ores, and
2. Arsenic and antimony oxidation and selective precipitation with iron from leach solutions.

4.2 Description of Experiments

All tests were performed with the TRIO ore sample, which among all other Delta ore samples has the highest arsenic content. The metals concentration and mineralogical composition of the TRIO sample are presented in Table 4.2.

The tests on arsenic and antimony leaching, oxidation, precipitation and crystallization were performed on a bench scale in both a batch and a continuous manner. All batch experiments were carried out under atmospheric pressure and at a temperature below the boiling point of the solution, in a glass reactor or a beaker with a stirrer. All continuous experiments under elevated oxygen pressure, were carried out in the two column reactor system described in Chapter 3 and at the annual AIME meeting in Phoenix, February 1988 [4.8]. Two modifications to the system are shown in Figure 4.10. The first modification consisted of the addition of a horizontal, cooled separator that improved crystal formation and particle sedimentation from the recirculated solutions. The second modification was a horizontal heated separator for the sedimentation/separation of hydrolysis products from oxidized solution.

The solutions used in the laboratory experiments contained variable elemental concentrations:

Fe from 2.5 to 71 g/l
Cu from 0.06 to 2.6 g/l
Zn from 1.5 to 196 g/l
Pb from 0.8 to 6.6 g/l
Ag from 4 to 28.1 mg/l
Sb from 1.6 to 130 mg/l
As from 0.16 to 10 g/l
Ca from 0.8 to 45 g/l
Mg below 15 g/l
Cl from 3.5 to 8.0 mol/l
SO_4^{2-} from 3.5 to 0.15 mol/l

Table 4.2. Elemental and mineralogical composition of the ore sample used in experiments. Delta Ore, sample TRIO, size 270-400 mesh

A) Elemental composition of the ore sample.

Fe	25.03%	Ca	4.39 %
Cu	1.35%	Sb	0.14 %
Zn	7.50%	Ag	118.8 ppm
Pb	7.30%	Au	3.98 ppm
As	6.99%	Total Sulfur	27.52%

B) Mineralogic composition of the ore sample.

ZnS	11.18%
PbS	8.42%
FeS	2.36%
$CuFeS_2$	3.89%
FeAsS	15.14%
FeS_2	32.75%
Fe (oxidized)	1.91%
Insoluble Residue	4.67%
Total Identified	91.65%

Tetrahedrite and Tenanite were confirmed as minor minerals.

4.3 Arsenic and Antimony Behavior During Chloride Leaching

The leachability of arsenic and antimony in acidic chloride solutions was tested under the following specific conditions:

- low temperature (70-80°C) leaching under elevated oxygen pressure (p_{O_2} = 20-30 psig);
- leaching at higher temperature (90-100°C) and under atmospheric pressure of air;
- leaching at higher temperature and under elevated oxygen pressure (20-30 psig);
- leaching at higher temperature and under elevated oxygen pressure, activated by a small addition of nitric acid (5g HNO_3/l solution).

All pressure leaching tests were carried out in the installation shown in Figure 4.10 according to flowsheets presented in Figure 4.11 and 4.12. Each experiment was terminated

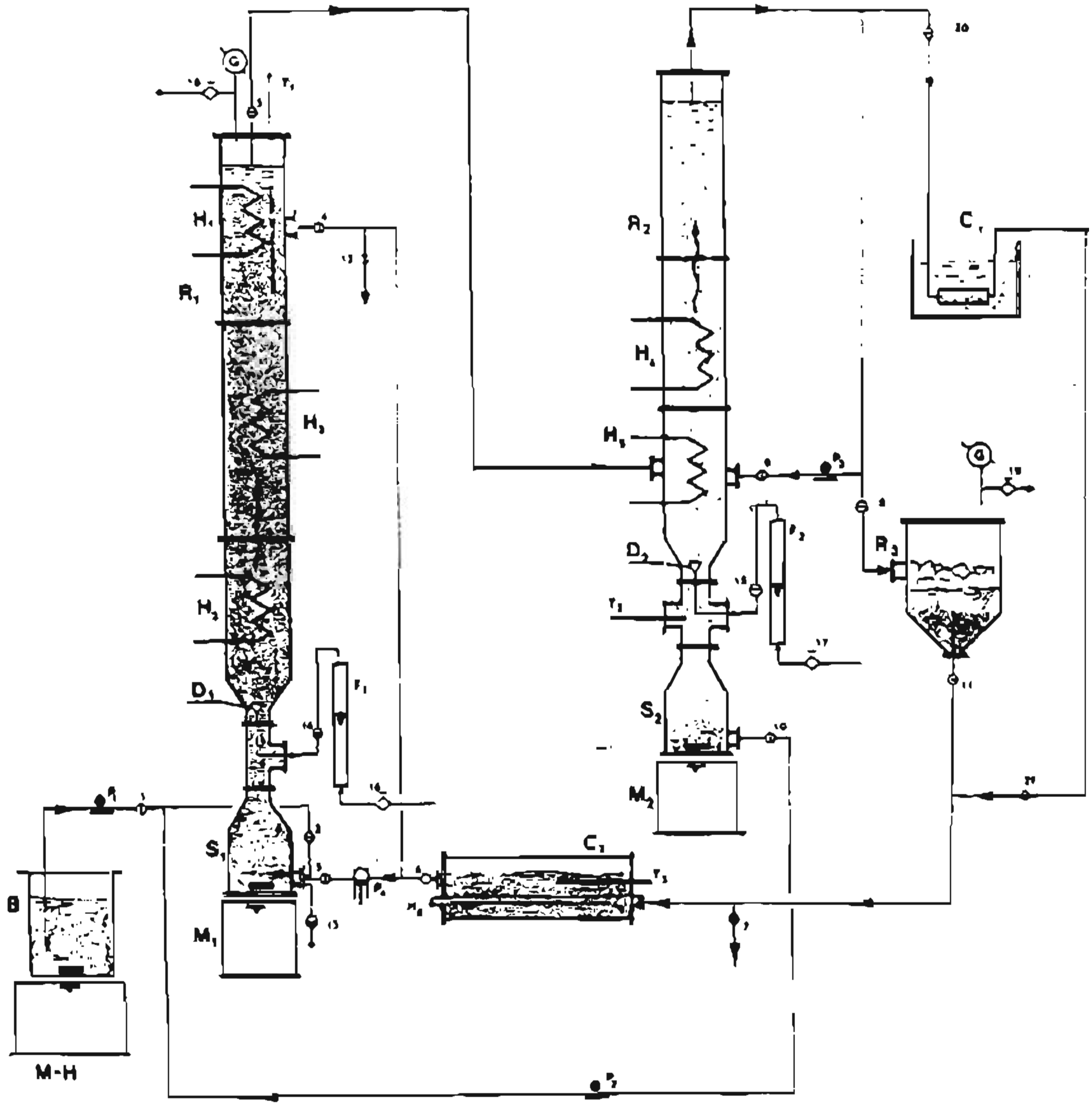


Figure 4.10. Laboratory installation for fluidized bed leaching, precipitation and flotation under elevated oxygen pressure.

R_1 and R_2 - Column reactors (dia. 4 inch, height 48 inch, max. pressure 50 psi)
R_3 - Pressure liquid/solid separator (150 psi)
S_1 and S_2 - Separators for sedimented fraction of suspension (50 psi)
B - Pulp preparation beaker
C_1 - Pressure crystallizer (100 psi)
C_2 - Separator for hydrolysis products sedimentation
D_1 and D_2 - Fritted-glass discs for oxygen dispersion in reactors (60 psi)
F_1 and F_2 - Oxygen flow-meters (150 psi)
G - Gauge (oxygen, 150 psi)
H_1-H_5 - Heating tapes
H_6 - Immersion heater (in fused quartz tube)
M_1 and M_2 - Magnetic stirrers
M-H - Hot plate with magnetic stirrer
P_1-P_3 - Tubing pumps Masterflex with Norprene tube, adapted to pulp transportation under 40 psi pressure
P_4 - Piston metering pump for solution (150 psi)
T_1-T_3 - Thermometers
1-21-Teflon valves

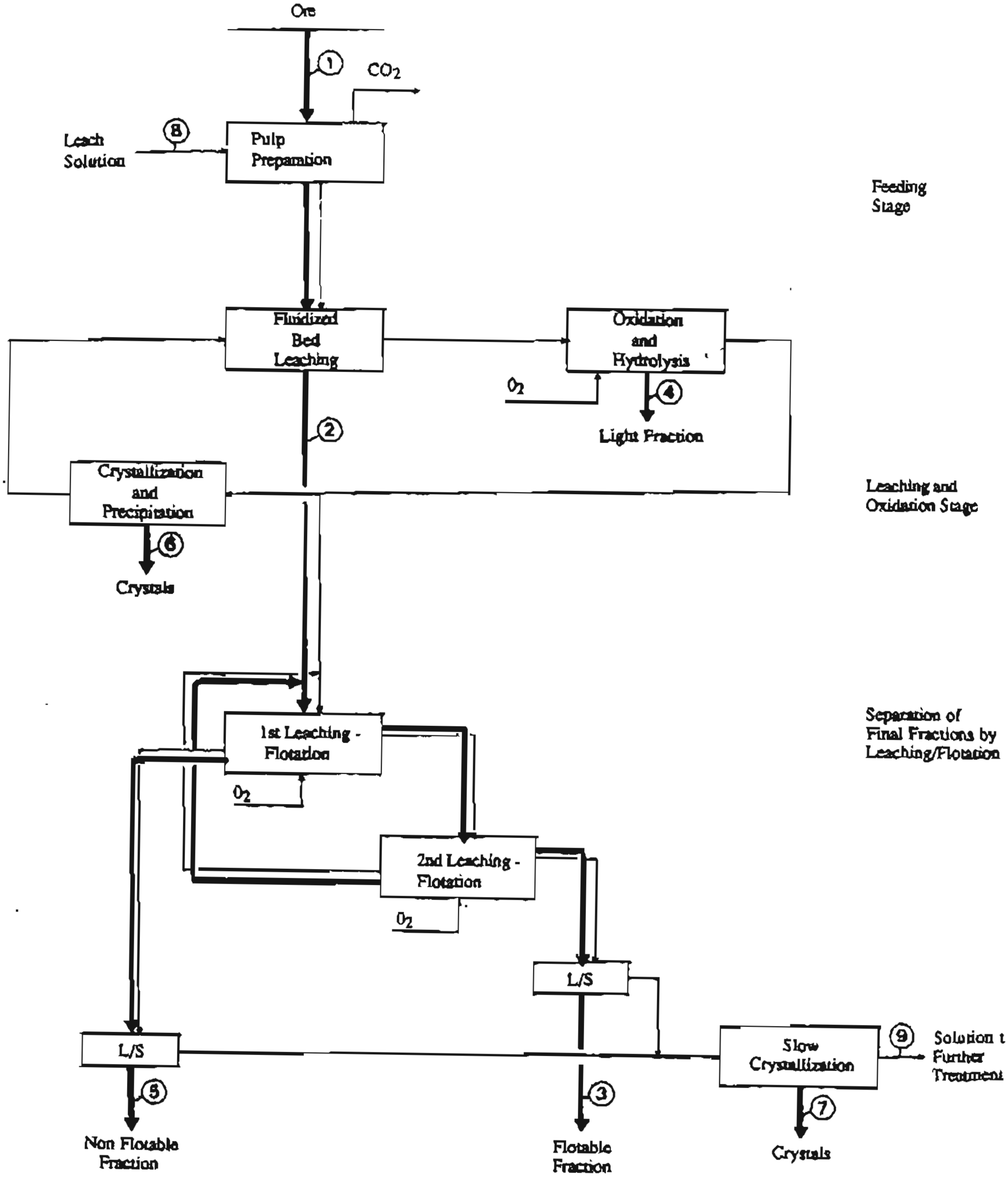


Figure 4.11. General flowsheet of experiments on leaching/precipitation/flotation carried out in pressure installation presented in Figure 4.10.

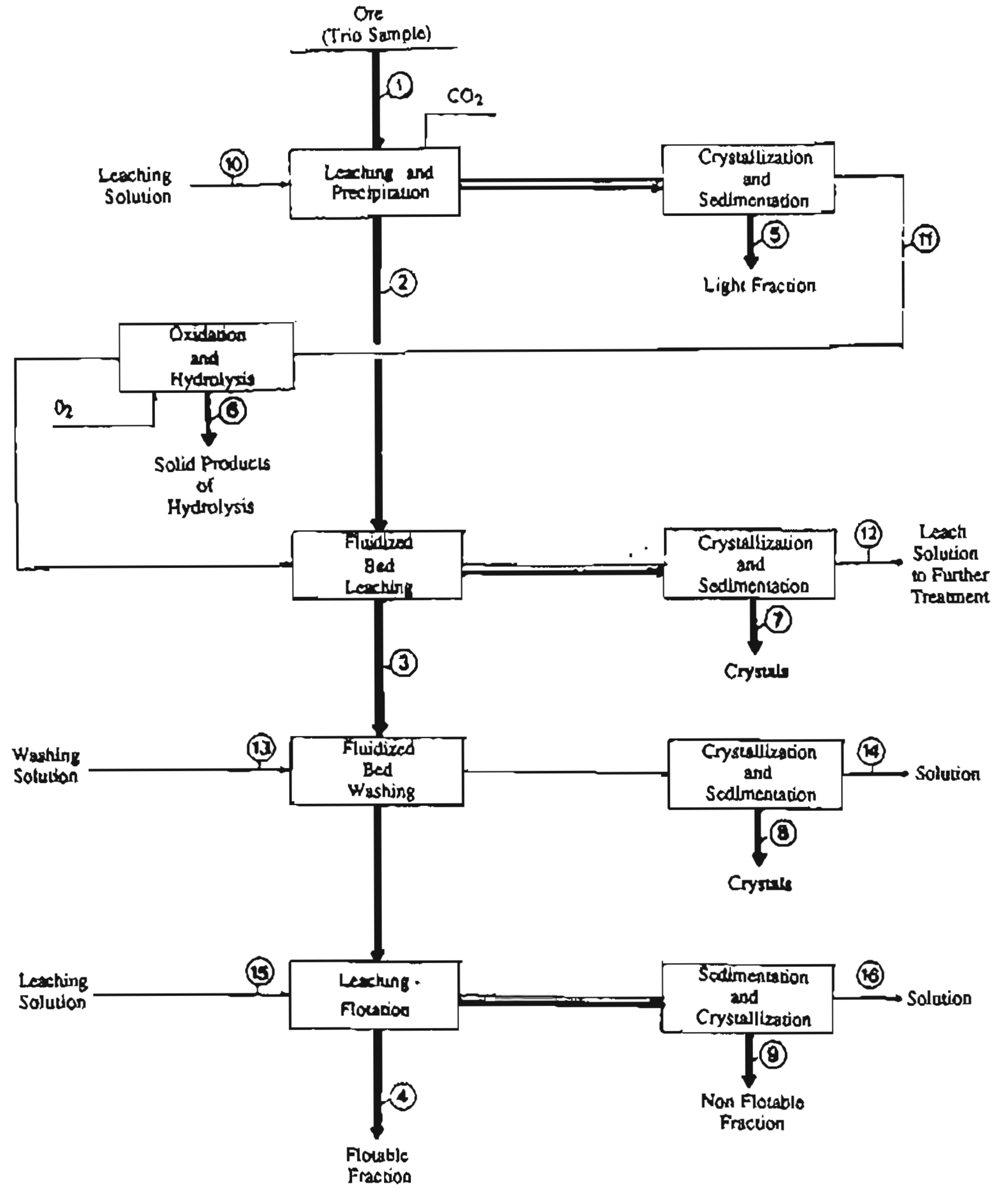


Figure 4.12. General flowsheet of mixed bath/continuous experiment (Table 4.6) carried out in the fluidized bed reactor and in a static reactor (3 liter beaker).

a segregation of solid particles by a leaching/flotation stage, conducted with oxygen dispersed in the solution under elevated pressure (20-30 psig). For improved separation of the final solids fractions, the leaching/flotation was repeated in some cases under atmospheric pressure of air in the installation described in Chapter 2. The results of six tests are presented in Tables 4.3 through 4.8. Specific leaching conditions and parameters are given.

The atmospheric pressure leaching tests (Tables 4.4 and 4.5) are included in the combined leaching/precipitation experiments and the general flowsheet is presented in Figure 4.12. These are:

- the fluidized bed leaching of ore with the solution identified in Figure 4.12 as flow (1), and bench scale leaching of succeeding intermediate products, flows 2 and 3, conducted in a large beaker (3 liter) with the solutions of flows 13 and 15. The nonflotable fractions from both experiments (Tables 4.4 and 4.5) were combined. This joint fraction (Flow 5) was divided between two experiments proportionately to the amount of fresh ore used in both experiments.

Table 4.3. Metals concentration in the flows during leaching tests carried out in the laboratory (FBL) installation (Figure 4.10) according to the flowsheet in Figure 4.11.
Chloride solution; Initial pH = 0.2; temp. 70-80°C; time 2 hours

Specification of Flow	Flow * No.	CONCENTRATION (%) (Au, Ag in ppm)											Amount of Total Flow [Grams]
		Fe	Cu	Zn	Pb	Ag	Sb	As	Ca	Au	SO_4^{2-}	S°	
Raw Material (Ore) to Processing	1	25.03	1.35	7.50	7.30	118.8	0.14	6.99	3.3	3.98	-	-	1500
Product (Ore) after Leaching	2	-	-	-	-	-	-	-	-	-	-	-	-
Final Product - Flotable Fraction	3	31.4	1.57	5.25	2.60	150	0.18	8.26	0.21				540**
Light Fraction of Products	4	6.4	0.26	1.2	45.2	26	0.05	1.2	3.2				20**
Non Flotable Fraction of Products	5	32.5	1.73	9.3	10.6	115	0.15	8.2	0.31				380**
Immediate Crystallization and Precipitation Product	6	1.9	0.12	2.17	28.1	10	0.02	0.6	7.80				60**
Slow Crystallization Products	7	2.15	0.10	8.0	31.5	9.01	0.02	<0.4	4.52				40**
		CONCENTRATION (g/l)											(Liters)
Leaching Solution (Inlet)	8	19.2	0.98	196	0.8	3.16	0.034	1.02	5.54		1.55		7.4
Leach Solution (Outlet)	9	34.7	1.25	232	0.8	9.76	0.077	0.16	2.15				7.0

* Identification numbers in the flowsheet (Figure 4.11)

** Approximate weight of fraction (not totally recovered after experiment).

Calculated Concentrations in the Flows (Calculated from AA analyses, mass balance considerations and assumptions):

		(%)			(%)			(%)			(%)
(1)	FeS_2	32.75	(4)	$PbCl_2$	55.32	(6)	$CaSO_4 \cdot 2H_2O$	33.54	(7)	$PbSO_4$	23.50
	$FeAsS$	15.14		$PbSO_4$	14.6		$PbCl_2$	20.76		$PbCl_2$	20.68
	ZnS	11.18		PbS	4.69		$PbSO_4$	7.51		$CaSO_4 \cdot 2H_2O$	19.44
	PbS	8.42		$CaSO_4 \cdot 2H_2O$	13.76		$FeOOH$	2.31		$FeOOH$	3.42
	$CuFeS_2$	3.89		$FeOOH$	1.59		$FeAsO_4 \cdot 2H_2O$	1.82			
	Insoluble (SiO_2)	4.67		$FeAsO_4 \cdot 2H_2O$	0.55		$ZnSO_4 \cdot 7H_2O$	9.53			
				$FeAsS$	1.73						

Table 4.4. The nonpressure, batch leaching/precipitation test. Chloride solution;
initial pH = 0.2, temp. 90-98°C, time 90 min.

Specification of Flow	Flow * No.	CONCENTRATION (%) (Au, Ag in ppm)											Amount of Total Flow [Grams]**
		Fe	Cu	Zn	Pb	Ag	Sb	As	Ca	Au	SO_4^{2-}	S°	
Raw Material (Ore) to Processing	1	25.03	1.35	7.50	7.30	118.8	0.14	6.99	3.3	3.98	-	-	539
Intermediate Product After Leaching	2												
Flotable Fraction After Processing	3	24.0	1.15	3.60	1.94	104.3	0.21	12.93	0.04				381.8
Light Fraction of Solid Particles	4												
Non Flotable Fraction After Processing	5	6.29	1.67	0.57	19.01	12.21	0.14	4.57	5.56				128**
Immediate Crystallization and Precipitation Product	6												
Slow Crystallization Products	7												
		CONCENTRATION IN SOLUTION, Grams Per Liter (Au, Ag in ppm)											Volume*** (Liters)
Leaching Solution (Inlet)	10	31.8	2.3	118	0.82	16	0.124	10	0.80				2
Leach Solution (Outlet)	11	32.3	2.13	119	1.38	27.2	0.004	4.36	1.26				1.8

* The numbers as in the flowsheet (Figure 4.12).

** The part of common flow of 274g. The second part in the same flow in Table 4.4.

*** Approximate amount or volume; not precise enough for a balance calculation.

Table 4.5. The nonpressure batch leaching/precipitation test. Chloride solution; initial pH=0.8; temp. 90-104°C, time 60 min.

Specification of Flow	Flow * No.	CONCENTRATION (%) (Au, Ag in ppm) Fe	Cu	Zn	Pb	Ag	Sb	As	Ca	Au	SO_4^{2-}	S°	Amount of Total Flow (Grams)
Raw Material (Ore) to Processing	1	25.03	1.35	7.50	7.30	118.8	0.14	6.99	3.3	3.98	-	-	613.5
Intermediate Product After Leaching	2	-	-	-	-	-	-	-	-	-	-	-	-
Flotable Fraction After Processing	3	22.4	1.64	8.31	3.08	140.1	0.19	10.24	0.12				
Light Fraction of Solid Particles	4												
Non Flotable Fraction After Processing	5	6.29	1.67	0.57	19.01	12.21	0.14	4.57	5.53				146**
Immediate Crystallization and Precipitation Product	6												
Slow Crystallization Products	7												
		CONCENTRATION IN SOLUTION, g/l											Volume*** (Liters)
Leaching Solution (Inlet)	10	28.7	2.42	115.6	1.46	20.46	0.088	6.59	1.48				2.6
Leach Solution (Outlet)	11	29.14	2.60	103.8	1.00	25.30	0.004	2.28	1.70				2.5

* The numbers as in the flowsheet (Figure 4.12).

** One part from total amount of 274g. The second part (128g) is indicated in Table 4.5 (Flow 5).

*** Approximate volume; not precise enough for a balance calculation.

Calculated Concentrations in the Flows (Calculated from AA analyses, mass balance considerations and assumptions):

$FeAsO_4 \cdot 2H_2O$	14.1
$FeOOH$	4.5
$PbSO_4$	20.4
$CaSO_4 \cdot 2H_2O$	23.9

Arsenic was not extracted from the fresh ore to the leach solution when:

- fresh ore was leached in a weak oxidative condition at temperatures below 90°C;
- pH of the solution is higher than 0.2.

Arsenic precipitates from the leach solution from the previous tests under these conditions and this behavior seems independent of the arsenic concentration in solution. In the above experiments arsenic concentration diminished:

from 1.02 g/l to 0.16 g/l (experiment: Table 4.3)
from 6.59 g/l to 2.28 g/l (Table 4.4), and
from 10.00 g/l to 4.36 g/l (Table 4.5).

In moderate oxidative conditions created by ferric chloride and oxygen under elevated pressure, a slow extraction of arsenic to solution was observed:

from 1.97 g/l to 4.80 g/l (Table 4.7), and
from 0.39 g/l to 3.05 g/l (Table 4.6, Flows 15 and 16).

In the second case, i.e. carried out according to the 2nd flowsheet (Figure 4.12) and described in Table 4.6, arsenic was leached from an intermediate product; the solid residue from the previous leaching/precipitation stage. In this case, arsenic extraction to solution can be attributed to dissolution of the precipitated products of hydrolysis and not to decomposition of the primary arsenopyrite or other refractory arsenic-sulfides.

Under strongly oxidative conditions, those created by nitric oxides or nitric acid activation, arsenic as well as antimony are partly extracted to the acid solution. In the experiment described in Table 4.8, their concentrations in the leach solution increased:

Table 4.6. Cumulative data from combined batch/continuous nonquantitative experiments carried out according to the 2nd Flowsheet (Figure 4.12). Chloride solution, temp. 90-98°C

Specification of Flow	Flow* No.	Fe	Cu	Zn	Pb	Ag	Sb	As	Ca	Au	$S0_4^{2-}$	S°	Total Amount [Grams]
		CONCENTRATION IN SOLIDS (%) (Au, Ag in ppm)											
Ore, Sample TRIO	1**	25.03	1.35	7.50	7.30	118.8	0.140	6.99	3.3	3.98	-	-	1,152.5
Ore After Leaching/Precipitation Stage	2**	23.11	1.33	6.24	5.53	120.	0.217	11.48	0.43				1,054.8
Ore After Leaching	3	27.52	1.51	10.87	3.45	98.40	0.211	10.12	0.52				1,060.0***
Flotable Fraction After Processing	4	31.65	1.44	2.60	0.13	142.7	0.220	8.55	0.12				485
Light Fraction	5	6.29	1.67	0.57	19.01	12.21	0.14	4.57	5.56				274
Products of Hydrolysis	6	14.96	0.41	6.85	4.37	37.78	0.078	5.95	0.17				111.2
Light and Crystalline Fraction	7	1.72	0.01	0.02	15.71	-	-	-	13.56				25.12
Crystals	8	10.52	0.56	0.20	20.86	75.25	0.39	7.67	2.46				116.1
Light and Non Flotable Fraction	9	23.05	0.27	0.86	1.86	27.47	0.10	4.85	6.25				108.4
		CONCENTRATION IN SOLUTION, g/l (Au, Ag in mg/L)											Volume (Liters)
Leaching Solution (Inlet)	10**	31.8	2.30	118	0.82	16.0	0.124	10.0	0.8				6.1
Leach Solution After Crystallization	11	28.51	2.73	148	2.31	23.42	0.011	5.25	1.46		8.44		5.9
Leach Solution (Outlet)	12	19.43	3.34	156.8	1.13	28.12	0.012	6.79	0.60		13.71		5.5
Washing Solution	13	2.52	0.07	1.51	6.4	11.60	0.120	0.16	44				4.8
Wash Solution After Crystallization	14	7.46	0.42	14.48	2.77	15.40	0.092	3.03	2.36				4.7
2nd Leaching Solution	15	28	0.82	5.9	2.3	4.12	0.090	0.39	36.0				4.0
2nd Leach Solution After Crystallization	16	21.4	0.80	7.94	3.96	6.72	0.155	3.05	21.7				4.2

* The same numbers as in the flowsheet in Figure 4.12.

** Cumulative data from 3 experiments performed with fresh ore: Two similar batch tests documented in Table 4.4 and 4.5 as well as in Figure 4.14; and one fluidized bed leaching test (314g fresh TRIO sample) with mixed solution after both experiments (Table 4.4 and 4.5) and 1.8 liters of the same solution as used in above experiments.

*** Only about 70% of total flow 3, was directed to the next stage of treatment (see Figure 4.12).

Calculated Concentrations in the Flows (Calculated from AA analyses, mass balance considerations and assumptions):

		(%)			(%)			(%)			(%)			(%)
(4)	FeAsS	18.6	(5)	$FeAs0_4\cdot 2H_20$	14.1	(6)	$FeAs0_4\cdot 2H_20$	18.3	(8)	$FeAs0_4\cdot 2H_20$	23.7	(9)	$FeAs0_4\cdot 2H_20$	14.9
	FeS_2	54.3		Fe00H	4.6		Fe00H	16.7		Fe00H	7.6		Fe00H	3.09
	$4Cu_2S\cdot Sb_2O_3$	0.9		$PbSO_4$	20.4		$PbSO_4$	6.4		$PbSO_4$	30.4		$PbSO_4$	2.7
	$CuFeS_2$	2.9		$CaS0_4\cdot 2H_20$	23.9		$CaS0_4\cdot 2H_20$	0.7		$CaS0_4\cdot 2H_20$	10.6		$CaS0_4\cdot 2H_20$	26.8
	ZnS	3.9					$ZnS0_4\cdot 7H_20$	30.1						
	S	10												

As from 4.8 g/l to 10 g/l
Sb from 8 ppm to 124 ppm.

The concentration of antimony decreased in the atmospheric pressure experiments:

from 88 ppm to 4 ppm (Table 4.4), and
from 124 ppm to 4 ppm (Table 4.5)
and increased slowly during leaching under elevated oxygen pressure:

from 34 ppm to 77 ppm (Table 4.3),
from 90 ppm to 155 ppm (Table 4.6, Flows 15 and 16), and
from 80 ppm to 124 ppm (Table 4.8).

However, the behavior of antimony during chloride leaching is not clear. It was precipitated from solution under oxidative

Table 4.7. Metals concentration in the flows during leaching and precipitation tests carried out according to the Flowsheet in Figure 4.11.
Chloride solution; initial pH = 0.2; temp. 90°C; oxygen pressure 20-30 psig; time 2 hrs.

Specification of Flow	Flow * No.	Fe	Cu	Zn	Pb	Ag	Sb	As	Ca	Au	SO_4^{2-}	S°	Amount of Total Flow [Grams]**
		CONCENTRATION (%) (Au, Ag in ppm)											
Raw Material (Ore) to Processing	1	30.16	1.58	7.88	7.25	130.4	0.16	8.40	1.52				1,568.0
Intermediate Product After Leaching	2	24.52	1.27	5.58	4.15	153.0	0.21	8.45	0.25			-	
Flotable Fraction After Processing	3	27.42	1.45	1.40	2.91	137.9	0.26	10.57		5.66		11.57	1,041.5
Light Fraction of Solid Products	4	22.12			1.45		-	0.12	14.3				~120
Non Flotable Fraction After Processing	5	41.02	1.59	1.89	14.68	152	0.35	3.97	0.14	0.82	33.2		106.4
Crystallization and Precipitation Products	6 & 7	8.54	-	-	23.96	-	-	0.61	31.36	-	48.0		96.47
		CONCENTRATION IN SOLUTION, grams per liter											Volume (Liters)**
Leaching Solution (Inlet)	8	21.7	0.52	126	0.77	3.18	0.03	1.97	3.36	- -		-	6.6
Leach Solution (Outlet)	9	31.6	2.5	144	0.74	8.6	0.08	4.8	-	-		-	6.4

* The numbers as in the flowsheet (Figure 4.11).
** Approximate amount or volume; not precise enough for a balance calculation.

Calculated Concentrations in the Flows (Calculated from AA analyses, mass balance considerations and assumptions):

		(%)			(%)			(%)
(4)	$CaSO_4 \cdot 2H_2O$	61.5	(5)	$CaSO_4 \cdot 2H_2O$	0.6	(6)	$CaSO_4.2H_2O$	65.6
	$FeOOH$	35.2		$FeOOH$	60.6		$FeOOH$	9.9
	Pb (as $PbCl_2$ or $PbSO_4$)	1.9-2.1		Pb (as $PbCl_2$ or $PbSO_4$)	19.7-21.4		Pb (as $PbCl_2$ or $PbSO_4$)	12.8-14.0
	$FeAsO_4 \cdot 2H_2O$	0.37		$FeAsO_4.2H_2O$	12.0		$FeAsO_4.2H_2O$	1.8

Table 4.8. Metals concentration in the Flows during leaching and precipitation tests, according to the Flowsheet in Figure 4.11.
Chloride solution activated by HNO_3 ($5 g HNO_3/l$). Initial pH = 0; oxygen pressure 20-30 psi; temp. 90-98°C; time 0.5 hr.

Specification of Flow	Flow * No.	Fe	Cu	Zn	Pb	Ag	Sb	As	Ca	Au	SO_4^{2-}	S°	Amount of Total Flow [Grams]**
		CONCENTRATION (%) (Au, Ag in ppm)											
Raw Material (Ore) to Processing	1	27.42	1.45	1.40	2.91	137.9	0.26	10.57		5.66		11.57	1030.
Intermediate Product After Leaching	2												
Flotable Fraction After Processing	3	42.7	1.59	0.41	0.21	160.3	0.23	6.66	-	6.07		16.1	534.2
Light Fraction of Solid Particles	4	17.29	0.20	0.11	41.38	0.02	0.25	5.01					33.0
Non Flotable Fraction After Processing	5	38.86	1.47	0.53	0.39	144.34	0.20	6.74	-	5.67			108.8
Immediate Crystallization and Precipitation Product	6	Together With Flow (4)											
Slow Crystallization Products	7	23.74	0.17	0.11	37.04	-	0.07	1.54	0.08				35.45
		CONCENTRATION IN SOLUTION, g/l (Ag, Au in mg/L)											Volume (Liters)**
Leaching Solution (Inlet)	8	31.6	2.5	144	0.74	8.6	0.08	4.8	0.97	-		-	6.6
Leach Solution (Outlet)	9	31.8	2.3	118	0.82	16.0	0.124	10.0	0.82	-		-	6.4

* The numbers as in the flowsheet (Figure 4.11).
** Approximate amount or volume; not precise enough for a balance calculation.

Calculated Concentrations in the Flows (Calculated from AA analyses, mass balance considerations and assumptions):

		(%)			(%)
(4)	$PbSO_4$	60.4	(7)	$PbSO_4$	54.1
	$FeOOH$	21.5		$FeOOH$	35.9
	$FeAsO_4 \cdot 2H_2O$	15.4		$FeAsO_4 \cdot 2H_2O$	4.7
				$CaSO_4.2H_2O$	0.4

conditions (Table 4.7). It seems, that precipitation or dissolution of antimony depends more on pH and other soluble component concentrations, than of oxidative conditions in solution.

4.4 Arsenic and Antimony Precipitation from Chloride Solution

Arsenic and antimony precipitation with iron by oxidation and hydrolysis of ferric ions were tested in the following experiments:

1. Precipitation from pure solutions without chemical addition and simultaneous precipitation and leaching, under elevated oxygen pressure.
2. Precipitation with iron by fresh ore addition.
3. Precipitation with iron by calcium oxide addition.

Only results of the tests on arsenic and antimony precipitation with calcium oxide are presented in this section. The other tests on arsenic and antimony precipitation are included in the leaching/precipitation experiments carried out according to the flowsheet presented in Figure 4.11 and 4.12. Their results are documented in the previous section in Tables 4.3 through 4.8.

The precipitation of arsenic with iron was caused by oxygen dispersed in the second reactor, subsequent to the fluidized bed leaching that had been run in the first reactor (Figure 4.10). The solid products of iron hydrolysis and ferric arsenate formed in the second reactor were transported with the solution to separator R_4, where larger particles of solids settled. This portion of the precipitated solids was then separated together with other crystallized products as "the light fraction". These are represented by flow (4) in the first flowsheet (Figure 4.11) and by flow (6) in the second flowsheet (Figure 4.12). The concentration of components in the product separated by this manner are given under the numbers of the flows: in Tables 4.3, 4.7, and 4.8 - Flow (4), and in Table 4.6 - Flow (6).

The iron hydrolysis products and ferric arsenate are also found in the nonflotable fractions after leaching/flotation stages. However, a part of the fine precipitated particles was not retained in the separator (R_4) but were circulated with the solution to the first reactor. These nonflotable particles were further separated by flotation from flotable particles of the leached ore and sulfur; - flow 5 in the first flowsheet and flow 8 in the second flowsheet. This is the case for experiments documented in Tables 4.4 and 4.5 in which a fraction of precipitated products was not separated in flow 4 but in the nonflotable fraction flow 5.

Precipitation of arsenic and antimony by fresh ore was also tested in a three stage experiment performed according to the flowsheet presented in Figure 4.13. The initial concentration of other metals was as follows: Fe 31.8 g/l, Zn 118 g/l, Cu 2.3 g/l and Ag 20 mg/l. Their concentration had not varied significantly during the precipitation tests conducted at the initial pH of 0. Near total antimony (97%) and about 60% of arsenic were precipitated during 0.5h of the first stage of processing. The degree of arsenic precipitation increased to 77% after one hour of the 2nd stage of precipitation.

Iron hydrolysis and ferric arsenate formation occurs during leaching if hydrogen ion concentration diminishes, thus iron precipitation was observed in many experiments. However, only in one test, carried out according to the second flowsheet (Figure 4.12), was a quantitative analysis of iron and arsenic precipitation made. The data of this experiment are presented in Table 4.6.

In this experiment the fresh ore (Flow 1) was contacted in the fluidized bed state with leaching solution having high arsenic concentration (Flow 10). During this leaching/precipitation stage about 65% of total arsenic, and about 95% of antimony were precipitated from solution.

During this experiment the concentration of both elements diminished in the solution:

arsenic from 10 g/l to 5.25 g/l, and
antimony from 124 ppm to 11 ppm.

A portion of precipitated arsenic and antimony was separated in the light fraction (Flow 5) together with the gypsum crystals

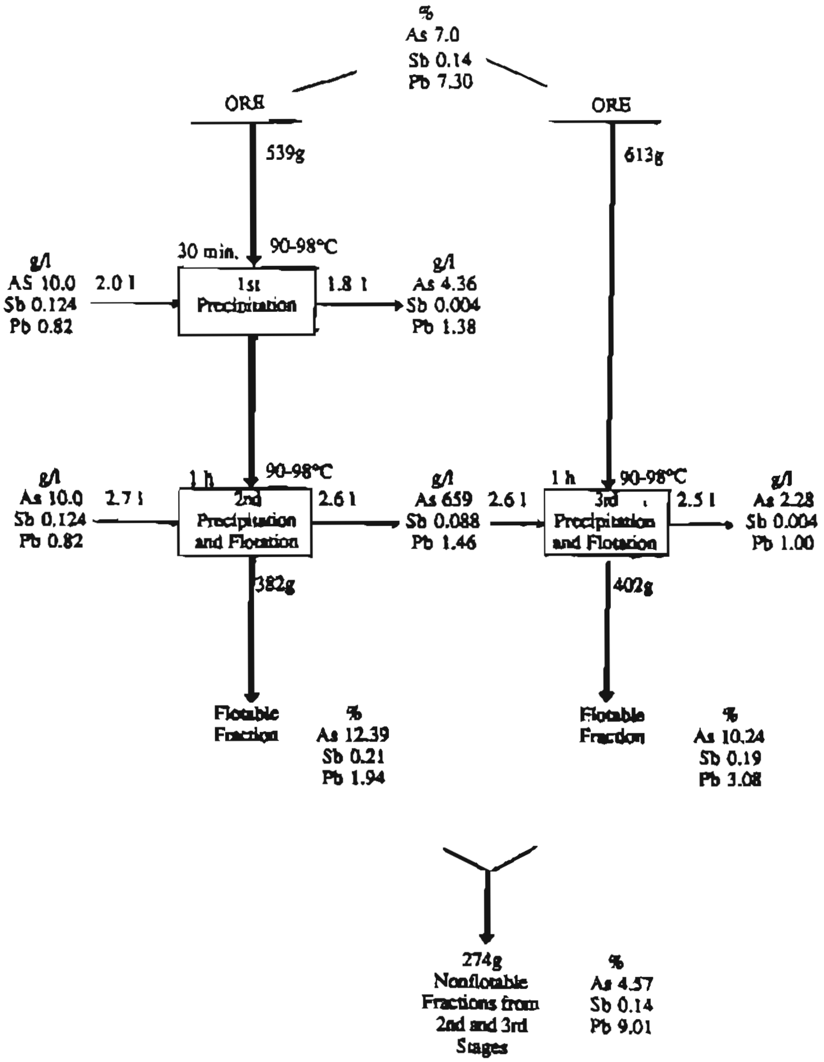


Figure 4.13. **Arsenic and antimony precipitation by fresh ore (sample TRIO) and separation of solid products in the flotable and nonflotable fractions.**

and other "light" particles. The rest remained in the flow of partially leached ore (Flow 2) that was subjected to three consecutive leaching stages:

- leaching in the same (Flow 11), but reoxidized solution with pH at about 1;
- leaching in the acidic (pH=0) calcium chloride solution, containing only small concentration of ferric ions (Flow 13);
- leaching in the acidic (pH=0) solution with the moderate concentration of ferric chloride (Flow 15), also containing calcium and magnesium chlorides, and ended by separation of solid residue by flotation into flotable fraction (Flow 4) and nonflotable fraction (Flow 9).

The analysis of results presented in Table 4.6 indicates that precipitated arsenic can be eliminated from the flow of leached ore in a separate nonflotable fraction together with iron and lead or by leaching in different chloride solutions with respectively low pH. The behavior of antimony cannot be uniquivocally confirmed on the basis of this experiment, because of its very low concentration in solution.

Arsenic and Antimony Precipitation by Calcium Oxide

The tests on arsenic and antimony precipitation by addition of calcium oxide were carried out on a bench scale, in a glass beaker. A small portion of powdered CaO had been added gradually to the solution at temperatures 90-98°C. After about 2 hours, precipitated solid particles were separated from the solution by filtration. In some cases a flocculant had been added for better separation of solid particles.

The results of the experiments conducted according to the flowsheet shown in Figure 4.14 are presented in Tables 4.9 through 4.12. The degree of precipitation of arsenic, antimony, iron and lead at different final pH of solution are shown in Table 4.13. The results indicate that precipitation of arsenic, antimony and iron depends strongly on pH and does not depend on the chloride ion concentration. It seems that observed lead coprecipitation does not depend significantly on pH in the investigated solutions. However, the degree of lead removal from solutions, increases with diminishing chloride ion concentration and the presence of sulfate ion.

Characteristic of the Precipitated and Crystallized Solids

Portions of solid particles precipitated and crystallized from the solutions during leaching, oxidation and neutralization had been collected in the separate fractions by three manners:

- by classification from the "bulk" suspension being leached in the fluidized bed owing to low specific gravity and small size of the precipitated particles. These were transported with solution beyond the fluidized bed leaching (FBL)-reactor;
- by selective flotation of flotable particles of treated ore and sulfur. Precipitated and crystallized nonflotable particles remained in the reactor;
- by the cooling of filtrated solution and crystallization. Several complexed salts had crystallized from pure solution after some days of retention at ambient temperature.

The newly formed solids were separated in the following fractions:

- the products of iron hydrolysis, also named the "light fraction":
  - Flows 4 and 6 in the 1st flowsheet (Figure 4.11), and
  - Flows 5 and 6 in the 2nd flowsheet (Figure 4.12);
- the fast crystallization or precipitation products (Flow 6 in the 1st flowsheet);
- slow crystallization products (Flow 7 in the 1st flowsheet).
- nonflotable fraction of solid, mostly products of hydrolysis and other crystals formed during leaching:
  - Flow 5 in the 1st flowsheet, and
  - Flow 9 in the 2nd flowsheet, and
- different mixed, not precisely defined, fractions of separated solids:
  - Flows 7 and 8 in the 2nd flowsheet.

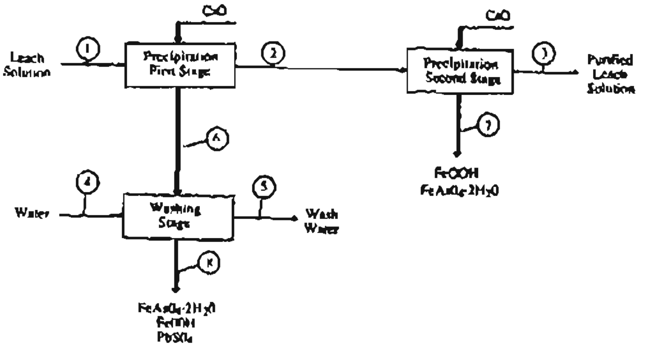


Figure 4.14. Flowsheet of the precipitation tests carried out with calcium oxide for the data presented in Tables 4.9 through 4.12.

The chemical analysis of each fraction is presented in Tables 4.3 through 4.12. However, because a portion of the precipitates was composed of very fine particles, as well as of amorphous particles, their crystallographic identification by x-ray analysis was very difficult. Only compounds that belong to the beaverite group and arsenosiderite were

Table 4.9. Metals concentration in the Flows during the test of precipitation by calcium oxide carried out according to the Flowsheet in Figure 4.14. Chloride solution, temp. 90-98°C, time of precipitation 2-3 hr.

Specification of Flow	Flow No.	Fe	Cu	Zn	Pb	Ag	Sb	As	Ca	SO_4^{2-}	pH	Volume of Solution [l]
		CONCENTRATION IN SOLUTION, g/l (Au, Ag in mg/l)										
Solution to Precipitation Stage	1	19.43	3.43	156.8	1.13	28.12	0.012	6.79	0.6	13.71	0.2	1.51
Solution After 1st Stage Precipitation	2	16.53	4.56	185.8	0.009	38.92	<0.02	4.49	26.16	n.a.		1.05
Solution After 2nd Stage Precipitation	3											
Washing Water	4	-	-	-	-	-	-	-	-	-	6.2	2.5
Spend Wash - Water	5	0.49	0.18	7.56	0.25	1.71	<0.8	0.07	0.38		2.2	2.4
		CONCENTRATION IN SOLID, % (Ag, Au - ppm)										Weight (g)
Product of 1st Stage Precipitation	6	7	0.3	12.2	1.12	27.	0.6	4	0.6			
Product of 2nd Stage Precipitation	7											
Precipitated Product After Washing	8	15.25	0.07	0.74	2.44	-	0.028	9.31	0.01			63.5g
		DEGREE OF PRECIPITATION, (%)										
Cumulative Degree of Elements Precipitation		33	0.8	0.2	90.6	-	100	57.7	0.7			

Calculated Concentrations in the Flow 8 (Calculated from AA analyses, mass balance considerations and assumptions):

	(%)
$FeAsO_4 \cdot 2H_2O$	28.7
FeOOH	13.2
$PbSO_4$	3.6

Table 4.10. Metals concentration in the Flows during the test of precipitation by calcium oxide carried out according to the Flowsheet in Figure 4.14. Chloride solution, temp. 90-98°C, time of precipitation in each stage 2-3 hrs.

Specification of Flow	Flow No.	Fe	Cu	Zn	Pb	Ag	Sb	As	Ca	SO_4^{2-}	pH	Volume of Solution [l]
		CONCENTRATION IN SOLUTION, g/l (Au, Ag in mg/l)										
Solution to Precipitation Stage	1	19.43	3.43	156.8	1.13	28.12	0.012	6.79	0.60	13.71	0.2	0.7
Solution After 1st Stage Precipitation	2	13.86	4.36	218	0.004	36.04	<0.02	3.65	2.01		0.36	0.77
Solution After 2nd Stage Precipitation	3										1.0	
Washing Water	4											2.5
Spend Wash - Water	5											
		CONCENTRATION IN SOLID, % (Ag, Au - ppm)										Weight (g)
Product of 1st Stage Precipitation	6	18.80	0.04	0.72	1.04	-	0.027	9.33	-			8.60
Product of 2nd Stage Precipitation	7	31.82	0.04	0.19	0.03	-	0.016	8.67	0.05			9.05
Precipitated Product After Washing	8											
		DEGREE OF PRECIPITATION, %										
Cumulativa Degree of Elements Precipitation		32.9	0.29	0.07	11.52	-	42.5	33.37	1.0			

Calculated Concentrations in the Flow 8 (Calculated from AA analyses, mass balance considerations and assumptions):

		(%)			(%)
(6)	$FeAsO_4 \cdot 2H_2O$	28.7	(7)	$FeAsO_4 \cdot 2H_2O$	26.7
	FeOOH	18.8		FeOOH	40.3
	$PbSO_4$	1.5		$PbSO_4$	0.05

Table 4.11. Metals concentration in the Flows during the tests of precipitation by calcium oxide according to the Flowsheet in Figure 4.14. Chloride solution; temp. 90-98°C, time of precipitation 2 hr.

Specification of Flow	Flow No.	Fe	Cu	Zn	Pb	Ag	Sb	As	Ca	SO_4^{2-}	pH	Volume of Solution [l]
		CONCENTRATION IN SOLUTION, g/l (Au, Ag in mg/l)										
Solution to Precipitation Stage	1	9.71	1.71	78.4	0.56	14.06	0.006	3.39	0.3	6.85	0.4	0.7
Solution After 1st Stage Precipitation	2	7.54	1.97	90.4	0.04	15.44	<0.01	0.22	1.77		1.7	0.43
Solution After 2nd Stage Precipitation	3											
Washing Water	4											
Spend Wash - Water	5											
		CONCENTRATION IN SOLID, % (Ag, Au - ppm)										Weight (g)
Product of 1st Stage Precipitation	6	15.31	0.04	0.29	2.23		n.a.	10.19	12.88			25.75
Product of 2nd Stage Precipitation	7											
Precipitated Product After Washing	8											
		DEGREE OF PRECIPITATION, (%)										
Cumulative Degree of Element Precipitation		53	1.1	0.2	37.3		n.a.	9.6				

Calculated Concentrations in the Flow 6 (Calculated from AA analyses, mass balance considerations and assumptions):

	(%)
$FeAsO_4 \cdot 2H_2O$	34.6
FeOOH	11.0
$PbSO_4$	3.3

Table 4.12. Metals concentration in the Flows during the test of precipitation by calcium oxide carried out according to the Flowsheet in Figure 4.14. Chloride solution; temp. 90-98°C, time of precipitation 2 hr.

Specification of Flow	Flow No.	Fe	Cu	Zn	Pb	Ag	Sb	As	Ca	SO_4^{2-}	pH	Volume of Solution [l]
		CONCENTRATION IN SOLUTION, g/l (Au, Ag in mg/l)										
Solution to Precipitation Stage	1	4.86	0.86	39.2	0.28	7.03	0.003	1.70	0.15	3.43	9.8	0.8
Solution After 1st Stage Precipitation	2	2.30	1.45	60	0.13	9.50	<0.01	3.98	3.16		0.9	0.43
Solution After 2nd Stage Precipitation	3											
Washing Water	4											
Spend Wash - Water	5											
		CONCENTRATION IN SOLID, % (Ag, Au - ppm)										Sample Weight (g)
Product of 1st Stage Precipitation	6	16.22	0.065	0.14	3.16	-	0.025	12.32	<0.01			8.53g
Product of 2nd Stage Precipitation	7											
Precipitated Product After Washing	8											
		DEGREE OF PRECIPITATION, (%)										
Cumulative Degree of Element Precipitation		52.9	0.72	0.04	81.5	-	30.0	38.7				

Calculated concentration in the Flow 6 (calculated from AA analysis, mass balance considerations and assumptions):

	(%)
$FeAsO_4 \cdot 2H_2O$	37.9
FeOOH	11.2
$PbSO_4$	4.6

Table 4.13. Cumulative degree of some metals precipitation in function of pH, for different concentrations of chloride and sulfate ions.

	pH				
Final pH	0.38	0.8	1.0	1.2	1.7
	Anions Concentration (moles)				
[Cl-]	7	1.8	7	7	3.5
$[SO_4^{2-}]$	0.14	0.03	0.14111	0.14	0.07
	Cumulative degree of precipitation (%)				
As	16.8	38.7	33.5	57.7	96
Sb	25	30	42.5	100	n.a.
Fe	11.8	52.9	32.9	33	53
Pb	11.3	81.5	11.25	90.6	97.3

confirmed in this way in some samples of precipitates. In this situation any suggestions about crystallographic structures of compounds were based on the chemical analysis of these products.

The stoichiometric formulas of known complexed hydroxo-salts that could precipitate from leach solutions correspond to the following compositions of simple compounds:

Plumbojarosite:

$$\mathrm{Pb[Fe_3(SO_4)_2(OH)_6]_2} = \begin{array}{l} \mathrm{PbSO_4} \\ \mathrm{Fe_2(SO_4)3} \\ \mathrm{4Fe00H} \\ \mathrm{4H_20} \end{array}$$

$$\mathrm{Pb[Fe_{2.84}Zn_{0.3}Cu_{0.03}(SO_4)_2(OH)_6]_2} = \begin{array}{l} \mathrm{PbS0_4} \\ \mathrm{0.6\ ZnS0_4} \\ \mathrm{0.06\ CuS0_4} \\ \mathrm{0.78\ Fe_2(S0_4)_3} \\ \mathrm{4.12\ Fe00H} \\ \mathrm{\sim 2\ H_20} \end{array}$$

Arsenosiderite:

$$\mathrm{Ca_3Fe_4(As0_4)_4(OH)_6{\cdot}3H_20} = \begin{array}{l} \mathrm{2\ FeAs0_4.2H_20} \\ \mathrm{Ca_3(As0_4)_2} \\ \mathrm{2FeOOH} \\ \mathrm{3H_20} \end{array}$$

Hydronium jarosite:

$$\mathrm{H_30{\cdot}Fe_3(SO_4)_2(OH)_6} = \begin{array}{l} \mathrm{0.67\ Fe_2(S0_4)_3} \\ \mathrm{1.67\ FeOOH} \\ \mathrm{3.67\ H_20} \end{array}$$

Beudantite:

$$\mathrm{PbFe_3(As0_4)(S04)(OH)_6} = \begin{array}{l} \mathrm{FeAS0_4.2H_20} \\ \mathrm{PbS0_4} \\ \mathrm{2FeOOH} \end{array}$$

Beudantite substituted by Ca:

$$\mathrm{CaFe_3(As0_4)(S0_4)(OH)_6} = \begin{array}{l} \mathrm{FeAs0_4{\cdot}2H_20} \\ \mathrm{CaS0_4{\cdot}2H_20} \\ \mathrm{2FeOOH} \end{array}$$

Beaverite:

$$\mathrm{PbCuFe_2(S0_4)_2(OH)_6} = \begin{array}{l} \mathrm{PbSO_4} \\ \mathrm{CuS0_4} \\ \mathrm{2FeOOH} \\ \mathrm{2H_20} \end{array}$$

Plumbojarosite substituted by Zn:

$$\mathrm{Pb[Fe_3Zn_3(SO_4)_2(OH)]} = \begin{array}{l} \mathrm{PbSO_4} \\ \mathrm{3ZnS0_4} \\ \mathrm{3FeOOH} \\ \mathrm{5H_20} \end{array}$$

Crandallite:

$$\mathrm{Ca\ Fe_3(As0_4)_2(OH)_5{\cdot}H_20} = \begin{array}{l} \mathrm{1.33\ FeAs0_4.2H_20} \\ \mathrm{0.33\ Ca_3(As0_4)_2} \\ \mathrm{1.67\ FeOOH} \end{array}$$

4.5 Summary and Conclusions

1. Arsenic extraction from Delta complex sulfide ores during typical atmospheric leaching with ferric chloride solution is about 6% [4.4].

   Arsenic extraction from the same ore by low concentration ferric chloride solution (below 30g Fe/l) under 20-30 psig of oxygen pressure is about 13% after 2 hours of leaching at 70-80°C (Table 4.3), followed by 2 hours of leaching at 90-96°C. During the same time, i.e., after running the 4-hour leach, about 86% of zinc was extracted.

   Arsenic extraction to the same solution increases sharply to about 60% after 30 minutes of the activated leaching at 90-104°C, in which the catalytic action of nitric oxides and nitric acid is applied (Table 4.5). In the experiment, the concentration of this catalyst was lower than 0.1 mol NO_3/l, that corresponds to about 5g HNO_3/l. It was demonstrated that the regeneration of the catalyst is rapid during leaching conducted under elevated oxygen pressure (30 psig).

2. Simultaneous extractions of antimony, zinc, and lead ore is about 50%, 96% and 99% respectively. Rough calculations made on the basis of analytical results indicate that during this experiment about 23% of the pyritic and other refractory sulfides matrix, was decomposed. At the same time about 86% of sulfur liberated from sulfides was oxidized to elemental form and 14% to sulfates. The concentration of sulfur in the final flotable fraction was 16.1% and the concentration of sulfate ion derived from sulfide sulfur oxidation was about 14g SO_4^{2-} per liter. The sulfate concentration in the final solution does not correspond to the total amount of sulfate generated during processing. According to the mass balance calculations, about 50% of generated sulfate accumulates in solid phases. Sulfate ions cause removal of lead and calcium from the leach solution in amounts relating to the solubilities of their sulfates.

   Owing to the formation of lead sulfate, the concentration of lead in the leaching solution was controlled at the level of about 1 g/l Pb, and lead sulfate as well as crystallized lead chloride, if any, were collected in a separate fraction during fluidized bed leaching and flotation stages (Tables 4.3 through 4.8). Lead extraction from these products to high concentration chloride solution containing $CaCl_2$, $MgCl_2$ or NaCl, is fast and easy, and pure $PbCl_2$ was then crystallized from the brine. Silver did accumulate with the lead as any light crystalline or nonflotable fraction.

3. Gold extraction from the leach residues after by routine cyanide leaching was as follows:
   - from the nonflotable fraction (Table 4.8, Flow 5): 75.1%
   - from flotable fraction containing total (16.1%) generated elemental sulfur (Table 4.8, Flow 3): 66.1%;
   - from flotable fraction after elemental sulfur extraction: 77.2 ± 16.6% (average extraction from 3 analyses).

4. Arsenic oxidation in solution from arsenite ion AsO_3^{3-} to arsenate AsO_4^{3-} follows ferrous ion oxidation to ferric ion or to the products of Fe(III) hydrolysis.

5. Arsenic removal from chloride leach solutions is fast under elevated oxygen pressure by precipitation with iron as mixed hydrolysis products and ferric arsenate. Such a precipitation is accelerated by neutralizing action of fresh ore or calcium oxide. Both neutralizing agents can be applied in a nonpressure process if arsenic and iron are respectively at 5 and 3 states of oxidation (AsO_4^{-3} and Fe^{3+} ions). The degree of arsenic precipitation depends on pH and concentration of ferric ion. In this research, only rough precipitation of arsenic from the acidic solution with pH lower than 2 has been performed.

   The highest degree of the arsenic precipitation achieved during pressure fluidized bed leaching was 84% with a final arsenic concentration of 166 ppm As and pH = 1.83. The highest degree of arsenic removal by calcium oxide addition in the atmospheric pressure experiments was 97% with a final arsenic concentration of 70 ppm at pH=2.

6. Antimony behavior was different. It is difficult to conclude its precipitation or dissolution behavior in the performed leaching/precipitation experiments. However, during the experiments in which maximum of arsenic was precipitated, the concentration of antimony increased from 34 to 77 ppm.

Precipitation of antimony did not exceed 50% in any experiment where neutralization by calcium oxide was employed. Nevertheless, total precipitation of antimony was achieved by dilution of solution during washing of the precipitates (Table 4.9). During this operation antimony chloride hydrolysed to insoluble oxy-chloride:

$$SbCl_3 + H_2O = SbOCl + 2HCl$$

7. Concerning the selectivity of precipitation, generally the arsenic-iron precipitate is a very good collector for other nonferrous metals. In the concentrated chloride solution containing sulfate ions, generated during oxidative leaching of sulfide ores, a significant portion of lead and calcium are precipitated together with iron and arsenic. In this case, further leaching of lead from this precipitate is required.

Lead coprecipitation does not depend substantially on pH, but coprecipitation of copper and zinc does. However, even at high pH, copper and zinc are precipitated together with iron and arsenic. Both metals can be relatively easily withdrawn from precipitates by simple washing or repulping with acidic chloride solution. In the experiment documented in Table 4.6, initially precipitated zinc was in the next stage of processing washed from the precipitated hydrolysis products. Coprecipitation of zinc does not depend on zinc concentration in solution (Tables 4.10 - 4.13) but on pH. The degree of zinc coprecipitation with arsenic, iron and lead, from the solution containing 157g Zn/l was 0.07% at final pH=1 and 0.2% at final pH=2. The concentration of zinc in precipitates was 0.19% and 0.74% respectively in the first and second case (Tables 4.9 and 4.10). The precipitation of arsenic from about 100 ppm to several ppm requires increasing pH to about 5. However, it is not possible to avoid in this way, a simultaneous precipitation of zinc and copper. When theFe/As ratio in solution is higher than 12:1, the concentration of arsenic can be diminished to about 1 ppm. The time required for this precipitation is about 12h [4.8].

If arsenic precipitation is carried out by addition of fresh ore to the solution, coprecipitation of the hydrolysis products of zinc and copper, having higher solubility than their sulfides, can have a secondary importance, because: 1) as a rule, such a process is carried out for the purpose of solution purification; and 2) the precipitating agent, fresh ore, must then be leached and the product of precipitation will be dissolved during leaching together with all or only a part of the precipitated arsenic and iron. A portion of the lead, calcium and iron crystallized from leach solutions was retained some days at room temperature. No significant amount of arsenic was identified in these crystalline products, with the exception that a small quantity of arsenic was found in crystals crystallized from solution containing 10g As/l (Table 4.8).

8. It may be possible to avoid dissolution of iron, arsenic, lead and calcium that were precipitated by the addition of fresh ore or were precipitated during leaching under oxygen pressure by a process of leaching, precipitation and flotation in the fluidized-bed reactor. During fluidized bed leaching a portion of precipitated or crystallized particles is selectively transported with solution and separated in the fractions collected beyond the FBL-reactor (Figure 4.10). During the leaching-flotation process, the flotable fraction of leached ore is transported in froth beyond the reactor; the nonflotable fraction of precipitated and crystallized compounds remains in the suspension in the reactor and can be separated by known techniques.

9. Only the chemical composition and not crystallographic structure was calculated from the metal and sulfate concentrations in the raw material and precipitated or crystallized solids. The amounts of principal components correspond to the following chemical formulas:

   $PbSO_4$ or $PbCl_2$
   $CaSO_4 \cdot 2H_2O$
   $FeAsO_4 \cdot 2H_2O$
   $FeOOH$

   in proportions given in Tables 4.3 through 4.13.

Because the specific gravity of $PbSO_4$ and $PbCl_2$ is two to three times higher than other components, the most probable explanation for their accumulation in the light fractions is that these compounds are of low density structure of the jarosite-type, beudantite-type or another complexed ferric-hydroxo-salt. However, in several cases, and particularly in the fractions separated during the leaching flotation stage as the nonflotable fractions, lead can occur as separate crystals of $PbSO_4$ or $PbCl_2$. The $PbSO_4$ and $PbCl_2$ crystals will be retained in the FBL-reactor together with leached ore because of high specific gravity (from 5.8 to 6.8). The sulfate or lead chloride, as well as other nonflotable particles, settle from the solution and can be separated in the nonflotable fraction. Because the total concentration of lead in some nonflotable fractions is higher than those corresponding to the stoichiometry of plumbojarotite or beudantite and the calculated total iron in the fractions, a part of the lead must occur as $PbSO_4$, $PbCl_2$ or as another unidentified compound.

10. Caution is suggested in interpreting the experimental data of Tables 4.3 through 4.12. Though the accuracy of analyses of the metal concentrations in solid and solutions was good, the solid products and spent solutions were not quantitatively recovered following experiments. The described continuous installation and the manner of experimentation were not suitable for collecting data for mass balance calculations and the weight of solids and volumes of solutions presented in the tables are illustrative of the experiments scale. Difficulties in mass balance calculations did not detract from the general purpose of this research.

4.6 Supplementary Research

Supplementary Tests on the Zinc-Chloride Leaching Process

Routine leaching kinetic tests on the LP ore sample in concentrated zinc chloride solution were performed in a 1 liter glass reactor equipped with a stirrer at temperatures 21, 60, 90 and 103°C. 50g ore samples of size fraction 325-400 mesh, that contained:

Fe	30.72 %
Cu	0.28 %
Zn	6.80 %
Pb	3.52 %
Ag	87.08 ppm

were leached in 0.7 liters of a solution containing:

Fe(III): 15.2 - 20 g/l
Cu: 4.6 - 7.2 g/l
Zn: 133 - 216 g/l.

Four samples of the solution were taken for analyses during leaching. Amounts of extracted metals were balanced with their concentrations in solid residues. Because of the high zinc concentration in solution, its extraction kinetics were calculated from Zn analyses of solid residues taken at different times during the leach experiments, (30, 60, 120 and 240 minutes).

The results of 4 hour leaching tests at 90 and 103°C are as follows:

Temp.		Extraction, %			
°C	Cu	Ag	Pb	Fe	Zn
90	63	81	99	n.a.	98
103	59	72	99	13	98

The results confirm the very good leachability of metals at high $ZnCl_2$ concentration, observed in previous experiments [Chapter 3].

The average values for the apparent energies of activation, calculated from laboratory data, for the temperature region of 21 to 103°C are as follow:

Zinc Sulfide: 1.54 kcal/mol Zn
Copper Sulfide: from 4.7 to 5.01 kcal/mol Cu
Silver in Sulfidic Matrix: from 2.88 to 3.65 kcal/mol Ag.

Exceptionally low temperature dependence of zinc extraction from ore to the high concentration solution that contains 280-450g of $ZnCl_2$ per liter deserves more in depth attention. Documentation of this research has been prepared in the form of a short paper that will be published when disclosure of this material is approved by the research sponsor.

Zinc Electrolysis From Chloride Solution

A small laboratory electrolyser was designed and constructed. Some research on the stability of different anode materials was performed in this stage of the project. The electrolysis process will be carried out according to two systems of electrolyte transportation shown in a simplified sketch in Figure 4.15. In the first system the solution is transported from the cathodic to the anodic compartment through the high porosity diaphragm (~10 µm). In the second, the electrolysis process is carried out without direct solution transportation through the low porosity diaphragm (~0.2 µm). The simplified design of the manufactured electrolyser is presented in Figure 4.16. This project is seen as the future subject of an MS thesis for Mr. Wang Zhao Fang. Mr. Wang is now preparing the electrolysis system.

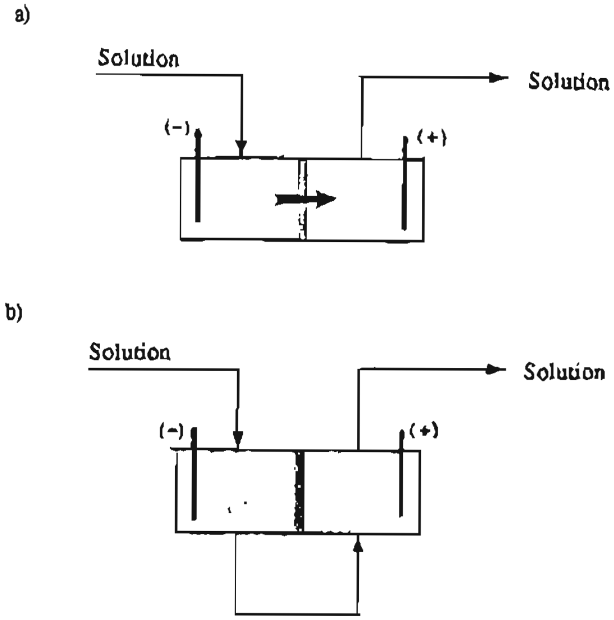


Figure 4.15. **Transport systems of the electrolytic cell:**
a) with solution transportation through high porosity diaphragm;
b) without solution transportation through low porosity diaphragm.

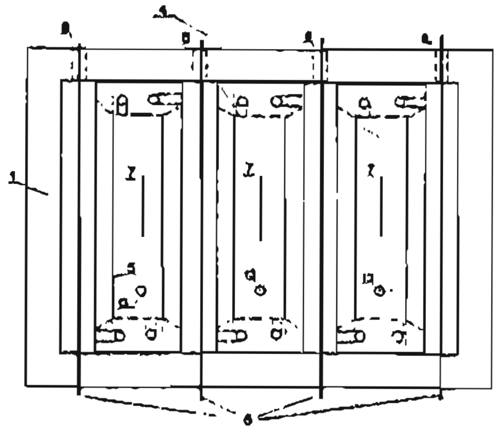
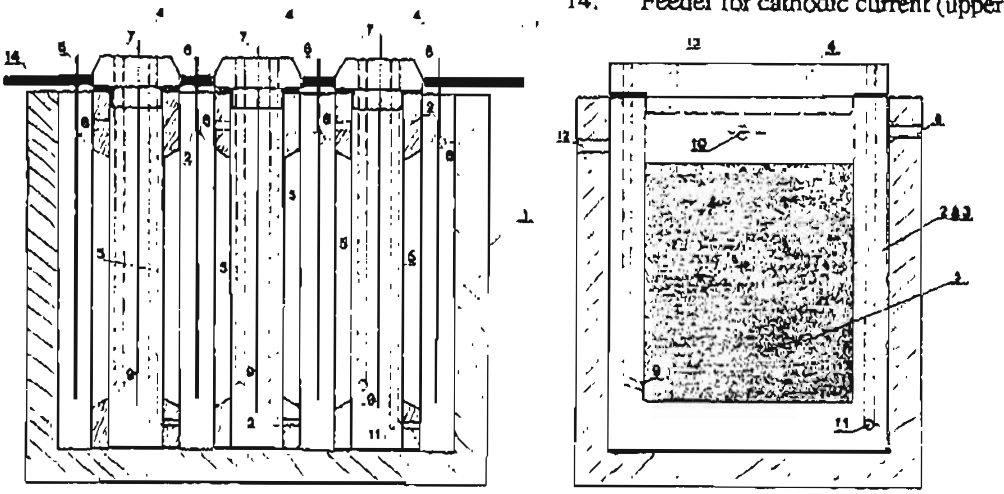


Figure 4.16. **Simplified design of the electrolytic cell with 4 cathodic and 3 anodic compartment for zinc electrowinning from chloride solution.**

1. Electrolyser casing (bath, plexiglass).
2. Diaphragm frame (polyprophylene).
3. Anodic compartment casing (polypropylene).
4. Cover of the anodic compartment (polypropylene).
5. Diaphragm (separator, polypropylene).
6. Zinc cathode.
7. Platinized titanium anode.
8. Catholyte inlet or outlet.
9. Anolyte inlet.
10. Anolyte outlet (connected with flexible pipe with 12).
11. Catholyte inlet.
12. Anolyte pipe outlet.
13. Chlorine/oxygen outlet.
14. Feeder for cathodic current (upper).



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Chapter 5

FERRIC CHLORIDE LEACHING OF THE DELTA SULFIDE ORES AND GOLD EXTRACTION FROM THE LEACHING RESIDUE

H.K. Lin and P.D. Rao

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5.1 Introduction

Conventional differential and bulk flotation processes have difficulties in achieving high recoveries with acceptable grades for zinc, lead and copper from the complex sulfide ores found at Tok, Alaska[5.1]. Furthermore, gold and silver, which account for a significant fraction of total value of the ores, are distributed evenly in the flotation tailings and concentrate. Therefore, processing both flotation tailings and concentrate would be necessary to obtain high recoveries of gold and silver.

A mineralogical study revealed that the economic sulfide minerals are interstitially associated with a large preponderance of pyrite. The economic sulfide minerals are 10 to 40 microns in size. These mineralogical facts explain the difficulties encountered in the flotation process.

A hydrometallurgical method involving ferric chloride leaching and subsequent steps to recover lead, zinc, silver and copper from the leach liquor has been studied at the Mineral Industry Research Laboratory, University of Alaska Fairbanks for the treatment of Delta ores. This alternative is attractive for processing complex sulfide ores which conventional flotation and smelting cannot handle. In addition, the liberation of sulfur in the environmentally acceptable elemental form, rather than as sulfur dioxide, may prove a major advantage of this hydrometallurgical method because of stringent environmental regulations.

As early as 1923, ferric chloride leaching was applied to one sulfide mineral[5.2] and was recognized as a highly efficient process. Chloride leaching has become more practical during the past decade, as corrosion problems of concentrated chloride solution have been partially overcome by the advent of modern materials of construction.

The United States Bureau of Mines has conducted extensive tests on ferric chloride leaching of chalcopyrite concentrates[5.3,5.4] and galena concentrates[5.5,5.6]. A hydrometallurgical test involving ferric chloride leaching of galena concentrates, purification of the resulting solution and direct electrolysis of the purified lead chloride solution was performed in the Minemet Research Laboratory[5.7].

Lucas and Shimano[5.8] have investigated two-stage ferric chloride leaching of a pyritic Zn-Pb-Cu-Ag bulk concentrate and found that more than 92% of zinc, lead, copper and silver could be extracted in 7.5 hours. The primary leaching reactions of sulfide minerals have been proposed as:

$$PbS + 2FeCl_3 = PbCl_2 + 2FeCl_2 + S^\circ \qquad (5.1)$$

$$ZnS + 2FeCl_3 = ZnCl_2 + 2FeCl_2 + S^\circ \qquad (5.2)$$

and $$CuFeS_2 + 4FeCl_3 = CuCl_2 + 5FeCl_2 + 2S^\circ \qquad (5.3)$$

Many other chloride-based hydrometallurgical processes such as: Clear, Cymet, Elken and Phelps Dodge, have been developed to treat copper or copper-zinc-lead concentrates on pilot-plant scale. But a direct ferric chloride leaching process for complex sulfide ores has yet to be developed.

The proposed chloride leaching process for the treatment of Delta complex sulfide ores is shown in Figure 5.1. In the proposed flowsheet, the ores are treated by single and two stage ferric chloride leaching to dissolve zinc, lead, copper and silver. The leach residue is treated for gold recovery while the leach liquor will be directed to lead, copper, silver and zinc recovery steps. Lead chloride will be crystallized first followed by a solvent extraction and electrolysis step to produce metallic copper. Cementation, by adding zinc powder, is then applied to the liquor to precipitate silver. Zinc production is by solvent extraction and electrolysis. The leach solution is regenerated with chlorine gas produced in the electrolysis steps. If a large amount of iron coprecipitates with silver, a hot cementation with metallic lead can be applied prior to the lead chloride crystallization step in order to precipitate both silver and copper. Zinc cementation would then be removed from the process.

The results of a study on chloride leaching and gold recovery from the leaching residue are presented in this report.

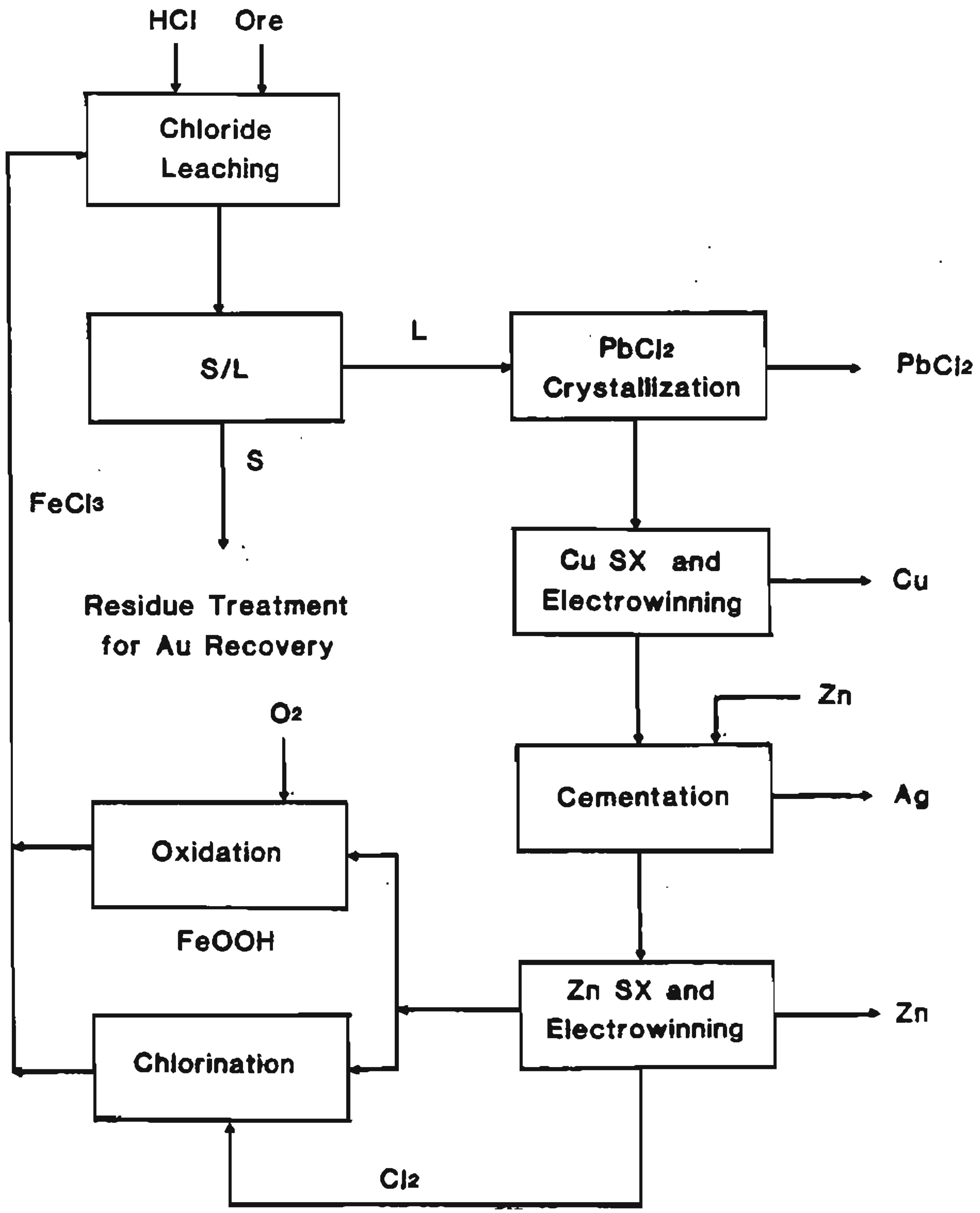

Figure 5.1. Proposed chloride leach process for treatment of Delta complex sulfide ores.

5.2 Experimental Work

5.2.1 Ores

Six samples of ore were collected from different locations in the Delta Massive sulfide deposit in 1985. These samples were named LPU, LPL, DDS, TRIO, DDN5 and DDN6. Their elemental compositions were presented in Chapter 2.

A sample of LP ore was collected in August, 1986. The sample was representative of the outcrop that was drilled and blasted a year earlier. A total of 1150 lbs of sample was brought to the laboratory. The sample was crushed in stages to 4 mesh. Further size reduction was carried out in a 8" dia x 7" ball mill. After a series of grinding tests a 7 1/2 minute grinding was selected. A 4.5 kg charge was used at 60% pulp density. About 170 kg of sample was ground in the ball mill and the product was deslimed in a 4" cyclone with a cut point at approximately 15 microns for gangue minerals. The cyclone overflow was flocculated, filtered and dried. The cyclone underflow was dried and sized using a sieve shaker down to 400 mesh. The minus 400 mesh material was further sized at 20μ sieve. These sized products were used in the leaching experiments. The concentrations of metals in various size fractions of the LP-86 ore sample are presented in Table 5.1.

The sized products were pelletized in epoxy for microscopic studies. Mineralogical composition was determined by point counting. A minimum of 1000 points were counted for each size fraction. Liberation study was conducted by grain counting of free and locked particles. Table 5.2 shows mineralogical composition of various size fractions.

Table 5.1. Concentration of Metals in the Different Sizes of LP-86 Ore.

Ore Size Mesh	Zn %	Pb %	Cu %	Au ppm	Ag ppm	Sb ppm
+30	4.90	2.96	0.20	2.10	67.3	355
200 x 270	5.10	2.84	0.19	1.70	64.2	375
325 x 400	5.90	2.76	0.21	1.90	69.1	470
400 x 20	6.80	3.52	0.28	2.10	86.8	630

Table 5.2. Mineralogical Analysis of LP-86 Ore.

	Mineral Composition Wt. %							
Size, Mesh	Sphalerite	Galena	Chalcopyrite	Tennanite	Arsenopyrite	Pyrite	Gangue Minerals	Total
70 x 100	10.6	3.6	0.8	1.3	<0.1	62.1	21.6	100.0
100 x 140	11.0	2.4	0.6	0.5	1.6	63.1	20.8	100.0
140 x 200	9.5	2.9	0.6	0.1	1.3	63.6	22.1	100.0
200 x 270	10.9	2.0	0.3	<0.1	0.6	63.6	22.6	100.0
270 x 325	11.4	2.5	0.6	0.3	0.7	68.0	16.5	100.0
325 x 400	11.3	2.4	0.6	0.7	1.1	69.9	14.0	100.0
400 x 20u	11.3	2.4	0.6	0.4	0.7	72.1	12.5	100.0

This mineralogical study revealed that pyrite comprises at least 60% by weight in every size fraction of ore particles. Sphalerite and galena are the predominant zinc and lead minerals respectively; chalcopyrite the major copper mineral and tennantite the major silver mineral. The gangue minerals consist mainly of quartz and dolomite.

Table 5.3 shows volume percent free grains of minerals as well as grains containing 2, 3, 4, or 5 minerals. Table 5.4 shows liberation of each mineral by size. It shows at 100 x 140 mesh there was no free sphalerite. At 400 x 20 µ there was only 59.6% free sphalerite. Even at 20 µ x 10 µ only 78.3% of the sphalerite is liberated. Galena is only 52% liberated even at 20 µ x 10 µ size. The only mineral that is totally liberated at 400 mesh and finer is arsenopyrite. This study shows that total liberation of valuable minerals is not possible until a 10 micron or finer is reached.

Table 5.3. Distribution of Locked and Free Grains in Ball Milled LP-86 Ore.

	Volume Percent										
	Locked grains - No. of minerals in a grain				Liberated grains						
Size, Mesh	5	4	3	2	Sphal-erite	Galena	Chalco-pyrite	Tennan-tite	Arseno-pyrite	Pyrite	Gangue Minerals
70 x 100	0.9	7.9	42.0	29.8	0.5	0.1	0	0	0	9.9	8.9
100 x 140	1.0	9.1	34.7	32.3	0	0	0.3	0	0.1	12.3	10.2
140 x 200		4.3	23.4	39.8	1.7	0.1	0	0.1	0	17.8	12.8
200 x 270	0.1	2.4	13.8	38.6	2.7	0.2	0.1	0.1	0.2	23.8	18.0
270 x 325		1.0	10.2	38.2	4.8	0.5	0.2	0.1	0.2	29.3	15.5
325 x 400		0.2	3.4	29.8	5.5	0.3	0.2	0.3	0.2	41.4	18.7
400 x 20u		0	2.8	24.1	7.4	0.6	0.4	0.1	0.5	51.6	12.5
20u x 10u		0	1.4	13.8	11.9	1.3	0.7	0.2	0.4	56.6	13.7

Table 5.4. Liberation Study of LP-86 Ore.
% Mineral Liberated in Each Size Fraction*

Size, Mesh	Sphal-erite	Galena	Chalco-pyrite	Tennan-tite	Arseno-pyrite	Pyrite	Gangue Minerals
70 x 100	4.6	5.0	0	0	0	19.3	2.6
100 x 140	0	0	50	0	9	23.6	30.8
140 x 200	11.5	6.3	0	100	0	34.1	36.6
200 x 270	24.3	18.2	33	100	50	46.0	50.8
270 x 325	39.3	35.7	33	33	40	50.6	57.4
325 x 400	44.7	21.4	33	50	25	68.1	79.6
400 x 20u	59.6	42.9	66	25	100	81.3	59.0
20u x 10u	78.3	52.0	58.3	50	100	89.0	87.5

* concentration of the minerals was determined by point count whereas concentration of free minerals was determined by grain count.

5.2.2 Leaching Procedure

Bench scale leaching tests were performed in a one-liter glass reaction vessel with a removable cover. The whole assembly consisted of a four-necked pyrex flask, a Friedrich's condenser, a sampling device and an agitator. The leach slurry in the reaction vessel was maintained at ±1°C of desired temperature in a constant temperature jar bath manufactured by Blue M Electric Company. Water is used as the medium in the bath when the desired system temperature is lower than 100°C. Prestone antifreeze is used when the temperature is greater than 100°C.

At the start of each test, lixiviant was added to the reaction vessel and was allowed to reach the thermal equilibrium within the bath. A weighed charge of the solid sample was loaded into the reaction vessel. The slurry temperature would rise as much as 2°C because of the heat evolved by the leaching reactions. However, the slurry temperature returned to the desired temperature rapidly.

At the end of each test, the slurry was filtered immediately using a vacuum filter. In a two-stage leaching test, a fresh ore sample was loaded for first stage leaching and the leach residue of first stage was used to charge the second stage. Newly prepared lixiviant was used in the second stage while the resultant leach liquor from the second stage was used as the lixiviant in the first stage.

During the test, solution samples were taken periodically from the reaction vessel. The soluble zinc, lead, copper, silver, calcium and total iron were determined by atomic absorption spectroscopy. Iron(II) concentration was determined by titration with standard $KMnO_4$ solution. Soluble sulfate concentration was gravimetrically determined with $BaCl_2$ solution. Metal values in the solid were determined by aqua regia digestion followed by atomic absorption spectroscopy. Elemental sulfur in the solid was determined using xylene dissolution complimented by evaporation.

5.2.3 Gold Dissolution Tests

Gold dissolution from the leach residue by cyanide or thiourea solution at atmospheric pressure was conducted in a reaction vessel similar to the one described above. An autoclave was used for the pressure leaching of gold. A solid/liquid ratio of 50 g/300 ml was applied to all the gold dissolution tests. Gold in solution was determined by extraction using a mixture of DIBK and Aliquat 336 followed by atomic absorption spectroscopy. Free cyanide was electrochemically determined using a pH/mV meter coupled to free cyanide and reference electrodes.

5.3 Results and Discussion

During leach tests involving the sulfide ore, solid/liquid ratio, particle size, ferric ion concentration and temperature were considered as variables. Cyanide or thiourea concentration, particle size and oxygen pressure were considered as variables in gold dissolution for the resulting chloride leach residue of the sulfide ore.

5.3.1 Leaching of Sulfide Ore

Sufficient agitation (400 rpm) for proper suspension of the slurry was applied in all tests.

(i) <u>$FeCl_3$ concentration</u> - The stoichiometric amount of $FeCl_3$ required for dissolving sphalerite, galena, chalcopyrite and pyrrhotite is approximately 0.3 mol/l based on the solid/liquid ratio of 50 g/500 ml. A larger stoichiometric amount was expected when partial dissolutions of pyrite and arsenopyrite were taken into consideration. The experimental results of lead, zinc, copper and silver leaching with ferric chloride concentrations of 0.3 mol/l to 1.0 mol/l are shown in Figures 5.2 and 5.3. Under these conditions, no significant effect of $FeCl_3$ concentration on metals extraction was observed from $FeCl_3$ concentrations higher than 0.5 mol/l. When a higher solid/liquid ratio is applied, the ferric chloride concentration would be adjusted accordingly.

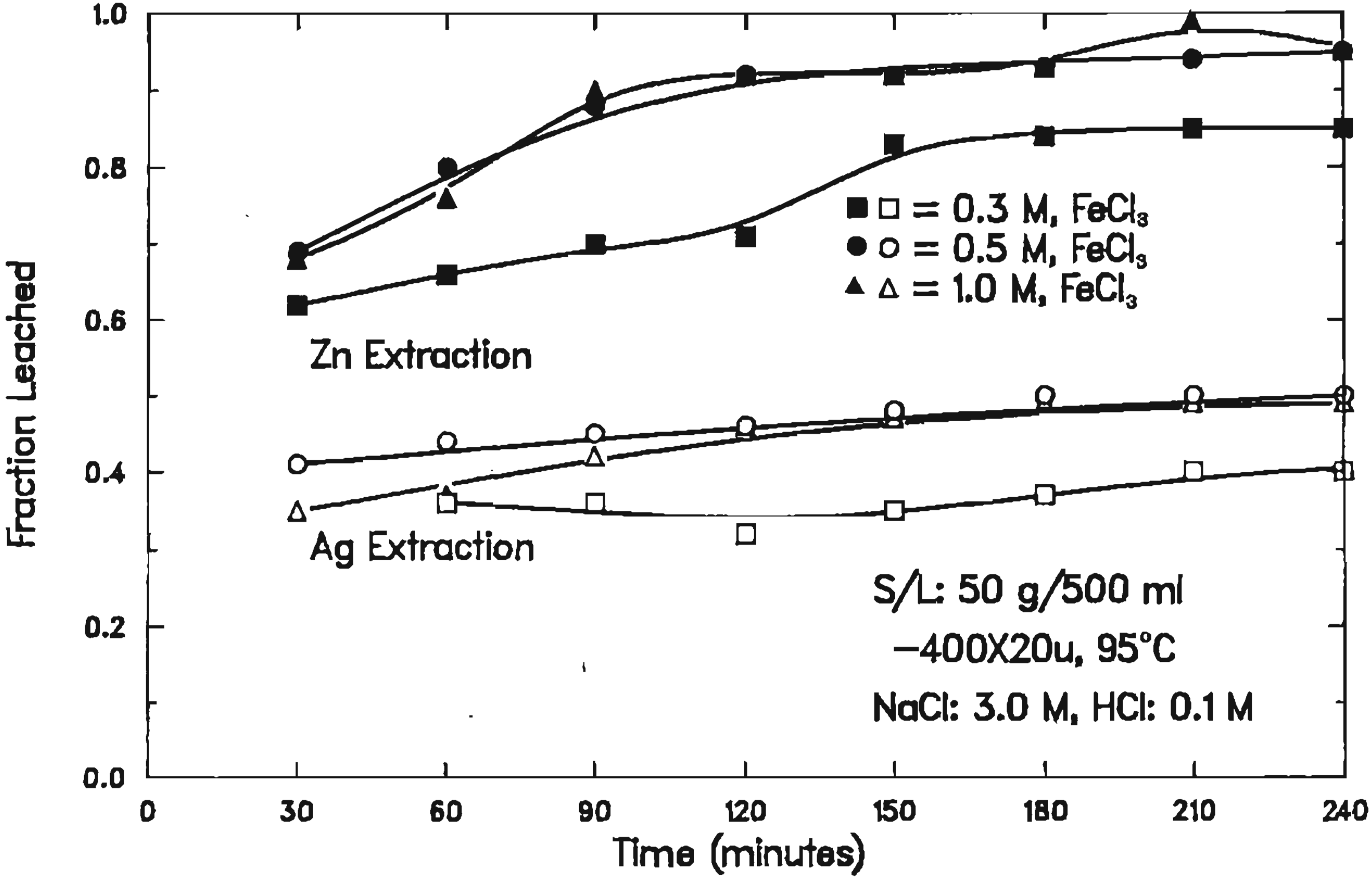

Figure 5.2. Effect of $FeC1_3$ concentration on the extraction of Zn and Ag from LP-86 ore.

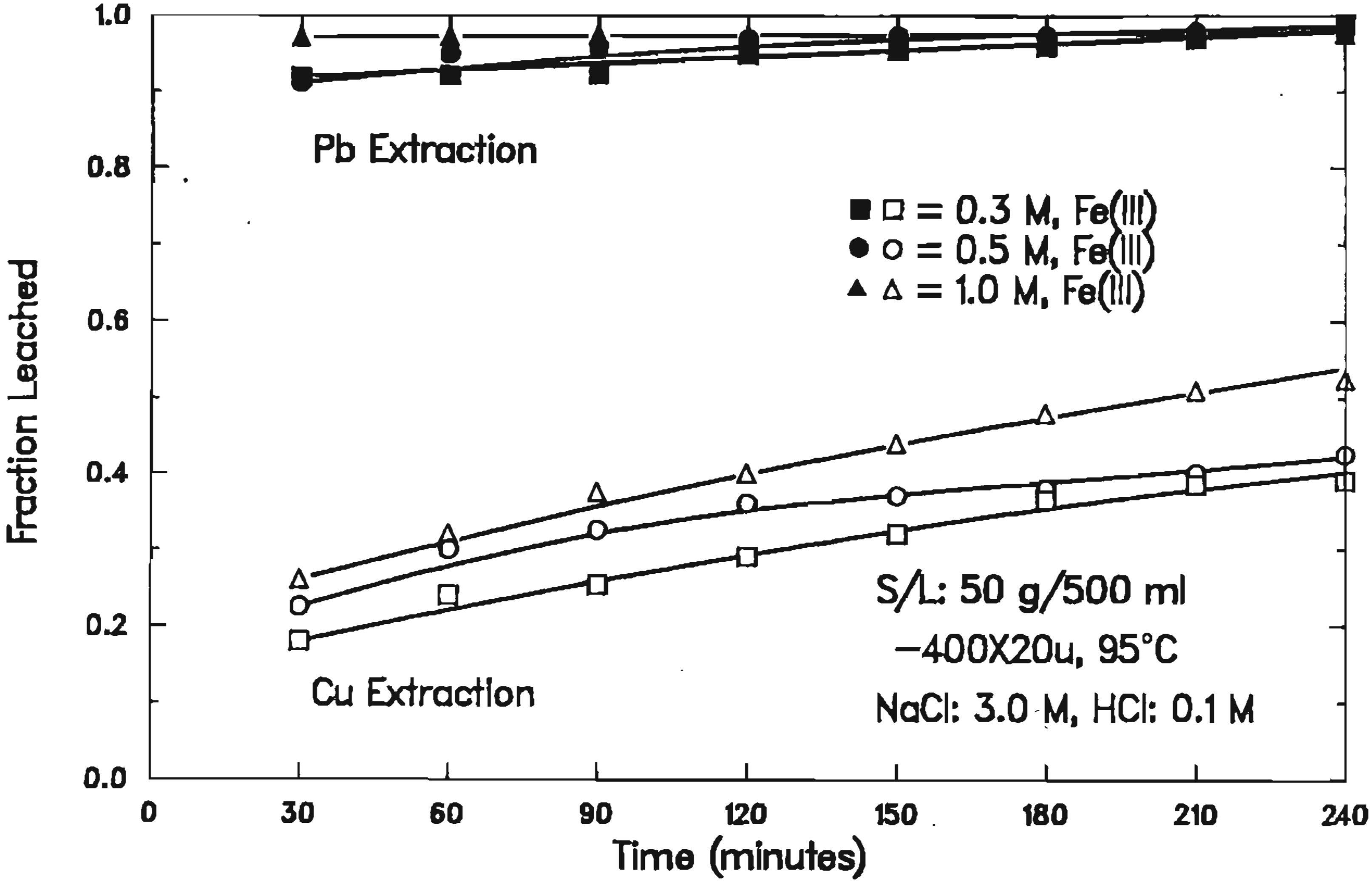

Figure 5.3. Effect of $FeCl_3$ concentration on the extraction of Pb and Cu from LP-86 ore.

(ii) Effect of solid/liquid ratio- Various solid/liquid ratios were tested while the $FeCl_3$/ore ratio was kept constant. The effect of the solid/liquid ratio on leaching at 90°C is shown in Figure 5.4. Particle interference at higher solid/liquid ratios hindered the dissolution rate of sphalerite significantly while only minor changes in the leaching rates of lead, silver and copper were observed.

(iii) Effect of particle size - To study the effect of particle size, two size fractions of the ore were leached. Figure 5.5 indicates that faster dissolution of zinc, silver and copper was observed for finer particle sizes. Dissolution of lead was too rapid to be differentiated between these two samples.

(iv) Effect of temperature- It is important to note that zinc is the most valuable component in the Delta ores and it is desirable to recover at least 90% of the zinc values. Acceptable zinc recoveries using a single-stage chloride leach do not seem attainable without very fine grinding and/or excessive retention time. Hence, two-stage leaching at 105°C was tested to improve the zinc extraction. The results, shown in Figure 5.6, indicate that at least 90% of the zinc can be extracted from LP-86 ore ground to minus 200 mesh and leached in two stages at 105°C with a solid/liquid ratio of 150 g/500 ml.

5.3.2 Silver Extraction and Microprobe Examination of its Occurrence

Silver extraction is low even in saturated NaCl solution (2 mol/l), as shown in Figure 5.7. Electron microprobe analysis was conducted for the minerals in LP-86. The results are presented in Table 5.5. They represent the average of several determinations on a single polished section. Arsenopyrite and tennantite data include the determinations made on polished sections of leach residue and subsequent cyanidation residue. Significant in these findings is that tennantite contains 0.75% silver and this mineral is unaffected during ferric chloride leaching as well as cyanidation.

Table 5.5. Electron Microprobe Analysis of Minerals in LP-86 ore.

	% by Weight								
	Zn	Pb	Cu	S	Fe	As	Sb	Ag	Total
Sphalerite	53.37	–	1.16	33.71	6.74	0.52	0.05	–	99.55
Galena	1.55	84.64	0.24	14.67	1.97	0.30	0.03	0.07	103.47
Chalcopyrite	0.31	--	34.14	34.95	29.70	--	–	0.02	99.12
Tennantite	3.39	–	41.54	27.97	5.08	15.50	5.85	0.75	100.08
Arsenopyrite	1.09	–	0.03	21.01	35.69	42.04	0.18	--	100.04
Pyrite	0.42	--	0.06	52.69	46.33	0.39	–	–	99.89
Bournonite	0.34	42.32	13.04	19.93	0.18	0.03	24.24	0.04	100.12

Oxidation of the silver-containing minerals may be needed for more rapid and complete silver extraction. Roasting the ore prior to leaching is one possibility. The ore was roasted at 750°C for 15 minutes before the leaching was conducted. About 75% of silver can be extracted in the first two hours of leaching with roasting compared to 45% of silver extraction without roasting (Figure 5.8).

Two-stage leaching was also applied to DDN-5 and TRIO ore samples. The results shown in Figures 5.9 and 5.10 indicate that zinc and lead extraction is greater than 90% for both samples while silver extraction is low on the TRIO ore sample.

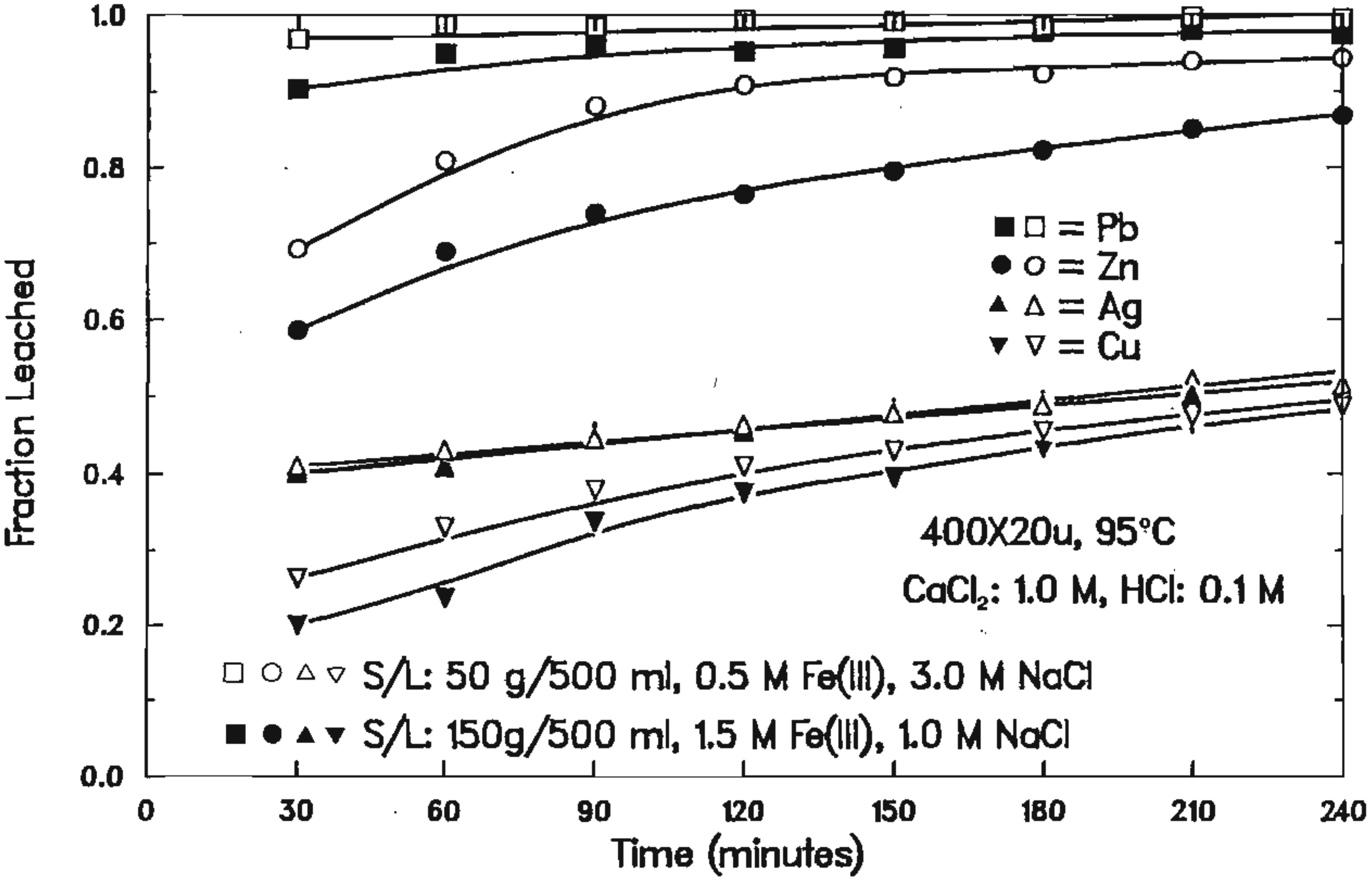

Figure 5.4. Effect of solid/liquid ratio on metal extraction of LP-86 ore.

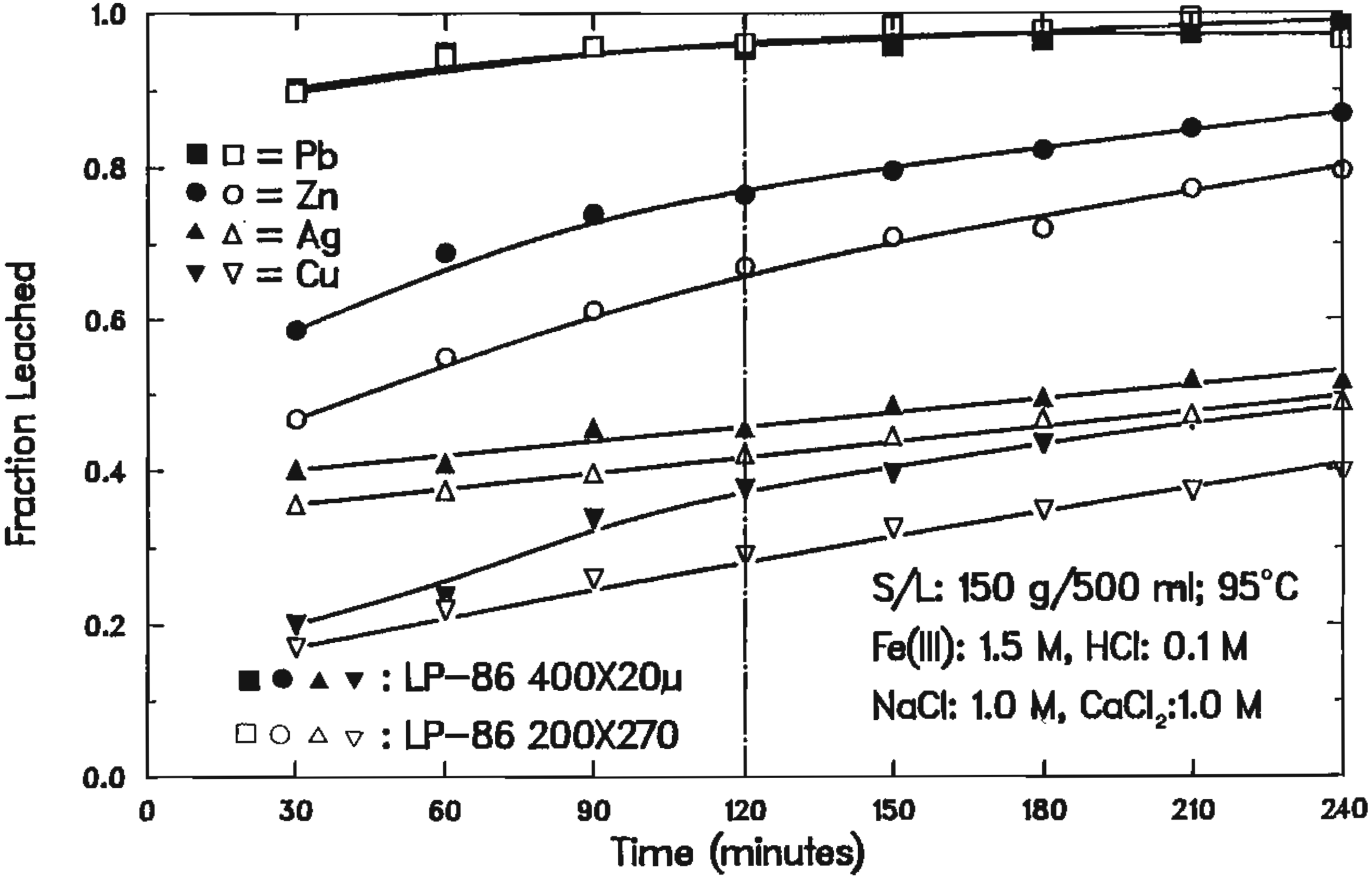

Figure 5.5. Effect of particle size on metal extraction of LP-86 ore.

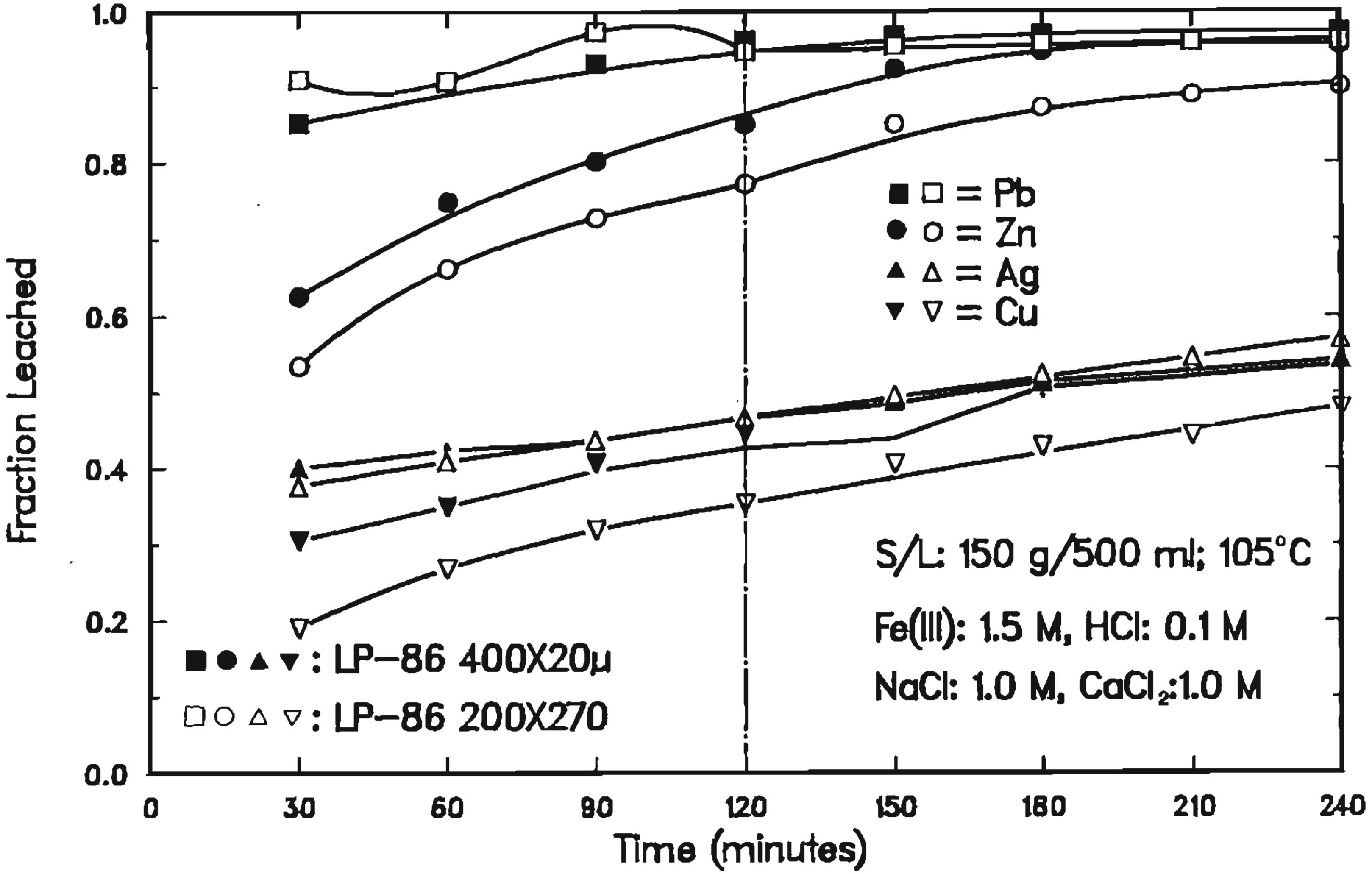

Figure 5.6. Metal extraction by two-stage leaching at 105∞C.

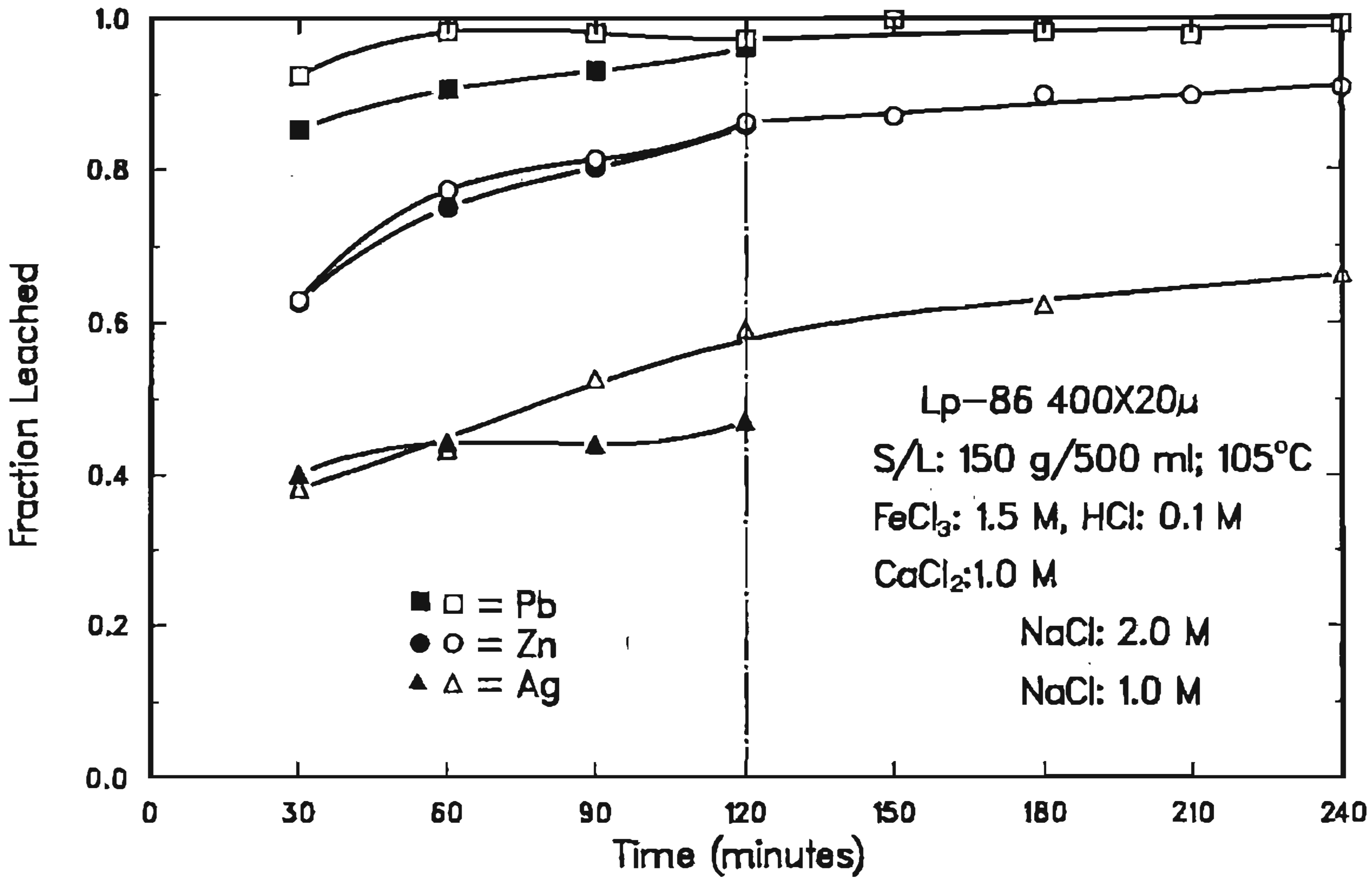

Figure 5.7. Effect of NaC1 concentration on metal extraction of LP-86 ore.

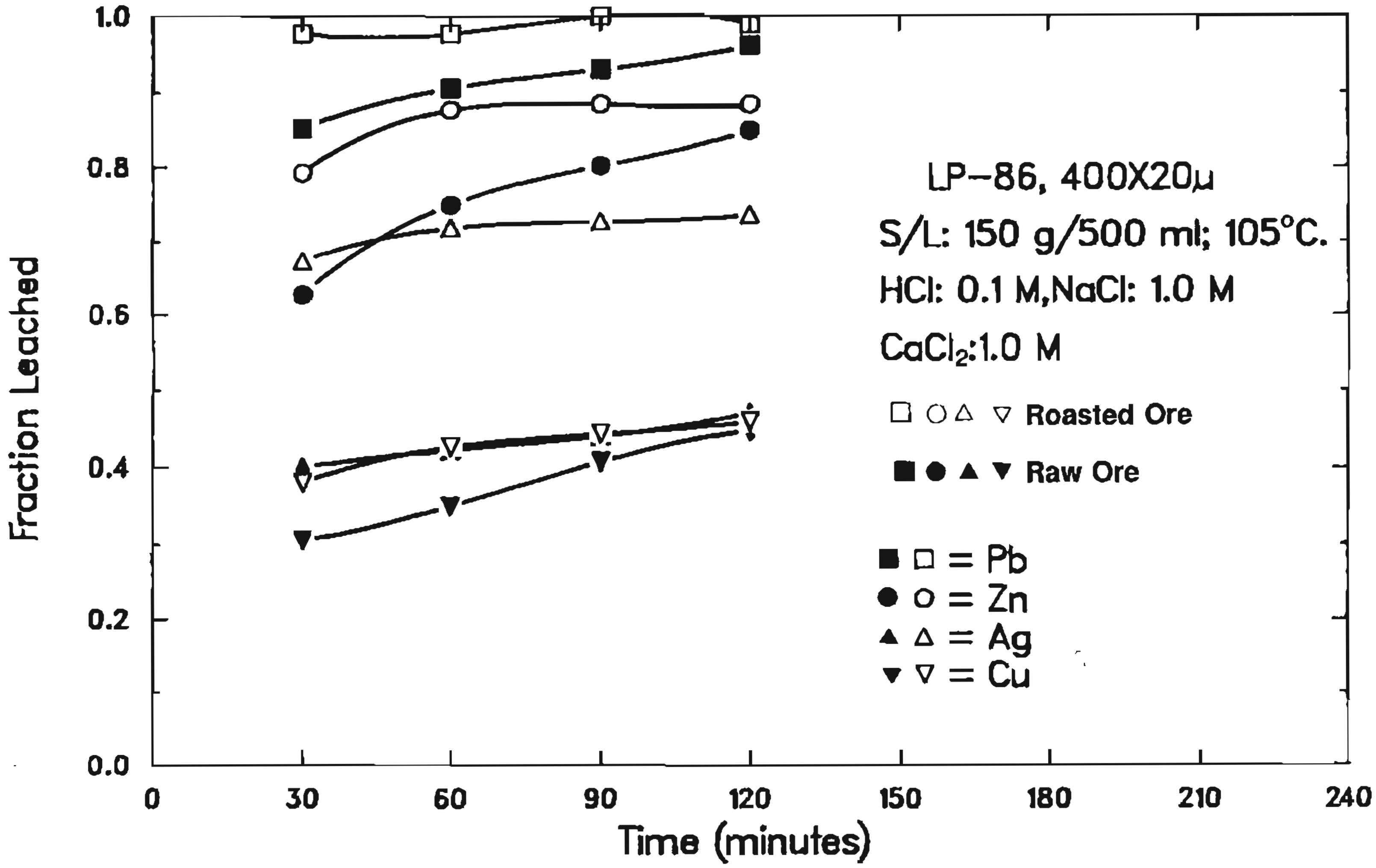

Figure 5.8. Comparison of metal extractions with and without roasting.

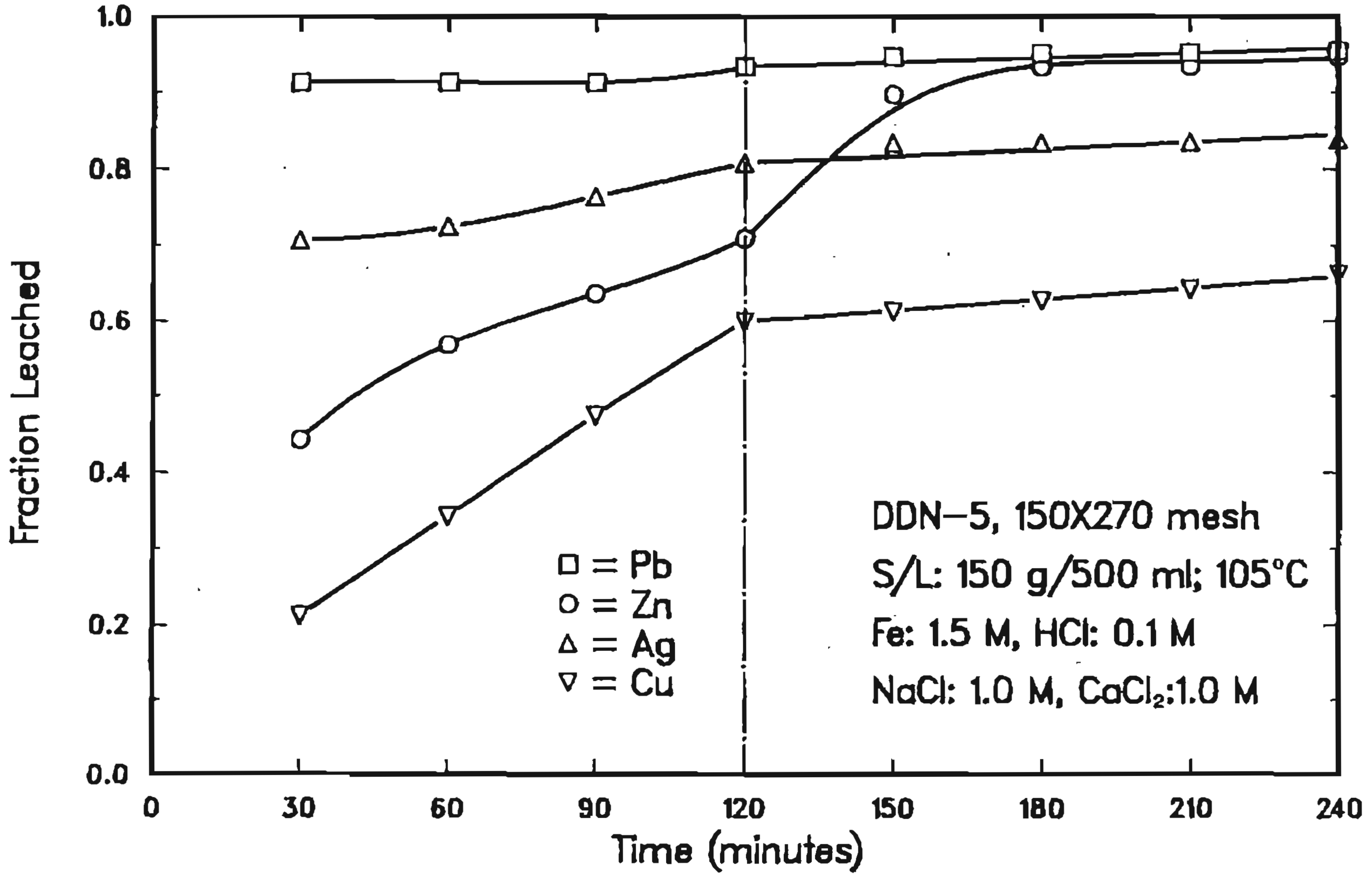

Figure 5.9. Metal extraction of DDN-5 ore.

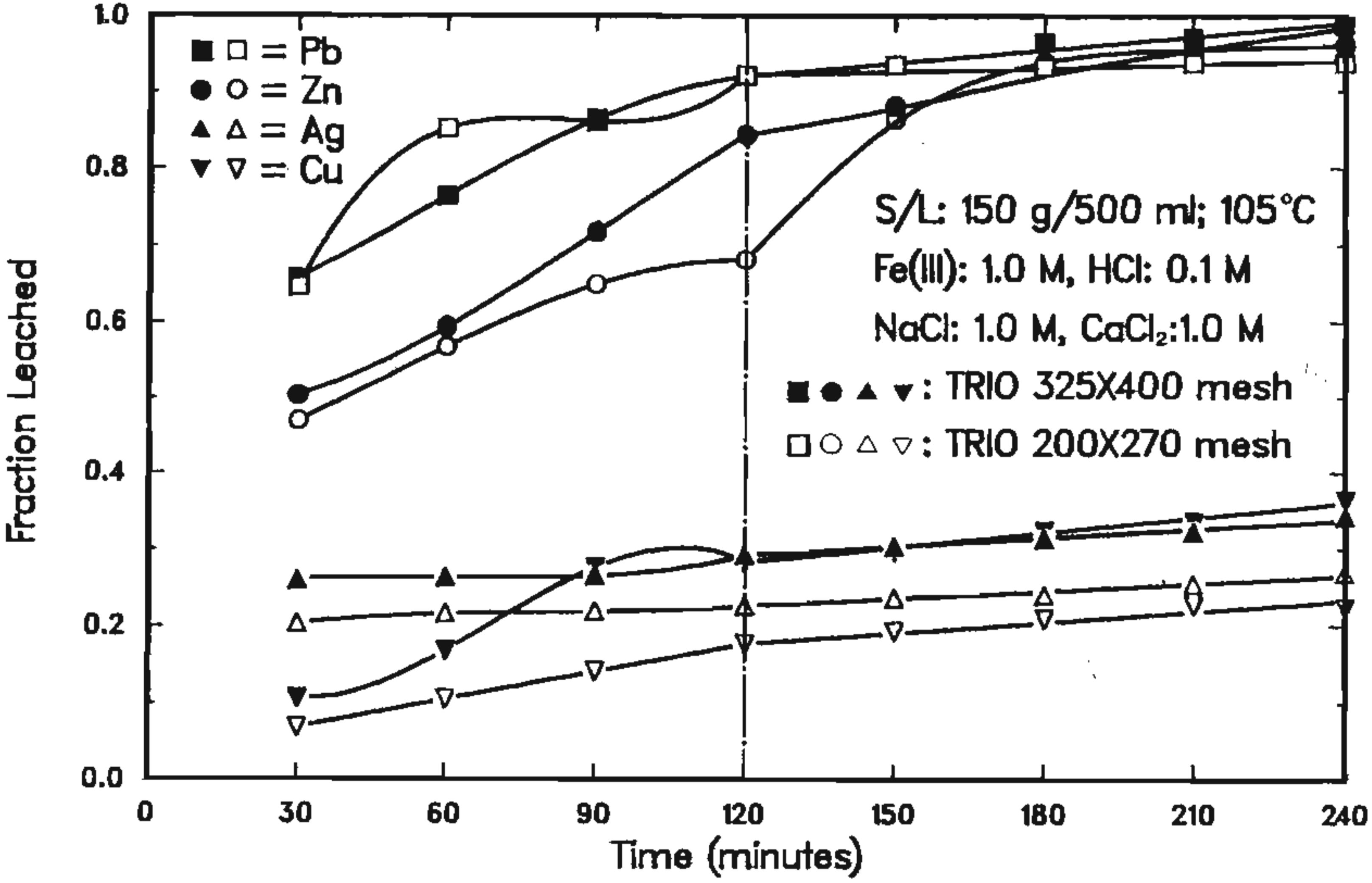

Figure 5.10. Metal extraction of TRIO ore.

5.3.3 Gold Dissolution Tests

The results of gold dissolution tests are listed in Table 5.6. All gold dissolution tests but one (test #1) were conducted using the $FeCl_3$ leaching residue as the solid feed. The high sulfide content in the ore might make direct cyanidation very difficult (test #1). Higher gold extraction can be obtained using higher cyanide and oxygen concentrations (tests #3, 4 and 5).

Increase in chloride leaching temperature to 105°C improved gold extraction in the cyanidation to 64% at 24 hours (test #5). Elemental sulfur extraction from the chloride leaching residue prior to cyanidation could not improve gold extraction (tests #5 and 6) under these conditions tested. Roasting of the ore at 750°C for 15 minutes prior to the chloride leaching was able to increase gold extraction to 71% (test #7) while thiourea leaching (test #8) and cyanidation under high pressure (test #9) did not have positive effects on gold extraction. No significant increase in gold extraction was observed on increasing the retention time beyond 24 hours.

Free cyanide measurements of the end solution of tests #3 - 7 and #9 indicated that at least 30% of total cyanide was unreacted and remained free in the solution. The lower gold extraction, hence, cannot be attributed to the insufficiency of the reactant species.

Table 5.6. Experimental Results of Gold Dissolution Tests.

Solid Feed		Leaching Conditions	Au Dissolution Conditions	Percent Au	Reacted Ag
1)	LP-86 400x20u		NaCN: 0.015% CaO: 0.020%	30 (18Hrs)	2
2)	LP-86 400x20u with leaching	95°C 4Hrs	"	31 (24Hrs)	10
3)	"	95°C 8Hrs	NaCN: 1g/l, NaOH: 2g/l Air Bubbling	53 (24Hrs) 47 (48Hrs)	25
4)	"	95°C 4Hrs	"	51 (24Hrs) 58 (48Hrs) 60 (72Hrs)	
5)	"	105°C 4Hrs	"	64 (24Hrs) 65 (47Hrs)	17
6)	LP-86 400x20u with leaching & S extraction	"	"	63 (48Hrs)	10
7)	Roasting&leaching of LP-86 400x20u	"	"	71 (16Hrs) 71 (24Hrs)	9
8)	LP-86 400x20u	"	Fe^{3+}: 2g/l H_2SO_4: 2g/l Thiourea: 2g/l	50 (24Hrs)	10
9)	"	"	NaCN: 1g/l NaOH: 2g/l O_2: 150 psi	57 (18Hrs) 58 (24Hrs)	

An experiment was designed to test the readsorption of the dissolved gold by carbonaceous matters in leaching residue. A volume of 300 ml aurocyanide solution containing 0.30 ppm gold was purged by nitrogen gas for 30 minutes before 50 gm of chloride leaching residue was charged to the solution. The solution was agitated and nitrogen purging was continued. Gold analysis of the solution samples taken at 2, 4 and 6 hours showed no significant change of gold concentration in the solution. Therefore, the possibility of readsorption of gold by the carbonaceous matter in the leach residue was excluded.

Dissemination of very fine gold grains in the pyrite grains was suspected to be the factor which caused the low gold extraction. A microprobe was used to examine the ore and residue for the occurrence of gold. Unfortunately, gold could not be detected in the ore or the leach residue because of its low concentration.

5.4 Summary

Over 95% of lead and 90% of zinc were extracted by a two-stage chloride leach of LP-86, TRIO and DDN-5 ore samples. The two-stage leach had a retention time of 4 hours, a temperature of 105°C, and used minus 200 mesh ore. Silver and copper extractions were below 60% for LP-86 and TRIO ore samples. 85% and 65% extractions for silver and copper respectively were achieved for DDN-5 ore sample. The difficulties with silver and copper extractions are probably attributable to their mineralogical occurrence.

About 64% gold extraction was obtained by conventional cyanidation of the chloride leach residue of LP-86 ore. Roasting the ore prior to the chloride leaching could increase the extractions of gold and silver drastically but roasting itself generates SO_2 and causes environmental problems.

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Chapter 6

ENGINEERING STUDY OF FAST HYDROMETALLURGICAL PROCESSES

F. Letowski

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ABSTRACT

The engineering research on fast hydrometallurgical processes is proposed to conduct at University of Alaska Fairbanks. The domain of the research is development of a new generation, 3-phase (liquid-solid-gas) continuous reactors and its application in following processes: (1) Thermal activation of refractory minerals by thermal shock and quasi-instantaneous leaching; (2) Leaching and leaching/flotation processes conducted under oxygen pressure; and (3) Precipitation of metals or lower valency metal oxides from aqueous solution under hydrogen pressure. The following systems will be tested: chalcopyrite decomposition and sulfate leaching (1); sulfide complex ore leaching/flotation in sulfate solution (2); and copper precipitation from sulfate solution (3). Advanced actually topics (2) and (3) will be carried out in a continuous pilot mini-plant.

6.1 General Introduction

A number of different possibilities of extractive metallurgy is connected both with development of high temperature technologies and their application in pyrometallurgical processes and in chemical metallurgy processes as well as with developments of low temperature technologies and their application in leaching processes, solvent extraction, ionic exchange or ionic flotation processes and all scale of electrochemical processes.

These processes are successfully incorporated into technologies of rare metals production. However, regardless of the extremely important contribution of titanium, tungsten, uranium and other rare metals to our modern way of life and technology, their production volume is relatively small and does not compare with other more common nonferrous metals. The application of the above processes to large production of copper, zinc, lead or nickel from its sulfide concentrates are acceptable if conditions of economy and environmental protection will be filled.

High capital costs and high sulfur emission characterize the pyrometallurgical smelting processes. Low capital costs characterize hydrometallurgical processes based on heap leaching or "in situ" leaching. Nevertheless, because of relatively low metals recovery, their application is limited to low grade ores. These processes can operate in technically undeveloped regions, but carry some risks of contamination of the aquatic systems and cannot operate successfully under the arctic climatic conditions.

At the same time certain hydrometallurgical technologies require a pyrometallurgical preparation of the raw material for leaching. Unfortunately there are important disadvantages of such expanded hydrometallurgy: long time of roasting with difficult to avoid emission of sulfur dioxide in oxidative conditions or with high heat consumption in endothermic nonoxidative conditions. Eventual commercial success can be expected from "pure" hydrometallurgical processes conducted under elevated pressure of gaseous reagents, which apply compact installations and operate with small volume of circulating leach solutions.

In such processes traditional barriers between mineral processing and metallurgy should disappear, the sulfur dioxide emission must be replaced with the generation of elemental sulfur and the fast, low energy processes should be introduced to the final metal winning stage.

The following research topics are proposed for development at the University of Alaska Fairbanks:

1. Thermal activation of refractory minerals of the non-ferrous metals by thermal shock and quasi-instantaneous leaching, as an alternative route to the pressure leaching techniques.

2. Ore leaching processes conducted under elevated pressure of oxygen, which can considerably simplify or completely by pass some steps of minerals valorisation.

3. Continuous precipitation of metals (copper, nickel, cobalt and precious metals) or lower oxides of metals (uranium, molybdenum, tungsten, vanadium) from aqueous solutions under hydrogen pressure, as an alternative process to electrowinning and other chemical precipitation techniques.

A large accumulation of basic information is accessible in the scientific literature which makes it possible to omit some physico-chemical laboratory research and focus our attention on engineering problems and apparatus design. The project concerns research on a new generation of three phase (liquid- solid-gaseous) reactors for hydrometallurgical processes and their particular application in each of the above proposed topics. The same concept of the continuous reactor with similar hydrodynamics problems for resolving is proposed for quasi-instantaneous leaching with "thermal activation", as for leaching or leaching/flotation process conducted under elevated pressure of oxygen and for metals or their "lower valency" oxides precipitation from leach solutions. In the 1st proposed application of the reactor, the suspension of fine solid particles in gas is injected through a high temperature zone directly to the leach solution. In the 2nd the liquid/solid/gas mixture is injected under elevated pressure to the leach solution. In the 3rd proposed application of the reactor, only liquid/gas mixture is injected under high pressure to the solution.

The most advanced engineering studies have been carried out recently by the author on the reactor application to copper precipitation under hydrogen pressure and the most detailed is the 3rd research topic described in Section 6.4 of the proposal. The continuous process of copper precipitation by hydrogen is being investigated in the laboratory by other authors, too.

Only a conceptual engineering outline of the activation of refractory sulfides is presented in Section 6.2. No publication about such a process is known and no laboratory research was carried out by the author.

Application of the proposed reactor to the leaching/flotation process conducted under elevated pressure of oxygen described in Section 6.3 seems to be nearest to the commercial solution. The research on such processing of complex sulfide ores has been carried on since 1985 in the Mineral Industry Research Laboratory of the University of Alaska Fairbanks for the Nerco Minerals Company, Alaska.

The development of rapid leaching processes conducted under oxygen pressure which are promising in arctic climate conditions was recently proposed as one of the research topics of the project "Engineering Center of Arctic Resource Development" submitted by the University of Alaska Fairbanks to the National Science Foundation in September, 1986.

Alaska has enormous mineral resources and the University of Alaska Fairbanks has a good, established program covering Alaskan needs in geological engineering, mining engineering and mineral process engineering. However, it is not enough to merely discover and classify the mineral deposits and then to keep them as a reserve for the future. It is also not sufficient to develop the mining and mineral preparation techniques to produce initially enriched raw materials and to prepare them only for exportation. Extractive metallurgy is the missing link for domestic recovery of metals from Alaskan mineral resources and among different possibilities the fast hydrometallurgical processes will probably be the most applicable to climatic conditions in the arctic undeveloped regions. Just for this reason, the research on the fast hydrometallurgical engineering techniques is proposed here. Nevertheless, not every result of laboratory research can be transformed at once into viable technology. Therefore the importance of the engineering research becomes one of the decisive factors in its successful development to a commercial scale.

6.2 Thermal Activation of Refractory Minerals

6.2.1 Introduction

Many important metals are extremely difficult to produce because of low concentration, high degree of dispersion and chemical properties of their compounds in the ore. These metals are usually inaccessible by the pyrometallurgical route, and difficult to extract by a simple leaching.

This is the case with some important basic non-ferrous metals which are often recovered from difficult-to-dissolve compounds. For instance, nickel from millerite (NiS) or serpentinite ($FeO \cdot NiO \cdot MgO \cdot 3SiO_2$), copper from chalcopyrite ($CuFeS_2$), molybdenum from molybdenite (MoS_2) or perovskite ($CaMoO_4$), chromium from chromite ($FeO \cdot Cr_2O_3$) or titanium from ilmenite ($FeTiO_3$).

Many high value metals like gold, silver, platinum group metals or uranium have little chance to come into contact with leach solution because of their dispersion in nonsoluble or difficult-to-dissolve rock-matrix as pyrite (FeS_2), chalcopyrite, arsenopyrite (FeAsS), quartz or aluminosilicates.

When direct leaching of the ore or concentrate is ineffective, a thermal pretreatment of the raw material can be applied. The purpose of such "thermal activation" is to change hardly soluble metals compounds into easily soluble forms.

6.2.2 Theoretical Background

Many established processes based on "thermal activation" before leaching are actually applied in industry [6.1]. Long ago the roasting processes were used to decompose sulfidic, silicate, carbonate and other minerals prior to leaching. But there is an important disadvantage to the roast processes: environmental pollution by large volume of gases containing sulfur, arsenic, antimony or mercury compounds and high cost of containment. Different kinds of roasting can be applied before leaching. For instance:

- zinc sulfide oxidative roasting

$$ZnS + \begin{bmatrix} 3/2O_2 \\ 2O_2 \end{bmatrix} \xrightarrow{\underline{900\text{-}950^\circ C}} \begin{bmatrix} ZnO \\ ZnSO_4 \end{bmatrix} + SO_2$$

  followed by leaching with sulfuric acid and electrolysis. The roasting can be conducted in old-type multi-hearth roasters, drum roasters, flash roasters [6.1] and modern fluidized bed roasters [6.2,6.3]. Roasting can take from several minutes in the fluidized bed roasters to several hours in the older-type roasters;

- thermal oxidative decomposition of chalcopyrite sprayed with spent electrolyte in fluidized bed roaster and then sulfate leaching and electrolysis [6.4];

- oxidative, selective roasting of arsenical gold ores conducted to facilitate gold recovery by cyanide leaching, which is used in gold mining industry for many years [6.5,6.6];

- reductive roasting of nickel-containing serpentinite ores:

$$FeO{\cdot}NiO{\cdot}MgO{\cdot}3SiO_2 + CO + H_2 \xrightarrow{750^\circ C} Fe + Ni + MgO + CO_2 + 3SiO_2 + H_2O$$

  before ammoniacal oxidative leaching for the nickel extraction [6.7];

- chlorinating roasting with soluble chlorides ($CaCl_2$, NaCl, etc), volatilization of volatile chlorides of non-ferrous metals followed by selective leaching [6.8] or direct leaching of the roasted ore as in the case of uranium and vanadium recovery from carnotite ores [6.9].

Several research programs on the improvement of the "thermal activation" processes have been conducted during the last few years. In general the programs were carried out in response to legislative restrictions introduced in many countries to deal with environmental pollution caused during roasting and smelting. They are: oxidative roasting of chalcopyrite with transformation of the sulfide sulfur into soluble in water sulfates, as Dowa Min. Co. process, CSIRO (Australia) process, Anaconda-Treadwell process and other described by Subramanian and Jennings [6.10], oxidative roasting of arsenopyritic concentrates conducted for the arsenic, antimony and sulfur recovery [6.11] or platinum group metals and gold recovery [6.12], sulfatizing roasting of refractory uranium ores in an atmosphere containing SO_3 [6.13] and other [6.14-6.16].

The most likely profitable processes are the "thermal activation" processes of the chalcopyrite concentrates enacted in nonoxidative conditions and below the melting point of sulfides which lead to the decomposition of chalcopyrite or cubanite ($CuFe_2S_3$) into simple or easy to dissolve sulfides [6.10,6.17-6.21]. But the cost of such endothermic processes conducted in the conventional roasters presents a serious economic limitation.

In the Sherritt-Cominco process [6.14], thermal decomposition of chalcopyrite consists of the exothermic oxidation in the upper part of the furnace:

$$5CuFeS_2 + 2O_2 \longrightarrow Cu_5FeS_4 + 4FeS + 2SO_2$$

and then of endothermic reduction in the lower part:

$$5CuFeS_2 + 2H_2 \longrightarrow Cu_5FeS_4 + 4FeS + 2H_2S$$

The two gases are collected and conducted to the catalytic Claus' process:

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

The solid residue is treated in leaching steps:

- in the 1st, the bulk of the iron is removed as follows:

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$

- in the 2nd step, referred to as the "activation leach", the iron in the bornite is removed by leaching with copper sulfate solution from the next (3rd) step:

$$Cu_5FeS_4 + CuSO_4 = 2Cu_2S + 2CuS + FeSO_4$$

- in the 3rd, referred as the "oxidation leach", copper sulfides are dissolved in H_2SO_4 and $CuSO_4$ solution in the presence of oxygen:

$$Cu_2S + H_2SO_4 + 1/2\ O_2 = CuSO_4 + CuS + H_2O$$

$$CuS + H_2SO_4 + 1/2\ O_2 = CuSO_4 + S^\circ + H_2O$$

Copper is deposited by electrolysis. Ferrous sulfate solution had to be subjected to crystallization and the crystals obtained are decomposed for the recovery of Fe_2O_3 and SO_2.

Another proposition, also concerning the treatment of chalcopyrite [6.15] consists of five stages:

1) Thermal activation of chalcopyrite

$$2CuFeS_2 = Cu_2S + 2FeS + S$$

2) Reductive leaching of iron by hydrochloric acid

$$2FeS + 4HCl = 2FeCl_2 + 2H_2S$$

3) Oxidative conversion

$$Cu_2S + O_2 = 2Cu + SO_2$$

4) Catalytic Claus process

$$SO_2 + 2H_2S = 3S + 2H_2O$$

5) Chloride oxidation - "pyrohydrolysis"

$$2FeCl_2 + 1/2\ O_2 + 2H_2O = Fe_2O_3 + 4HCl$$

Many rare metals occur in nature as nearly insoluble compounds. For instance, zirconium in silicate $ZrSiO_4$, berylium in aluminosilicate $3BeO{\cdot}Al_2O_3{\cdot}6SiO_2$, tungsten in wolframite $FeWO_4$ or sheelite $CaWO_4$, tantalum and niobium in tantalite $(Fe,Mn)(TaO_3)_2$ or columbite $(Fe,Mn)(NbO_3)_2$, and other. For their transformation into compounds soluble in water or in fused salts the roasting, the alkaline fusion with hydroxides or carbonates or with fluorides and fluorosilicates is applied in industry [6.22].

As yet the "thermal activation" is not generally recognized as a viable alternative that can be applied for the metal recovery from sulfide minerals. The "thermal activation" processes are too costly and environmental protection against contamination by SO_2 is very difficult. The length of time of the processing is the most negative parameter. The most difficult to control are the oxidative roasting processes. In the sulfate roast process [6.16], concentration of sulfur dioxide in spent gases is from 4 to 6% and residence time of solids in experimental fluidized bed reactor is about 3 hours. In the Sherritt-Cominco oxidative/reductive roaster [6.14] the control of the temperature distribution in the reactor is most difficult. The retention time of concentrate in the reactor is about 1.5 h.

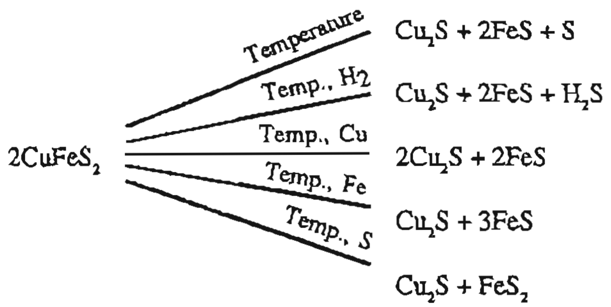
6.2.3 Description of Proposed Research

Research on "activation" of refractory sulfides by the thermal shock and instantaneous leaching is proposed to be developed at University of Alaska Fairbanks.

An idea of the thermal shock used to slacken the refractory structure of solids only, or with followed dissociation of refractory compounds, or their decomposition and formation of new phases in oxidative, reductive or inert conditions is not new [6.23-6.24]. Nevertheless many of such fast reactions have a reversible character in steady state conditions. To "freeze" a transistory structure or to direct the reaction equilibrium to the right side, a fast (instantaneous) alteration of parameters or introduction of some gaseous or liquid reagents is necessary. A leaching process in which a dispersed solid raw material is injected through a high temperature zone to a leach solution, is proposed for the refractory sulfides decomposition.

The high temperature zone can be generated in different ways according to the properties of raw material. It could be an electromagnetically induced thermal plasma, a high voltage spark, a high current arc, a corona, or a glow- type discharge, a high frequency oscillations or a laser beam.

One of the most important, hard to dissolve sulfides is obviously chalcopyrite. Its thermal activation below the melting point leads to different products as a function of additives:



The thermal decomposition can be more complicated, of course, and a wider spectrum of different compounds can be expected in reaction products [6.21]. At the same time the "thermal activation" of solids can be accompanied by activation of hydrogen, sulfur or another reagent used with raw material. It is known for instance, that very stable hydrogen molecules can be "excited" by high voltage discharge or can be dissociated into ionic forms in the plasma state, thus strongly increasing their reactivity.

The life-time of the thermally activated species is very short. In this case it will probably be important that raw material be contacted with the high temperature zone just before being injected into to the leach solution.

6.2.4 Expected Advantages

The following advantages of such an activation technique are expected:

- short time of contact with the high temperature (2,000 - 10,000°C) zone expressed in seconds, replaces long heating (minutes to several hours) in classical roasters;
- instantaneous contact of raw material with aqueous solution in high temperature forms the conditions like effective pressure leaching with good heat recovery;
- kinetic energy of the raw material injection, makes good hydrodynamic conditions (mixing);
- possibility of operating at elevated pressure allows for the design of a continuous, compact, three phase (liquid-solid-gaseous) reactor, proposed in the next two research topics;
- compact joint of high temperature generator with leaching reactor eliminates environmental contamination that characterizes classical roasting processes;
- possible application for any other thermal activation processes, as well as for precious metals and elemental sulfur recovery from pyrite ores.

6.3 Ore Leaching Processes Under Elevated Pressure of Oxygen

6.3.1 Introduction

Several research programs on the "pure" hydrometallurgical processing of nonferrous metals flotation concentrates have been initiated during the past 20 years. In the early 1980's the results of research into this type of technology have not been encouraging due to the high capital and operating cost of hydrometallurgical processes. Several chloride copper winning processes, such as the Cymet [6.25] Duval [6.26,6.27], Elkem [6.28], Minemet [6.29], Tecnicas Reunidas [6.30] and other new copper winning processes such as the nitric-sulfuric-leach process [6.31], Anaconda-Arbiter [6.32] and Parker-Murir [6.33] processes were discontinued after pilot plant studies, chiefly because of economic considerations, less frequently because of technical reasons. The greater part of these processes were then proposed or tested in pilot-plant for complex-sulfide-concentrates (Zn-Pb-Fe-Cu) processing [6.27-6.30,6.34-6.36].

Some published opinions indicate that the level of energy consumption is higher for hydrometallurgical than for pyrometallurgical processes [6.37,6.38]. These analyses pertain to the conversion of copper concentrate to refined copper cathodes, and the energy balance was compared between existing smelting technologies and several hydrometallurgical processes that with one exception (Roast-Leach-Electrowin Process) [6.4,6.39] were at the experimental stage of development.

The chief reason for misjudging the potential of hydrometallurgy falls under two tactic assumptions:

1) that the flotation concentrate produced for smelters and saleable on the open market is also most suitable as a feed material for leaching, and

2) that electrolytic winning of copper is, at present, the best final process for extracting copper from solution.

All the processes mentioned above [6.25-6.34] use the concentrates suitable for pyrometallurgical processes as feed material , despite the fact that requirements for leaching are not as precise as for smelting. Only two of the above processes [6.25,6.33], do not use electrolytic copper deposition. The flotation consumes about 20% and electrolysis about 20-40% of the total energy used in copper production. It is evident that hydrometallurgy associated with such expensive procedure cannot be economically competitive with the relatively less energy-intensive pyrometallurgy. There is no better situation with the selective flotation of complex-sulfide ores. The pyrometallurgical technologies require production of separate concentrates of copper, zinc and lead and rejecting of pyrite to the tailings. The production of the bulk, cheaper and suitable for leaching concentrate opens the way to economic challenge of hydrometallurgy [6.40,6.41].

6.3.2 Theoretical Background

Leaching of refractory minerals conducted at high temperature and under elevated pressure of gaseous reagents is an alternative to the normal pressure leaching below 100°C proceeded by thermal activation processing.

Temperature is the general parameter affecting the rate of leaching, but at the same time physical and physico-chemical properties of aqueous solutions change considerably with temperature [6.42]. The solubility of gases in aqueous solutions usually decreases with temperature and elevated pressure must be applied to keep its high concentration in solution. Gases that react with water, such as ammonia, sulfur dioxide, hydrogen sulfide and carbon dioxide, show a much higher solubility than oxygen, nitrogen, or hydrogen.

Among ionic solids the soluble chlorides increase their solubility with temperature whereas, for instance, solubility of sulfates of many nonferrous metals increase only to 100°C, and decrease strongly above this temperature. Only a few of them are soluble at temperatures higher than 200°C [6.43,6.44].

The spontaneous precipitation of scarcely soluble solid phases from aqueous solutions is an important phenomenon observed above 100°C. As a rule, there are either basic salts, oxides or hydroxides that precipitate because of hydrolysis [6.45-6.46].

The number of physico-chemical data and other fundamental information on the leaching under oxygen pressure [6.21,6.22,6.47-6.50] is probably sufficient to by-pass the study on equilibria, kinetics and reaction mechanisms and concentrate the research on the engineering problems of pressure leaching.

Hydrometallurgical processes at high temperature and pressure have been carried out in three general type-reactors:

- horizontal cylindrical autoclaves, volume 15-36m^3, with length/diameter ratio at least 3:1, equipped with mechanical stirrers and divided into three to five sections, e.g. autoclaves being in use by Sherritt Gordon for leaching, reduction and other hydrometallurgical processes [6.51];
- vertical column-reactors, volume 40-70m^3, with height/diameter ratio about 5:1 and with mixing by high-pressure steam (250°C, 650 psi) in use for leaching of nickel laterites (e.g. Moa Bay process) [6.52];
- horizontal tube autoclaves (VAW-Lurgi pipe reactors), capacity of 60-300m^3. The liquid-solid suspension, is mixed and transported through the reactor by piston or membrane high-pressure pumps. The tube reactors are in use for bauxite continuous leaching (West Germany) and uranium and gold ore leaching (South Africa) [6.53,6.54].

6.3.3 Description of Proposed Research

1. Present State of Research

A research, transgressing the traditional barriers between mineral processing and metallurgy, joining froth flotation and direct ore leaching under elevated oxygen pressure is proposed. In such a process direct leaching of complex sulfide ore with ferric sulfate solution followed by separation of different components of the solid suspension by flotation is applied. This example of the leaching-flotation association allows for: production of zinc sulfate solution; transformation of galena PbS to insoluble lead sulfate $PbSO_4$ and its accumulation in non-flotable fraction together with precipitated goethite, hematite or jarosite salt as well as with other insoluble gangue minerals; separation of sulfur and non-decomposed sulfides in the flotable fraction; and regeneration of the leaching agent under elevated oxygen pressure [6.55]. Research on pressure leaching and flotation and possible application to the direct processing of ores rich in nonferrous metals, from some pyrite Alaskan deposits, with special attention to the gold and silver recovery is being carried out since fall 1985 in the Mineral Industry Research Laboratory at the University of Alaska Fairbanks. Results [6.56] of the initial research funded by Nerco Minerals Company indicate a good recovery of metals in different products of the leaching-flotation process, applied directly to the ore. Rate of simultaneous ferric sulfate regeneration under 40-140 psig at 70-90°C is excellent too.

The laboratory installation actually used for leaching and flotation of the complex-sulfide ore under elevated pressure of oxygen is schematically shown in Fig. 6.1. It is composed of two tubular Corning-glass reactors (diameter 2 in., height 3 1/2 in. and 2 1/2 in. respectively), the peristaltic pump for the ore pulp feeding, the piston pump for recirculating the nonflotable fraction and the steel, teflon lined reservoir for collecting the flotable fraction. The oxygen is dispersed in both reactors by using the glass tubes with porous fritted, pyrex discs. The maximum pressure that can be applied in this glass installation is 50 psig (345 kPa).

2. Description of Reactor Project

The development of the leaching-flotation process could be expected to achieve satisfactory results if attention was to be focused on the engineering research and construction of the continuous reactors for leaching under oxygen pressure of 150-300 psig (1240-2070 kPa).

The vertical tubular reactor is proposed for an intense leaching-flotation process conducted under an elevated pressure of oxygen. The proposed L-F multi-step reactor has high/diameter ratio about 8/1. The volume of the reactor is divided into sections by special-form elements. The sections are equipped with injection systems of liquid and gaseous phase that assure good centrifugal mixing of fluid and high oxygen dispersion in solution. The constrained hydrodynamics of the reactive liquid-solid-gas mixture allows for a prolongation of the retention time of the leached ore particles and assumes the continuous selective separation of the solid leached particles by flotation. The leaching-flotation reactor will probably be a particular engineering solution of an apparatus due to a group of three phase (solid-liquid-gaseous) continuous reactors. Therefore the application of such reactors not only to other leaching processes but also to precipitation processes from aqueous solutions with the participation of gaseous reagents can have important technical significance. The first application of this kind of reactors, proposed in December 1982 for copper precipitation from solution under hydrogen pressure [6.57] is described as the next proposed topic.

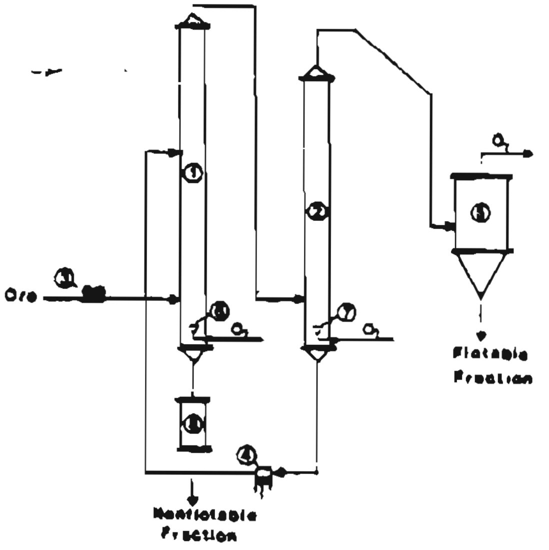


Figure 6.1. Simplified flowsheet of the laboratory installation used for leaching and flotation under elevated pressure of oxygen:
(1) and (2) - tubular Corning-glass leaching reactors;
(3) - 50 psi peristaltic pump; (4) 150 psi piston pump;
(5) - teflon lined reservoir for the flotable fraction;
(6) and (7) - fritted glass tubes for oxygen dispersion.
(8) - Glass separators for collecting non-flotable fraction.

6.3.4 Expected Results and Benefits

We expect that the new continuous reactor proposed here for leaching under oxygen pressure will have some advantages over known pressure reactors applied in industry. This is a simple construction of tubular elements of the reactor in which no mechanical mixing system is used. Required hydrodynamics is attained by:

- tangential injections of the liquid/gas or liquid/gas/solid mixture into reactor,
- upwardly directed hydrostatic transport of dispersed gas, and
- the construction of special form elements inside the reactor that constrain a prolongated retention time of the solid particles in fluidization phase.

The high dispersion of supplied oxygen and its fast and uniform saturation in the leaching solution, accelerates reactions controlled by oxygen pressure. For instance:

- the oxidation of ferrous ions to ferric ions conducted simultaneously with leaching of sulfides:

$$2Fe^{2+} + 1/2\,O_2 + 2H^+ = 2Fe^{3+} + H_2O$$

$$\left.\begin{matrix}ZnS\\PbS\\FeS\end{matrix}\right] + 1/2\,O_2 + 2H^+ = \left.\begin{matrix}Zn^{2+}\\Pb^{2+}\\Fe^{2+}\end{matrix}\right] + H_2O + S$$

- the oxidation of ferrous ions and goethite precipitation

$$2Fe^{2+} + 1/2\,O_2 + 3H_2O = 2FeOOH + 4H^+$$

- the oxidation of cuprous and ferrous chlorides with goethite precipitation

$$4CuCl + 2FeCl_2 + H_2O + 3/2\,O_2 = 4CuCl_2 + 2FeOOH$$

- the oxidation of cobaltous to cobaltic ammino-complexes:

$$2Co(NH_3)_6^{2+} + 1/2\,O_2 + 2H^+ = 2Co(NH_3)_5H_2O^{3+}$$

and others.

Among several possible applications of the proposed reactors leaching of the low grade ores of uranium or precious metals is particularly promising. Actually proposed and industrially built VAW tube autoclaves [6.58] give good results when high pressure of oxygen is applied. For instance:

- 98% of gold was extracted from the ore containing 10.2g Au/t after 15 min. of cyanide leaching under 300 psi (2068 kPa) of oxygen pressure at 20°C. Consumption of reactives 1mg NaCN/t and 6 mg O_2/t ore. Solid liquid ratios 1:2. The same yield of gold extraction in non-pressure leaching was obtained after 26 hours [6.52];

Of course the oxygen consumption will be higher if pyritic matrix must be broken down before gold extraction [6.59]. We suggest that in such a situation our proposed reactor will be better because the rate of oxygen delivery to the reactive medium and its dispersion in solution is one of the most decisive factors of oxidation.

We hope that the proposed reactor can be successfully applied in hydrometallurgical processes conducted in the Alaskan arctic conditions.

6.4 Continuous Copper Precipitation Under Hydrogen Pressure

6.4.1 Introduction

The continuous precipitation of metals or lower oxides of metals from aqueous solutions under hydrogen is the last sector of research connected with the new generation of the three phase reactors for hydrometallurgical processes proposed here. The precipitation of copper, nickel, cobalt and precious metals by hydrogen and other gas reducers is an alternative process to electrowinning and cementation [6.60-6.64] and precipitation by hydrogen of uranium dioxide (UO_2), vanadium oxide (V_2O_3) and lower oxides of molybdenum and tungsten is an alternative to other chemical precipitation techniques [6.65-6.69].

The reduction of aqueous solutions using gaseous reductors (hydrogen, sulfur dioxide, carbon monoxide) is a complex engineering problem. Attempts have been made previously to design such a continuous process, but were never carried out beyond laboratory scale models and apparatus [6.70-6.72]. Sherritt-Gordon Mines Ltd., who have pioneered in the field of hydrogen pressure reduction, were applying either a batch process or a semi-continuous process for precipitation of metal powder [6.60,6.64,6.73]. Such methods might be economically viable in the case of well priced nickel and cobalt [6.60,6.64], special composite powders [6.74-6.77] or rare metals "lower oxides" precipitation [6.65-6.69]. But for copper powder precipitation as a product alternative to cathodes [6.73,6.78,6.79], the batch process would be too costly.

The greatest difficulties which have stood, so far, in the way of achieving a continuous process are:

- the corrosivity of the reactive mixture;
- technical difficulties associated with the transport of reagents in a continuous process under elevated pressure of hydrogen and at relatively high temperature of aqueous solutions.

In spite of such inconveniences, there is a general consensus among specialists on the advantages of such processes: hydrogen reduction is much faster than the electrolysis and is completely pollution free.

Research on the continuous copper precipitation from sulfate solution under hydrogen pressure is proposed to be developed after the following arguments:

1. Chemical and electrochemical equilibria in the Cu-H_2SO_4-H_2O system at temperatures up to 200°C [6.42-6.45,6.80-6.83], kinetics and mechanisms of the two-step copper reduction by hydrogen under pressure [6.60,6.64,6.84-6.88] are known. Relatively simple interpretation of experimental results makes it possible to focus the attention on engineering problems and apparatus design.

2. Results obtained from the research on the copper continuous reduction will be carried into effect for other precipitation systems with gaseous reagent participation.

3. The copper reduction under hydrogen pressure was investigated by the author of this proposal [6.80,6.89,6.90] and process and equipment for the continuous procedure were presented in the proprietary report of authors in May 1983 [6.57] (formerly Cunit Hydrometal Inc.). The report contains the initial project for pilot plant capacity of 5,000 tons of copper powder per year, produced from a copper-base scrap and the design for a 3-phase pilot CHP-reactor (Copper Hydrogen Precipitation reactor) capacity of 10 kg Cu/h. Laboratory modeling experimentation and engineering calculation on the new 3- phase (liquid-solid-gas) reactor were completed in September 1983 [6.91].

A temporary caveat No. 83-1280 of the invention entitled "Method and Apparatus for Continuous Copper Precipitation" was deposited on April 12, 1983 in the names of F. Letowski and N. Korwin in the Canadian Patent Office. Since October 1983 the former owner of the research results, Cunit Hydrometal Inc., has been inactive and all rights were transferred to the partners (F. Letowski and M. Korwin).

4. Continuation of the project according to this proposal allows development of a more universal kind of the liquid-solid-gas reactor, based on CHP-reactor, equally for other precipitation processes, as well as for the leaching, the leaching-flotation or the instantaneous leaching preceded with thermal activation processes, described earlier (Sections 6.2 and 6.3).

6.4.2 Theoretical Background

The separation of copper from aqueous sulphate solutions obtained from ore, concentrate, or scrap leaching may be carried out in the following ways:

(1) as compact cathodes by classical electrolysis from copper sulphate solution; this type of copper electrowinning is applied or proposed in many hydrometallurgical processes [6.4,6.14,6.16,6.29,6.32,6.36,6.39] or by electolysis in diaphragm-electrolyzers from copper sulphate solutions, containing also a significant concentration of ferrous sulphate [6.92,6.93];

(2) as a copper powder by cementation with iron [6.92], by two stage pressure reduction with SO_2 in ammoniacal solution [6.33,6.62] and by hydrogen pressure reduction from ammoniacal solutions [6.73,6.78,6.79,6.84,6.89,6.94-6.98] or from sulphate acidic solution containing iron (II), zinc, magnesium or other metal sulphates [6.64, 6.88, 6.90, 6.94, 6.99-6.102].

If copper reduction by hydrogen is carried out using acid concentrated solution of $CuSO_4$, the purity of the precipitated copper powder is very high, of the order of 99.96% Cu or more [6.60,6.90,6.99,6.101], but the highly corrosive nature of the solution containing free sulphuric acid formed during the reduction

$$CuSO_4 + H_2 = Cu + H_2SO_4$$

presents a serious engineering problem. Because of the neutralizing effect of ammonia, copper powder precipitation is carried out more frequently using ammoniacal sulphate or carbonate solutions

$$Cu(NH_3)_2SO_4 + H_2 = Cu + (NH_4)_2SO_4$$

but the reduction is accompanied by the precipitation of solid products of the copper ion hydrolysis, which affect the purity of the precipitated metal [6.44,6.79,6.80,6.84,6.89].

The equilibria of reduction are influenced by the pH, cuprous and cupric ion concentrations and the concentration of the complexing agent - NH_3. The kinetics of reduction is influenced by temperature, hydrogen pressure, hydrodynamic conditions and the nucleation of metal crystals [6.84-6.88]. The slow progress of reduction at a low temperature and moderate hydrogen pressure is due to the great stability of H_2 molecules; this makes catalytic activation a necessity. The activation of molecular hydrogen is the principal means of controlling the first stage in the precipitation of the metal from solution. The activation energy of hydrogen reduction can be lowered by means of heterogeneous and homogeneous catalysis. Heterogeneous activation of hydrogen takes place mainly on solid surfaces that adsorb molecular hydrogen from solution. The homogeneous activation of hydrogen is an autocatalytic reaction with participation of copper ions in solution.

Another possibility of hydrogen activation by high voltage discharge, just before its injecting to solution was recently investigated by the author of the proposal [6.103]. In the initial laboratory tests the discharged electrodes were mounted inside a special construction injector for hydrogen injection to an autoclave. The results of the initial tests indicate that high voltage hydrogen activation accelerates the reduction of copper. This influence seems to be strong: the average rate of the copper precipitation from cupric sulfate solution under 400 psi (2758 kPa) of hydrogen pressure at 120°C is about 0.12 $gL^{-1}h^{-1}$ if

20,000 to 30,000 volt discharge with frequency 5.10^3 s^{-1} was applied, whereas without activation no reduction was observed. Also, the reduction rate with activation at 130-140°C, reached the same level (0.41 $gL^{-1}h^{-1}$) as at 160-180°C without high voltage activation.

Because of good activation of hydrogen on solid surfaces, an amount of fine copper powder is most frequently added to the reduced solution of copper sulfate. If the amount of such nucleating centers suspended in the solution is too small, some copper is deposited on the walls of the reactor and on other surfaces in contact with solution.

The reduction of copper from solution after acid leaching of a copper concentrate containing 68 g/l Cu, 15 g/l Fe^{2+}, and about 20 g/l H_2SO_4 is quite easy at 150-180°C and under partial hydrogen pressure of 510-560 psi (3550-3850 kPa) [6.90]. The effect of temperature and hydrogen pressure on the rate of reduction from this solution is presented in Fig. 6.2. Even though the rate of reaction increases with temperature and pressure, it depends much more on the mixing of the gaseous (hydrogen), liquid (solution) and solid (copper powder) phases.

The selectivity of copper precipitation, as compared to less noble metals, is very good. It is a little less in ammoniacal solution in comparison to other amminocomplex-forming metals, such as nickel and cobalt [6.60,6.64,6.84,6.94,6.97].

One of the first processes, developed by Sherritt-Gordon Mines Ltd. in the years 1956-1959, precipitated copper powder from the ammoniacal solution obtained from the Lynn Lake sulphidic copper concentrate by ammonia pressure leaching [6.73]. Copper powder has also been precipitated directly from amminosulphate or amminocarbonate solutions after leaching of copper scrap [6.60,6.78,6.79] or from an acidic sulphate solution obtained after solvent extraction from amminosulphate solution after leaching [6.101]. Other flowsheets of copper precipitation from acid solutions after sulphide concentrate leaching were proposed too, as an alternative to copper deposition, in electrolyzers with diaphragm [6.104-6.106].

As it was mentioned before copper reduction using hydrogen is carried out by a batch process. The possibility of metals reduction on a continuous basis is referred to in some patents [6.97,6.107-6.110] but no continuous process has been described. The study of the continuous process using a laboratory model was carried out at the University of Oklahoma [6.72,6.111].

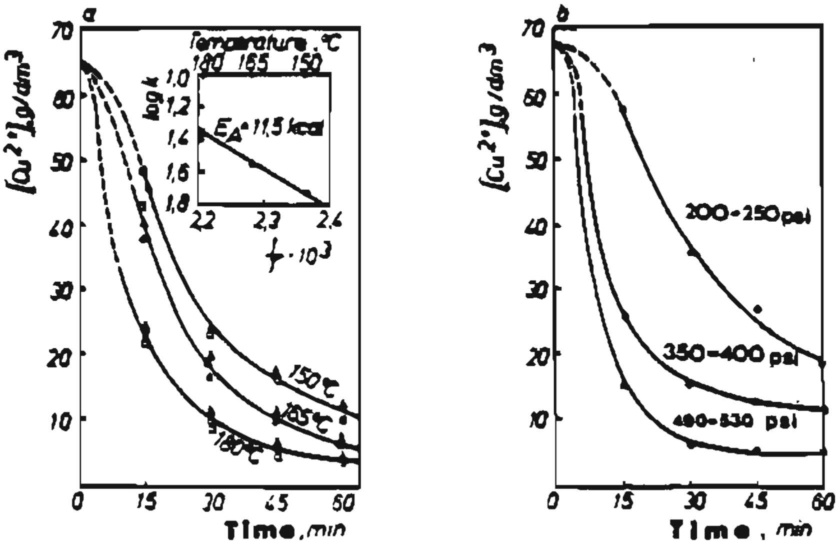


Figure 6.2. Effect of Temperature (a) and Hydrogen Pressure (b) on the Rate of Reduction from Acid Solutions [6.91]: (a) Progress of reduction at 150, 165 and 180°C, P_H = 490-530psi, nucleation 80 gpl Cu powder, Fe^{++} = 3 gpl, n - 600 Rpm, (b) Effect of hydrogen pressure on reduction rate: 200-250 psi, 350-400 psi, and 490-530 psi. Temp. 165°C, Cu^{++} - 68 gpl, nucleation 80 gpl Cu powder, Fe^{++} = 3 gpl, n = 600 Rpm.

Copper reduction [6.72] had been performed in a vertical tubular reactor 72 in. height and 1 in. in diameter. The flow of the acidified copper sulfate solution was directed concurrent with, or countercurrent to the upwardly directed flow of hydrogen under the total pressure of 413-512 psig (2850-3536 kPa) and at temperatures from 149 to 204°C. The amount of hydrogen is in excess of that required for stoichiometric reduction of copper and this circumstance provides sufficient mixing of the solid-liquid-gas mixture. A schematic diagram of the continuous reactor installation according to Sista and Sliepcevich [6.72] is given in Fig. 6.3. The copper powder suspension leaves the tubular reactor and after cooling in a heat-exchanger is collected in the liquid-solid separator. The results presented by Sista and Sliepcevich confirm the high purity of the product, if the pH of the reduced solution is below 1.8 units, and the high rate of continuous reduction, permitting 70-80% of copper to precipitate within the residence time of 10-20 minutes. The rate of reduction increases with increasing temperature (Fig. 6.4) but at the same time the co-precipitation of basic copper sulphate $Cu_3(OH)_4SO_4$ from the solution with high copper concentration requires its limiting to 12-22 g/l Cu. The basic copper sulphate precipitation as a function of temperature is shown in Fig.6.5 [6.45].

In spite of the clear superiority of the continuous process over batch or semi-continuous procedures, there still remain some difficulties in implementing the known continuous processes [6.70-6.72,6.111] on an industrial scale, and namely:

- troublesome excess of reducing gas under pressure;
- undesirable precipitated copper powder due to the short residence time of the particles and the unregulated motion of the solid-liquid-gas mixture;
- excessive surface resulting from high length-to-diameter ratio causes metal deposition on internal reactor walls.

6.4.3 Description of the Proposed Research

1. General Engineering Requirements [6.57]

The aim of the project is to study and develop the continuous process of the high purity copper powder precipitation under hydrogen pressure from solutions after leaching. The process will be developed on the basis of the 3-phase pressure reactor, which concept was proposed and investigated previously [6.57,6.91]. The study on application of the same kind of reactor for the pressure leaching was proposed too [Chapter 2], and it is presented in the 2nd part of the Proposal.

It has been stated in Section 6.4.2 that problems in the previously described, continuous precipitation processes [6.70-6.72,6.111] are of an engineering nature. In order to overcome them an essential change in the continuous copper reduction concept is required. The following conditions must be met for the CHP process to become viable:

a. The precipitation process must be carried out with a significant excess of copper in the solution than the amount required for almost total consumption of the supplied hydrogen, in order to eliminate its recycling.

b. A high rate of hydrogen supply to the solution is required, in order to assure good mixing of the solid-liquid-gas mixture, a high rate of hydrogen dissolution in solution, and a high rate of copper precipitation from solution.

c. Hydrodynamic conditions must assure the continuous selective separation of a given fraction of the copper powder particles.

2. Reactor Description [6.91]

The proposed reactor is a vertical column, whose height to diameter ratio does not exceed 10:1. The volume of the reactor is divided into sections by special-form elements. These sections are equipped with injection systems of liquid and gaseous phase, that assure good centrifugal mixing of fluid and high hydrogen dispersion in solution. The constrained hydrodynamics of the reactive liquid-solid-gas mixture allows to prolong the retention time of a given size copper powder particles and assures the continuous selective separation of the copper powder particles with a sufficiently large size, as a final product. The hydrogen gas is fed into the reactor in a sufficient quantity to assure constant pressure. The copper sulphate solution is fed into the reactor continuously through an inlet in the lower part, and is spent from the top of the reactor. The total quantity of the hydrogen gas which is supplied to the reactor, should react with the copper ions and precipitate 40 to 70% of copper

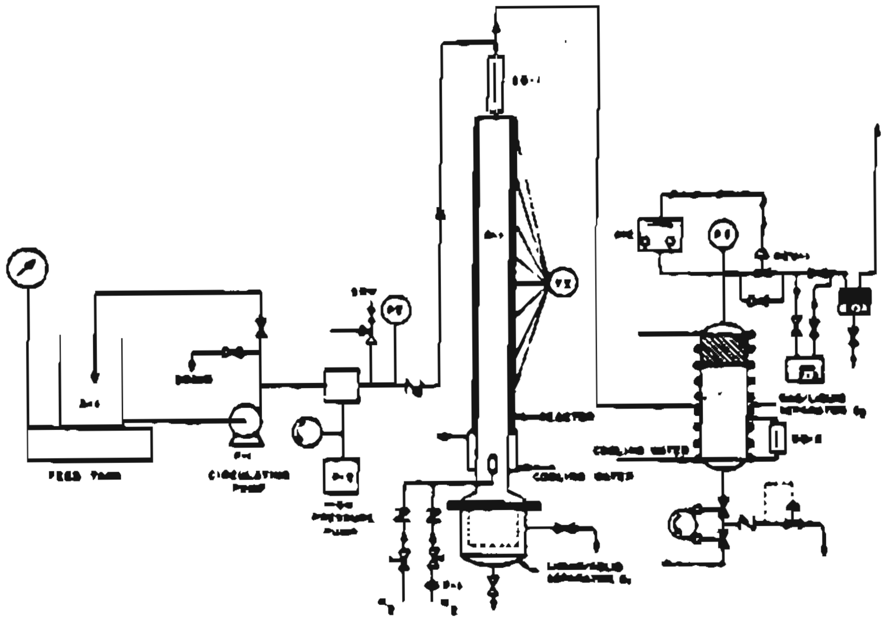


Figure 6.3. Schematic diagram of the laboratory continuous hydrogen reduction installation according to Sista and Sliepcevich [6.73].

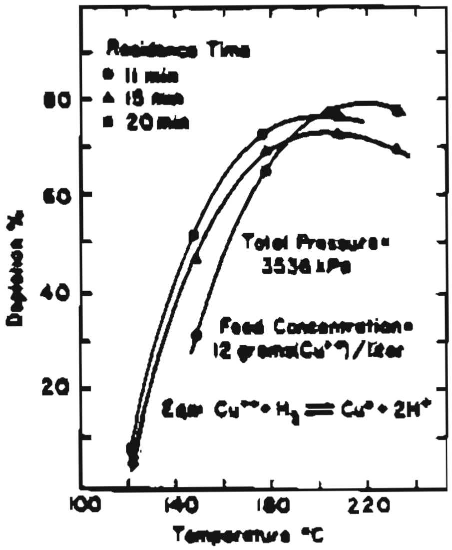


Figure 6.4. Effect of temperature on rate of hydrogen reduction (Sista and Sliepcevich) [6.73].

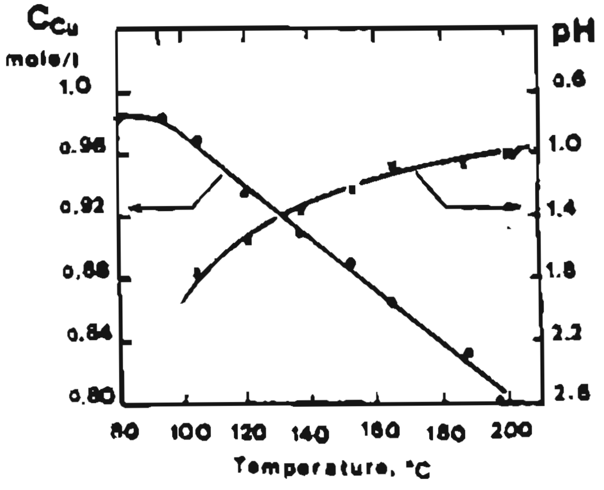


Figure 6.5. Effect of temperature on hydrolysis of copper sulphate solution. ($CuSO_4$) = 1 mol/l. [6.45].

from solution. Only a small proportion of unreacted hydrogen leaves the reactor in the form of the gas dissolved in the spent solution.

The copper powder particles growing inside the reactor during the reduction are subjected to a motion in two different flows of the solid-liquid-gas mixture:

- the small copper powder particles are carried off in the central part of the reactor, with the vertical flow of the solution-gas fluid flowing from the bottom to the top of the reactor;
- the larger copper powder particles move with a resultant of the gravitational and centrifugal forces and subsequently go down along the reactor wall. In every section the flow of larger copper powder particles is directed by the special form elements to the central part of the reactor, where centrifugal segregation of the copper particles is repeated. Finally, the largest particles leave the active mixing area and pass through the outlet in the bottom of the reactor to the separator, which is emptied periodically.

3. General Assumptions and Elementary Engineering Data [6.91]

The copper precipitation occurs according to the reaction:

$$CuSO_4(aq) + H_2(g) = Cu(s) + H_2SO_4(aq)$$

For the temperature range from 150 to 180°C the equilibrium constant expressed as

$$K = (H^+)^2(Cu^{2+})^{-1}p_{H2}^{-1}$$

is equal to 10^{10} [6.90]. The high value of K indicates that the reaction of copper reduction by hydrogen is practically irreversible. However, at low temperatures, i.e. below 100°C, the rate of copper reduction is extremely slow. The rate of reduction becomes sufficiently high to be used as a process of copper winning from solution, only when the temperature is above 130-150°C and the partial pressure of hydrogen is not less than 200 psi (1380 kPa).

The product of reduction - copper powder, has a suitable purity (99.96% Cu) if:

- the concentration of copper ions during the reduction exceeds 20-30 g/l Cu;
- the yield of copper precipitation does not exceed 50-70%;
- the growth of the copper particles develops on a suitably high surface of copper powder suspended in solution;
- and the rate of the nucleation centers arising in the solution is sufficiently high and constant.

The activation energy of the reaction equals to 11.5 kcal/mol [6.90] and the initial rate of reduction under 390-450 psi (2690-3100 kPa) of partial pressure of hydrogen, and with nucleation by 80 grams of copper powder (size 100-160 μm) per liter is equal:

$$4.3 \times 10^{-4}\ mol\ L^{-1}s^{-1}\ (150°C)$$

$$6.6 \times 10^{-4}\ mol\ L^{-1}s^{-1}\ (165°C)$$

$$9.3 \times 10^{-4}\ mol\ L^{-1}s^{-1}\ (180°C)$$

According to Sista and Sliepcevich [6.72] the rate of continuous copper precipitation under hydrogen pressure 450 psi (3100 kPa) from solution containing 70 g/l Cu, and at temperature 170°C is 7.5×10^{-4} to 1.2×10^{-3} kmol m^{-3} s^{-1}. These values were accepted in the assumptions.

The CHP process is carried out according to the following mass balance:

$1.11\ \text{kg}\ H_2$

$CuSO_4 = 274$ kg $CuSO_4 = 138$ kg

(Cu = 70 kg) $\xrightarrow[\text{solution}]{1\ m^3}$ CHP Reactor *) $\xrightarrow[\text{solution}]{1\ m^3}$ (Cu = 35 kg)

$H_2SO_4 = 33$ kg $H_2SO_4 = 88$ kg

copper powder
Cu = 35 kg

The residence time of the solution in the CHP reactor required to precipitate 35 kg of copper with the rate accepted below ($7.5 \cdot 10^{-4}$ kmol $m^{-3}s^{-1}$), could vary from 7.65 to 12.2 min:

$$\tau_1 = \frac{35}{63.5 \times 7.5 \times 10^{-4}} = 7.35 \times 10^2 S = 12.2 \text{ min};$$

$$\tau_2 = \frac{35}{63.5 \times 1.2 \times 10^{-3}} = 4.59 \times 10^2 S = 7.6 \text{ min}$$

For the process conducted under total pressure of 560 psi (3860 kPa), at temperature 170°C, 0.5 m^3 of hydrogen must be supplied to 1 m^3 of solution. This volume is equal to 0.65 of the hydrogen solubility in pure water in the same conditions, (0.86 cm^3 H_2/gH_2O under 50 atm (5066 kPa) at 170°C).

The proposed experimental reactor has a height of 57 inches and inside diameter of 5.7 inches. Its volume is 18.2 l. For the residence time from 7.6 to 12.2 min the rate of copper powder precipitation is from 2.5 to 4 kg Cu per hour if the average transport of the reactive medias through reactor (liquid/gas volumetric ratio is 2 and the volume of copper powder is neglected) is from $3 \times 10^{-5}\ m^3s^{-1}$ to $4.8 \times 10^{-5}\ m^3s^{-1}$ at the inlet and from $2 \times 10^{-5}\ m^3s^{-1}$ to $3.2 \times 10^{-5}\ m^3s^{-1}$ at the outlet. The rate of hydrogen supply is from $2.22 \times 10^{-2}\ g\ s^{-1}$ to $3.55\ g\ s^{-1}$.

4. Reactor Design [6.91]

Laboratory modeling experiments for the process of continuous copper precipitation by hydrogen [6.91] were carried out in the glass reactor (volume 20 l) with water - air modeling fluid. Some qualitative tests were performed also with sand fractions used as a solid phase. The results of these experimentations as well as the engineering calculations on the hydrodynamics in the CHP reactor, particularly on the fluid injection systems, vertical and centrifugal fluid transport, gaseous bubbles and solid particles classifications, were the basis for the reactor design.

The reactor of the volume and geometry described in assumptions (Section 6.4.3) is divided into three sections. The details of the sections are described in the Caveat. Three liquid-gas injectors and two high pressure injectors are set up inside the reactor. Hydrogen gas is injected in the pressure range from 900 psi (opening) to 800 psi (closing), and the rate of its injection by one injector is calculated. The type and size of nozzle will be adapted during the proposed research.

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*) Copper-Hydrogen-Precipitation Reactor

The liquid phase is discharged only from the top of the reactor with an average rate of 1.20-1.92 l min^{-1} if the assumed, total hydrogen-gas consumption will be confirmed.

The solid product in the form of copper powder particle size minus 200 mesh goes down to the liquid-solid pressure separator with the rate of 42-67.2 g min^{-1}. The residence time of the copper powder particles in the reactor is considerably higher than the residence time of the solution and this circumstance is very important for a good growth of crystals. Nevertheless, at the same time a relatively high concentration of fine copper particles in the highest section of the reactor can cause an over-loading for the liquid-solid filter at the solution outlet. If this circumstance were disadvantageous, a change in the height/diameter ratio of the reactor or only the higher part of reactor, could be necessary.

5. Project Development

The proposed reactor application to copper precipitation from sulfate solution by hydrogen should be continued according to the following program:

a. Construction and tests of the gas injectors and gas/liquid injectors.

b. Construction of the experimental pilot-unit for metals reduction by hydrogen.

c. Tests of continuous copper precipitation by hydrogen.

6.4.4 Expected Results and Benefits

At the present time it is still difficult to place the hydrogen reduction method in relation to other processes of copper reduction from solution. A great deal of additional research is needed into the engineering problems due to the continuous process. Nevertheless, it was felt that a qualitative comparison made on the basis of certain criteria might be useful at this stage. This comparison is presented in Table 6.1.

Table 6.1. Comparative classification of the methods of separation of copper from sulphate solutions

Criteria of Classification	Classical Electrowinning	Electrolysis with diaphragm	Hydrogen pressure reduction	Reduction by sulphur dioxide
Industrial application	+++	+	+	0
Intensity of process	+	+	+++	++
Technical difficulty	-	-	—	–
Materials / corrosion	-	-	–	—
Energy consumption	—	—	-	–
Purity of product	+	++	+++	-
Environmental pollution	-	–	0	–

Positive criteria: +++, ++, +

Negative criteria: ---, --, -

Do not occur: 0

Industrially Known Applications

Classical electrowinning of copper is the currently used industrial practice. The diaphragm-electrolysis is more frequently used in winning other nonferrous metals, e.g. Ni, Mn, but it is not often used in the electrowinning of copper from sulphate solution. Copper reduction by hydrogen pressure is a rarely used method in industry - its application is limited to fine copper powder or to the composite powders production. Precipitation by SO_2 is not used in industrial practice.

Intensity of Process

Classical and diaphragm-cells electrolysis processes are the slowest, whereas processes using copper precipitation with SO_2 are faster. Hydrogen reduction is a very fast process. It is approximately 20 times faster than electrolysis.

Technical Difficulty

The processes are rated as follow in the order of technical difficulty:

- hydrogen reduction, because of high pressure (300-700 psi), high temperature (140-200°C) and hydrogen gas utilization;
- reduction by sulphur dioxide, due to moderate pressure (100-180 psi), moderate temperature (100-120°C) and sulphur dioxide utilization;
- electrolysis with diaphragm;
- classical electrolysis.

Materials/Corrosion Problems

The process with SO_2 reduction is characterized by the highest corrosivity of the gaseous phase, while corrosivity at the liquid phase presents a moderate problem. The higher corrosivity of solution is associated with the process of hydrogen reduction from sulphate solution. Electrolytic processes have the lowest corrosion levels.

Energy Requirements

The principal sources of energy are fuels, electricity and chemicals. Electrowinning processes have the highest electrical energy requirement. Energy consumption expected in gaseous reduction processes will be lower, because of the high rate of metal precipitation.

Environmental Pollution

Because in every process solutions are recirculated in closed circuits, the greatest environmental threat is due to the emission of vapors, liquid suspensions in the air and gases during electrolysis processes. The possibility of environmental contamination during the SO_2 reduction process results from accidental, anomalous utilization of sulphur dioxide. The hydrogen reduction process does not threaten the environment.

The final conclusions deriving from this comparative analysis are very favorable to the hydrogen reduction process. It appears to be technically superior and more economical than other copper separation methods. It can be much better adapted to the climatic conditions in the arctic because of the compact and small installation. However, the reduction of copper by hydrogen is technically the most difficult process, and its industrial application as an alternative process of copper winning requires some non-conventional engineering solutions.

The anticipated benefits associated with the commercial application of the proposed reactor to copper precipitation by hydrogen are:

1. The Copper Hydrogen Precipitation (CHP) reactor will be capable of replacing classical electrolyzers in many known hydrometallurgical processes. The produced coarse size copper powder can be converted by casting into copper ingots. The proposed CHP process is less energy-intensive than copper electrolysis. The capital costs of the CHP unit built and operating costs of the CHP process will be smaller than these for the electrowinning tankhouse of the same capacity. A comparison of anticipated technical and economic factors of the hypothetical CHP-process proposed by CUNIT Hydrometal Inc. to copper recovery from copper scrap [6.57] with data of copper electrowinning from the solution after heap leaching and solvent extraction is presented in Table 6.2.

2. Minimal financial risk is associated with gradual development of the CHP process, step by step through its less hazardous experimental application for the composite copper scrap processing, to future large-scale for the concentrate processing.

3. The application of such reactors to other precipitation processes from aqueous or non-aqueous solutions with the participation of gaseous reagents other than hydrogen evidently acquires a commercial significance. The following applications for the such reactors could be taken into account:

   - nickel and cobalt powders precipitation from amminosulfate solutions by hydrogen;
   - precious metals precipitation from chloride solution by hydrogen;
   - nickel and cobalt sulfide precipitation by gaseous hydrogen sulfide;
   - copper powder or a double cupric-cuprous sulfite precipitation by sulfur dioxide;
   - uranium(IV) oxide -UO_2, precipitation from carbonate-uranyl- complex solution by hydrogen;
   - lower valency oxides of vanadium molybdenum and tungsten precipitation by hydrogen;
   - iron(III) oxide precipitation, i.e. as goethite FeOOH, during oxidation of ferrous sulfate and partial hydrolysis of iron(III) by oxygen.

6.5 Example of the Reactor Application

The simplified flowsheet of an hypothetical hydrometallurgical processing of a chalcopyrite concentrate is an illustration of possible applications of the proposed kind of reactors (Fig.6. 6). This kind of reactors is applied in the following unit processes:

- the fast thermal activation in the nonoxidative conditions (1) and instantaneous leaching (2) with spent solution after the hydrogen reduction process;
- the leaching-flotation process and iron hydrolysis (3) under elevated oxygen pressure (50-150 psi) at temperature 90-102°C; the principal leaching-flotation process (4) under the same conditions as (3); and
- the copper precipitation process (5) under hydrogen pressure of 400 psi (2756 kPa) at 170°C.

All unit processes are technically realizable. Very simplified chemistry of the processes can be described with the following principal reactions:

1. The fast thermal activation - chalcopyrite decomposition in the nonoxidative conditions:

$$2CuFeS_2 \longrightarrow Cu_2S + 2FeS + S$$

Table 6.2. Comparison of some anticipated technical and economic factors of the hypothetical CHP-process with data of copper electrowinning.

		Classical electrolysis BLUEBIRD, Miami (Arizona) Tankhouse for 5,000 t Cu/year*)	Hydrogen reduction, CHP Process; project for 5,000 t Cu/year
Unit capacity		625 kg Cu/h	640 kg Cu/h
Rate of solution recirculation		208 m^3/h	18 m^3/h
Concentrations in solution (inlet/outlet)	Cu	36/33 gpl	70/35 gpl
	Fe	1.5 gpl	15-20 gpl
	H_2SO_4	146/151 gpl	28/87 gpl
Temperature/pressure		45°C/atmospheric	170°C/600psi (4140kPa)
Principal elements of installation		48 cells (total volume 240m^3, 40 cathodes, 41 anodes; weight of one cathode 5 to 60 kg after 8 days	2 pressure reactors of total volume 2x1.2=2.4m^3, 2 pressure liquid/solid separators of 0.1m^3, pumps, compressors, other pressure equipment
Product, form and purity		Copper cathodes 99.9% Cu	Copper powder, size 200 um 99.96% Cu
Costs of direct energy and chemicals **)		Electricity in the electrolysis only, $0.117/kg Cu	Cost of heating and hydrogen only, $0.094/kg Cu
Capital costs of the copper winning section section only.		Electrowinning tankhouse only, $2,532,300.	CHP unit only, $1,359,000.
Approximate surface of the copper winning section		500 m^2	50 m^2

*) 1970 data, according to A.K. Biswas and W.G. Davenport, "Extractive Metallurgy of Copper", Pergamon Press 1976.

**) In constant Canadian dollars 1983 - Estimated by M.J. Corwin - Cunit Hydrometal Inc., Sept. 1983.

2. The instantaneous leaching of iron with copper precipitation in sulfidic form:

$$FeS + CuSO_4 = FeSO_4 + CuS$$

3. The fast leaching of easy to decompose copper sulfides:

$$Cu_2S + Fe_2(SO_4)_3 = CuS + CuSO_4 + 2FeSO_4$$

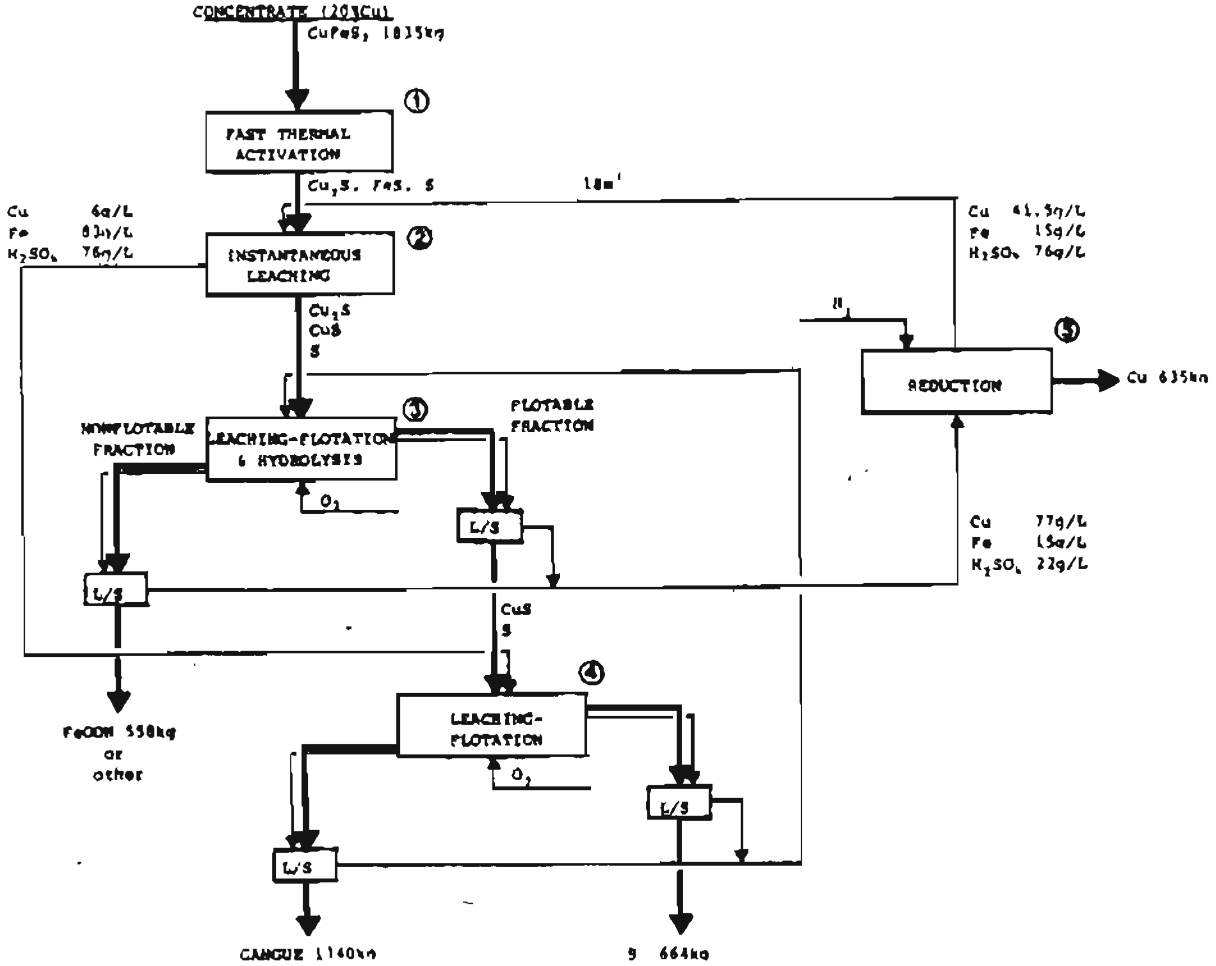


Figure 6.6. Simplified flowsheet of a hypothetical processing of chalcopyrite concentrate.

with partial precipitation of goethite (or jarosite-type salts):

$$2Cu_2S + 2FeSO_4 + 3/2\,O_2 + H_2O = 2FeOOH + 2CuS + 2CuSO_4$$

and with simultaneous separation of solid particles by flotation with oxygen:

- sulfur and non-decomposed sulfides in the flotable fraction, and
- goethite (or jarosite-type salts) and some gangue minerals in the nonflotable fraction.

4. The principal leaching of non-decomposed sulfides from flotable fraction:

$$CuS + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + S$$

with the simultaneous iron oxidation:

$$2FeSO_4 + 1/2\ O_2 + H_2SO_4 = Fe_2(SO_4)_3 + H_2O$$

and the sulfur separation from nonflotable gangue minerals by flotation with oxygen.

5. Copper precipitation under hydrogen pressure:

$$CuSO_4 + H_2 = Cu + H_2SO_4$$

The concentrations of copper, iron and sulfuric acid in solution calculated from the theoretical mass-balance of above chemical reactions are indicated in Figure 6.6. An example of application of this kind of reactors in different unit processes is shown in Figure 6.7. Numbers in circles correspond to the unit process numbers in Figure 6.6.

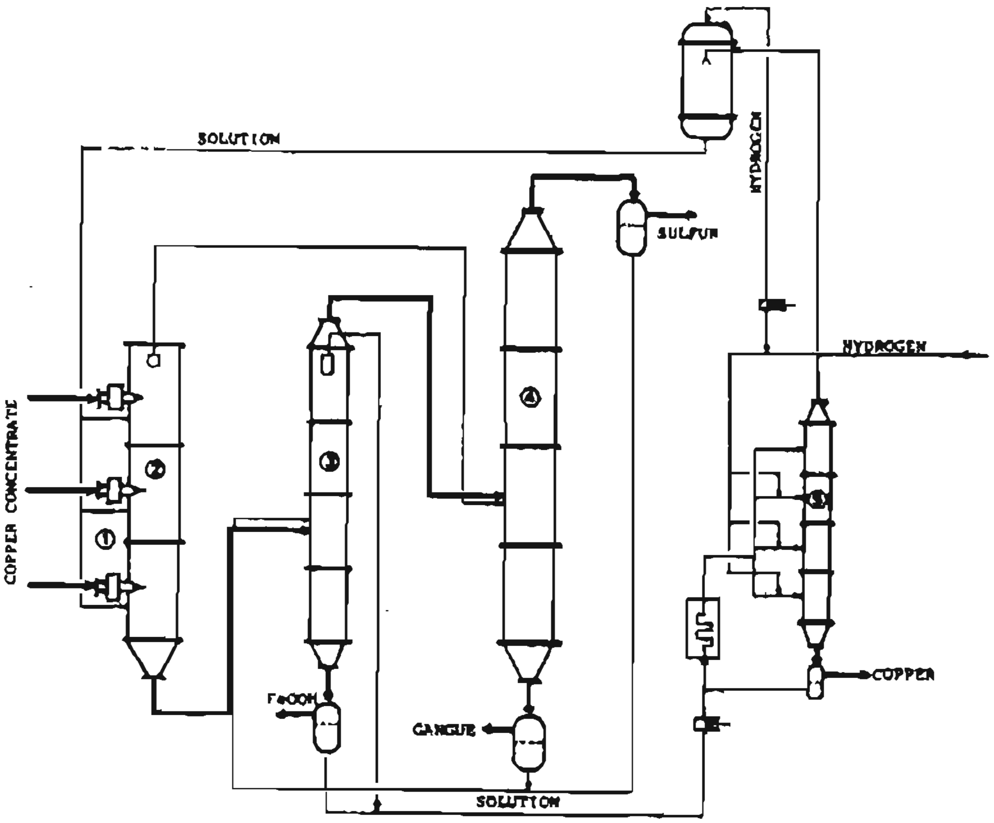
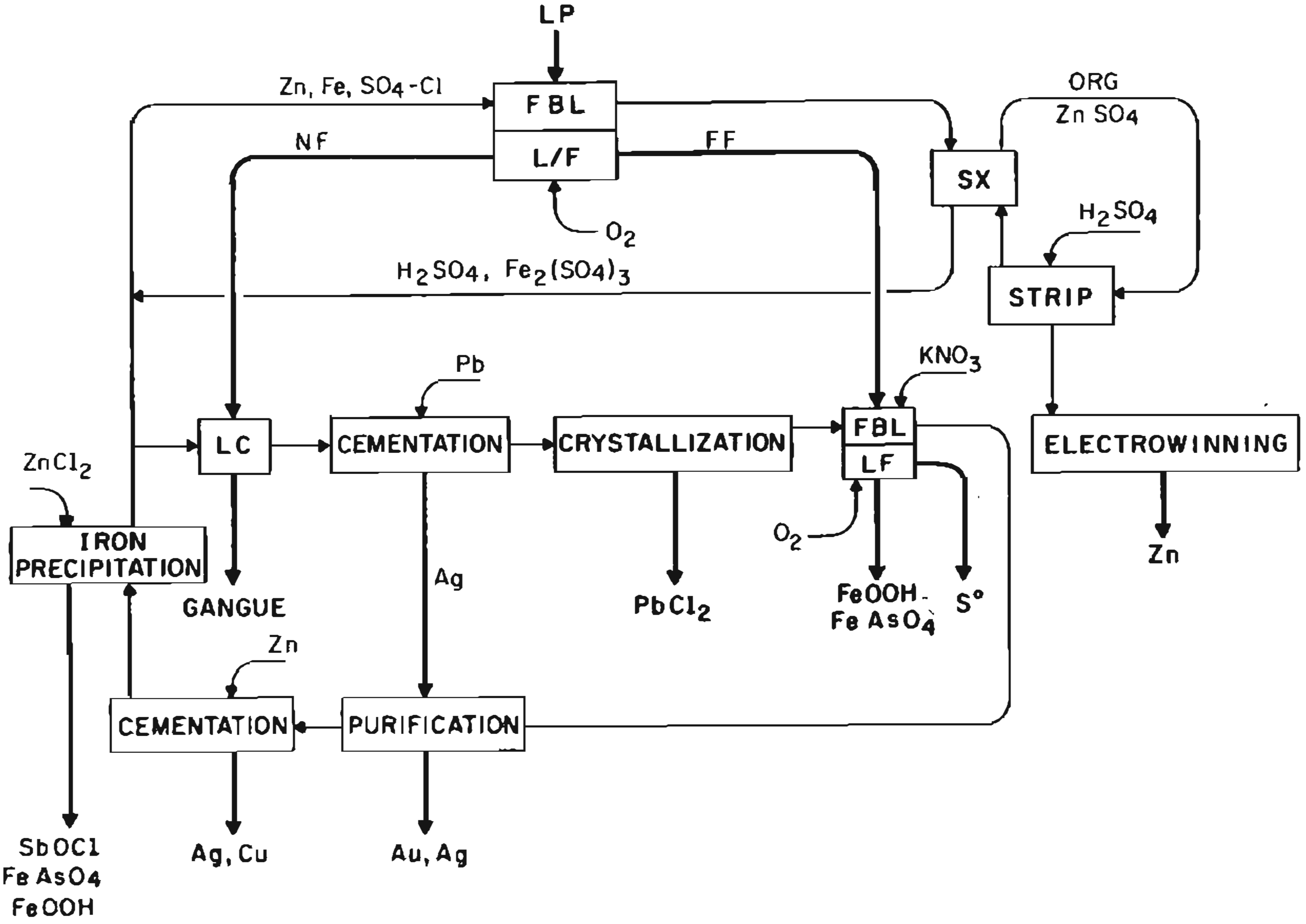


Figure 6.7. An idea of application of the new generation reactors in the chalcopyrite processing according to the flowsheet shown in Fig. 6.6.

6.6 APPENDICES

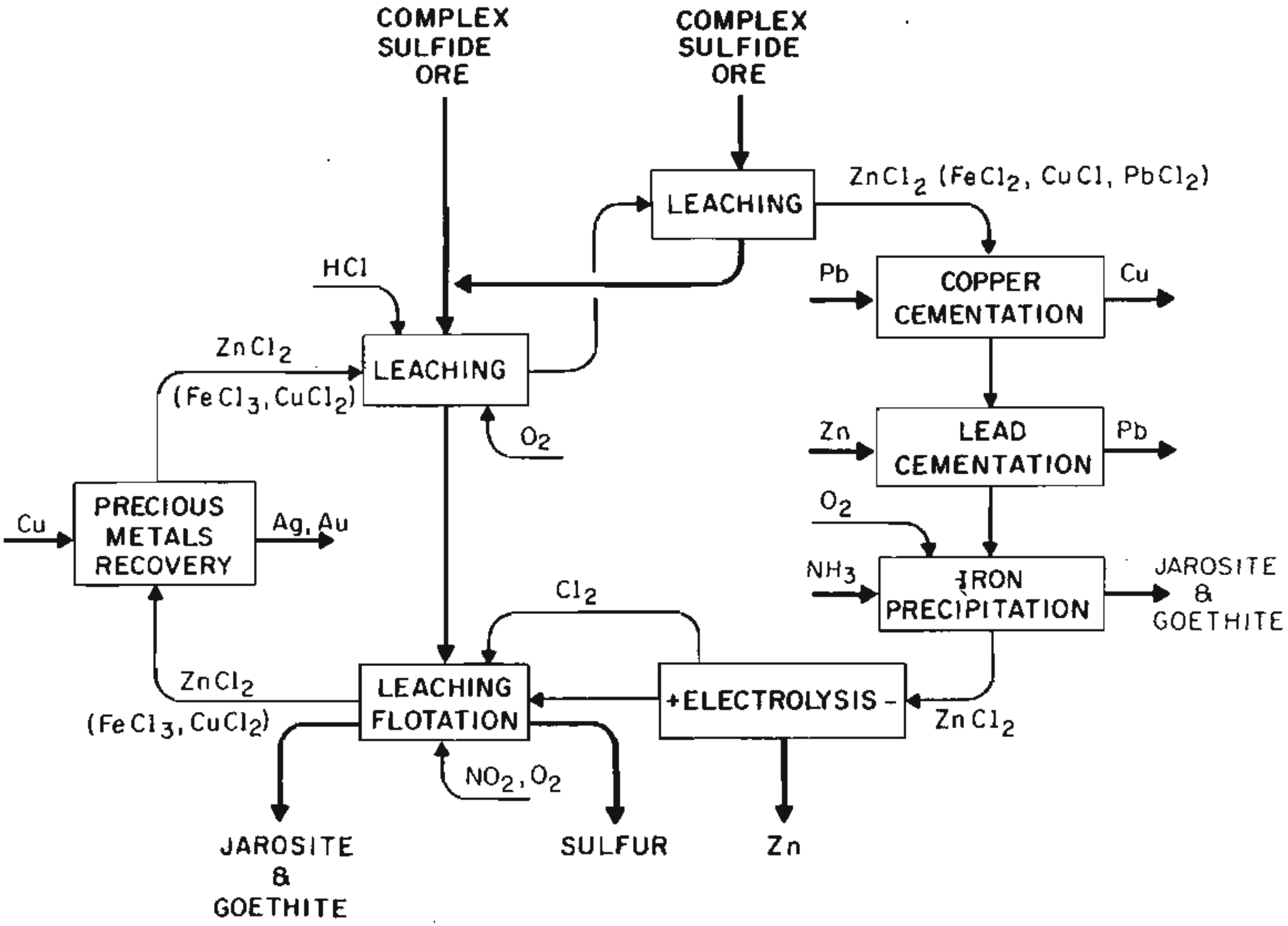
Appendix 1

A proposed flowsheet for treating the complex sulfide ore.



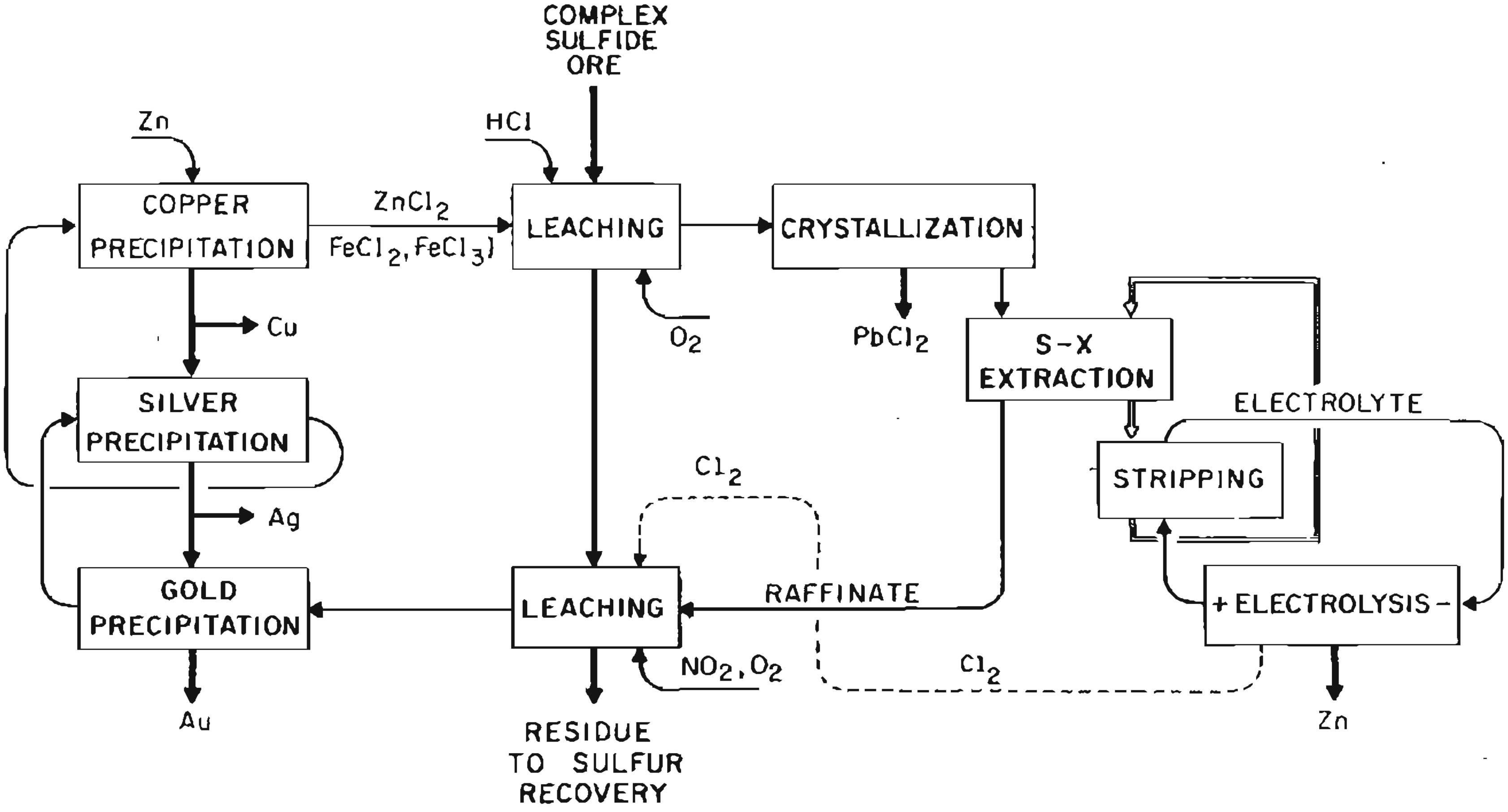
Appendix 2

A process designed for treating metal sulfides.



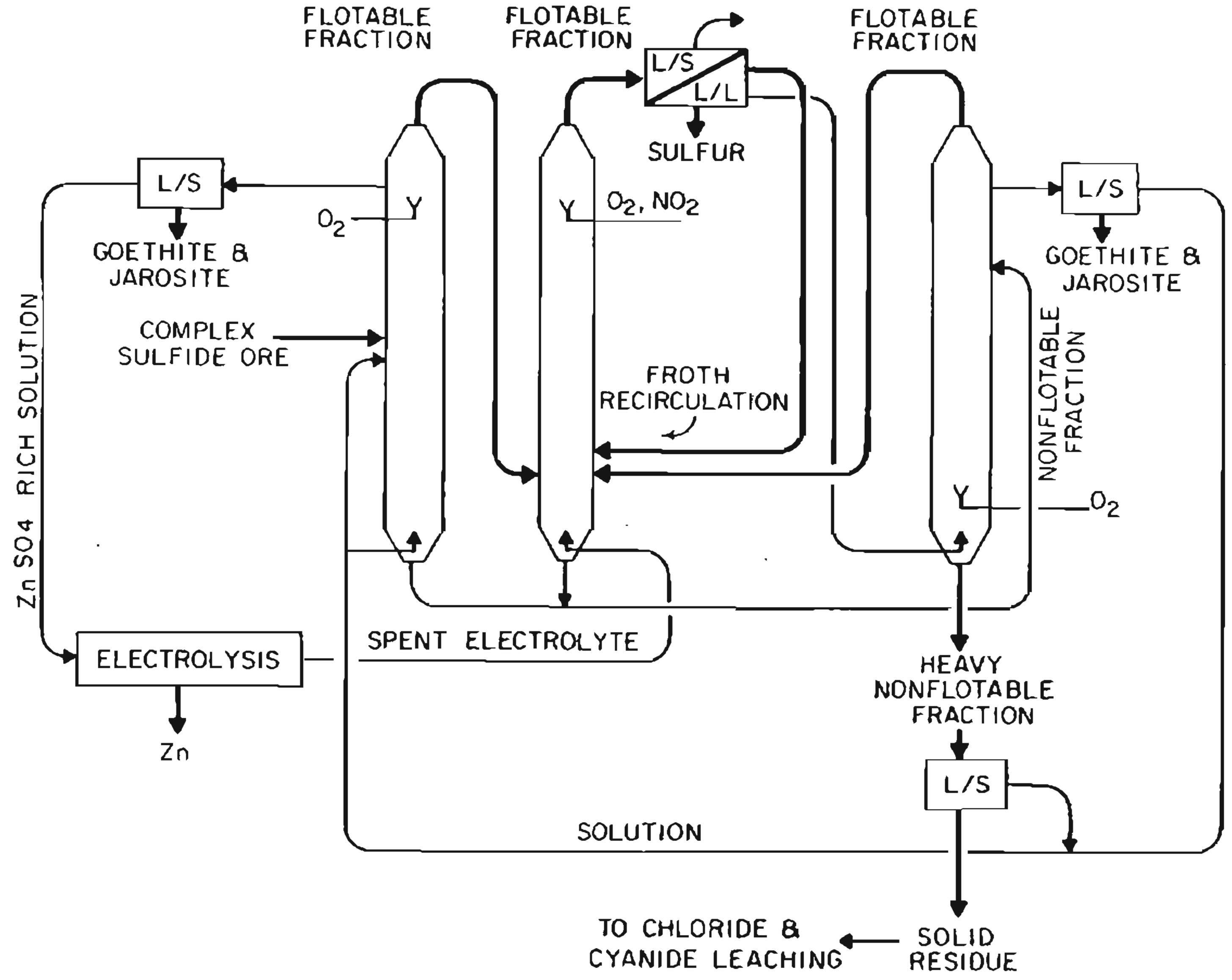
Appendix 3

An alternative for treating metal sulfides.



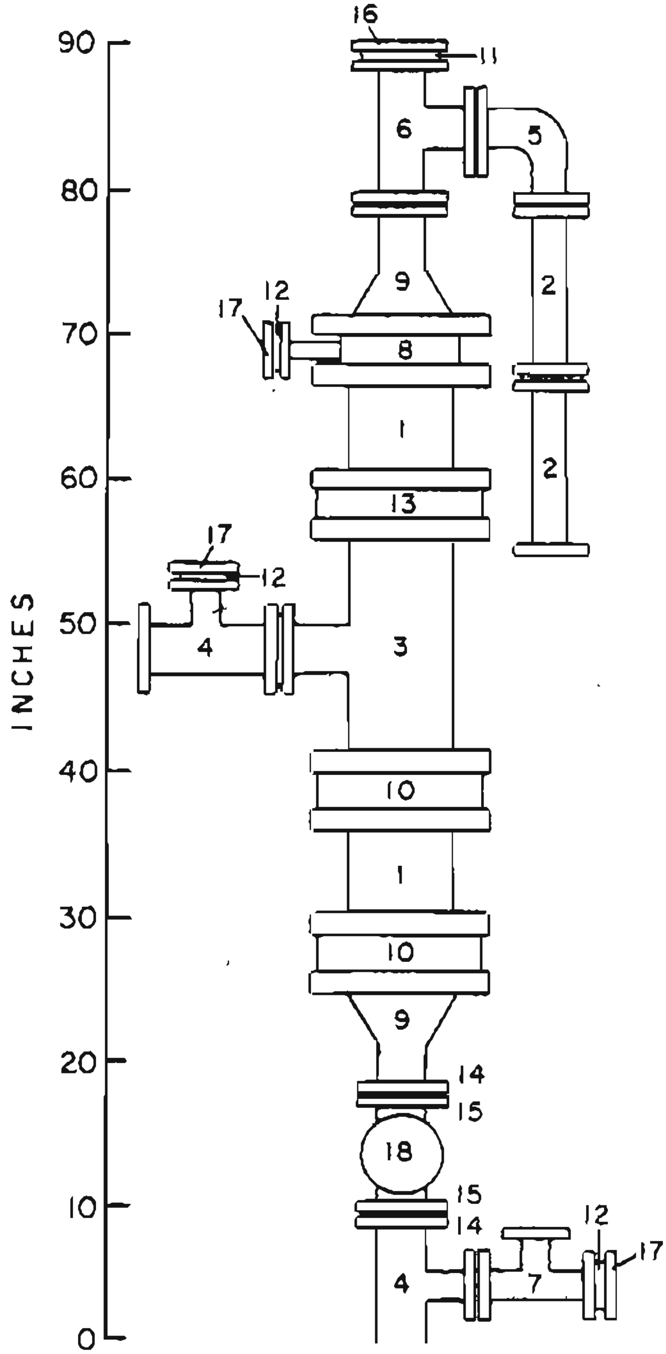
Appendix 4

A process for treating metal ores.



Appendix 5

Design of a reactor for larger pilot installation.

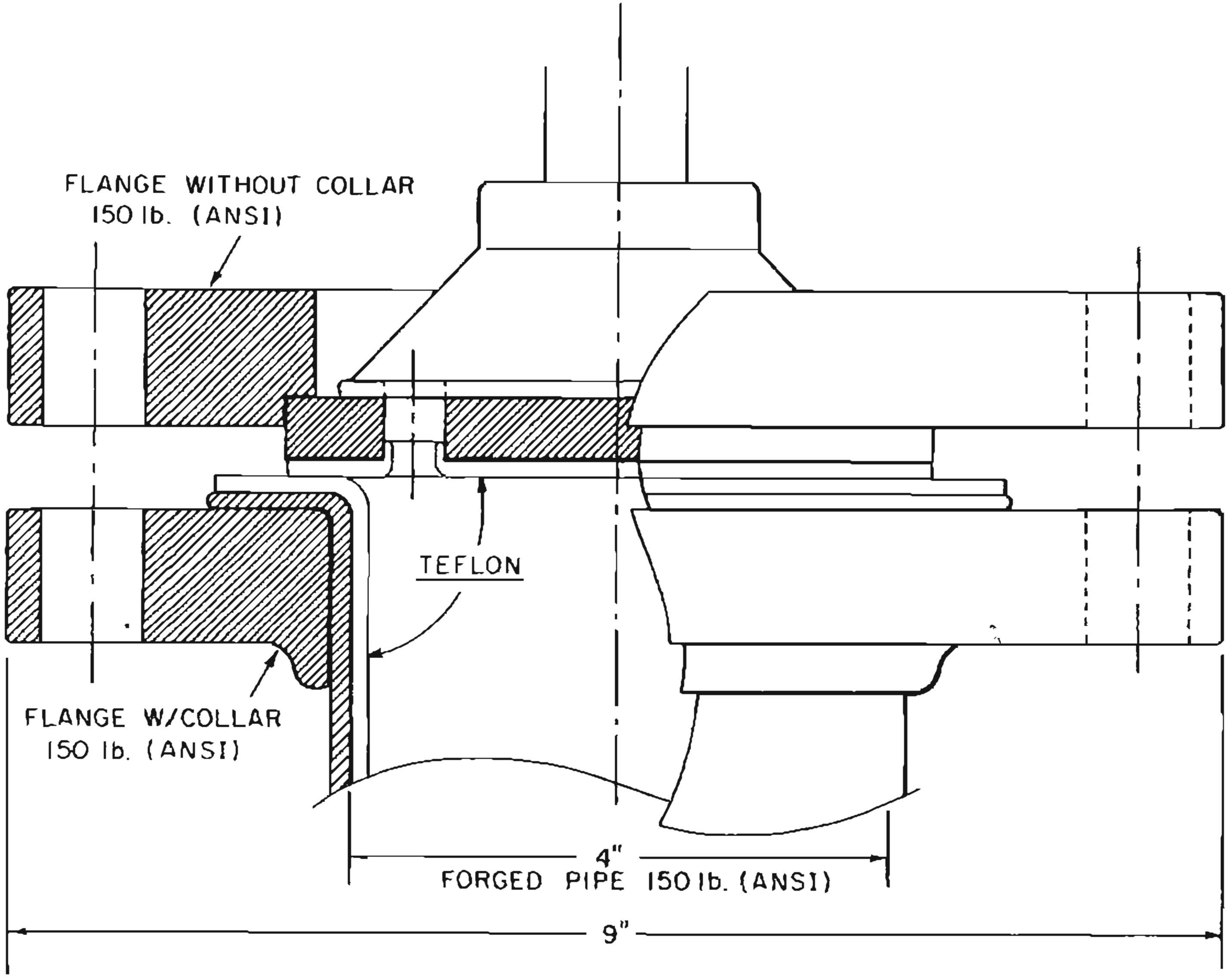


Legends:

1: 6" pipe, 8 1/2" long
2: 1" pipe, 1' long
3: Reducing tee, 6" x 2"
4: Reducing tee, 2" x 1".
5: Reducing elbow, 2" x 1"
6: Tee, 2"
7: Tee, 1"
8: Instrument tee, 6", R = 2", S = 7/8"
9: Concentric Taper Reducer, 6" x 2"
10: Full face spacer, 6" C = 2 1/2.
11: Standard full face spacer, 2".
12: Standard full face spacer, 1"
13: Armored full face spacer, 6", C=2 1/2"
14: Standard blind full face spacer, 6",C=1/2"
15: Blind Flange, 6"
16: Blind Flange, 2"
17: Blind Flange, 1"
18: Bull's eye sight flow, 2".

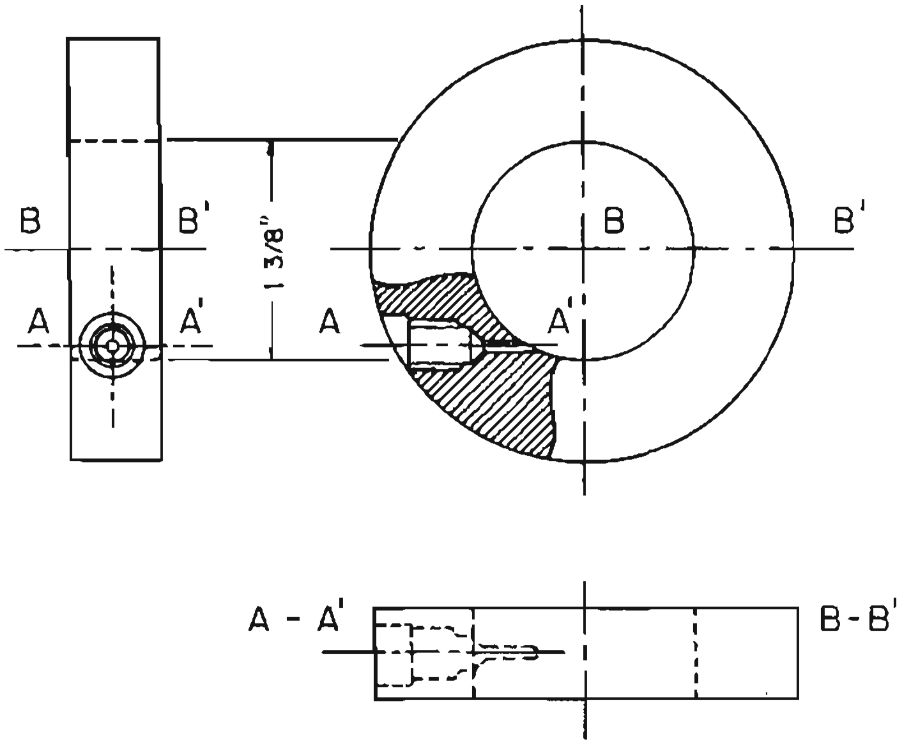
Appendix 6

Design of the teflon lined tubing element for autoclave.



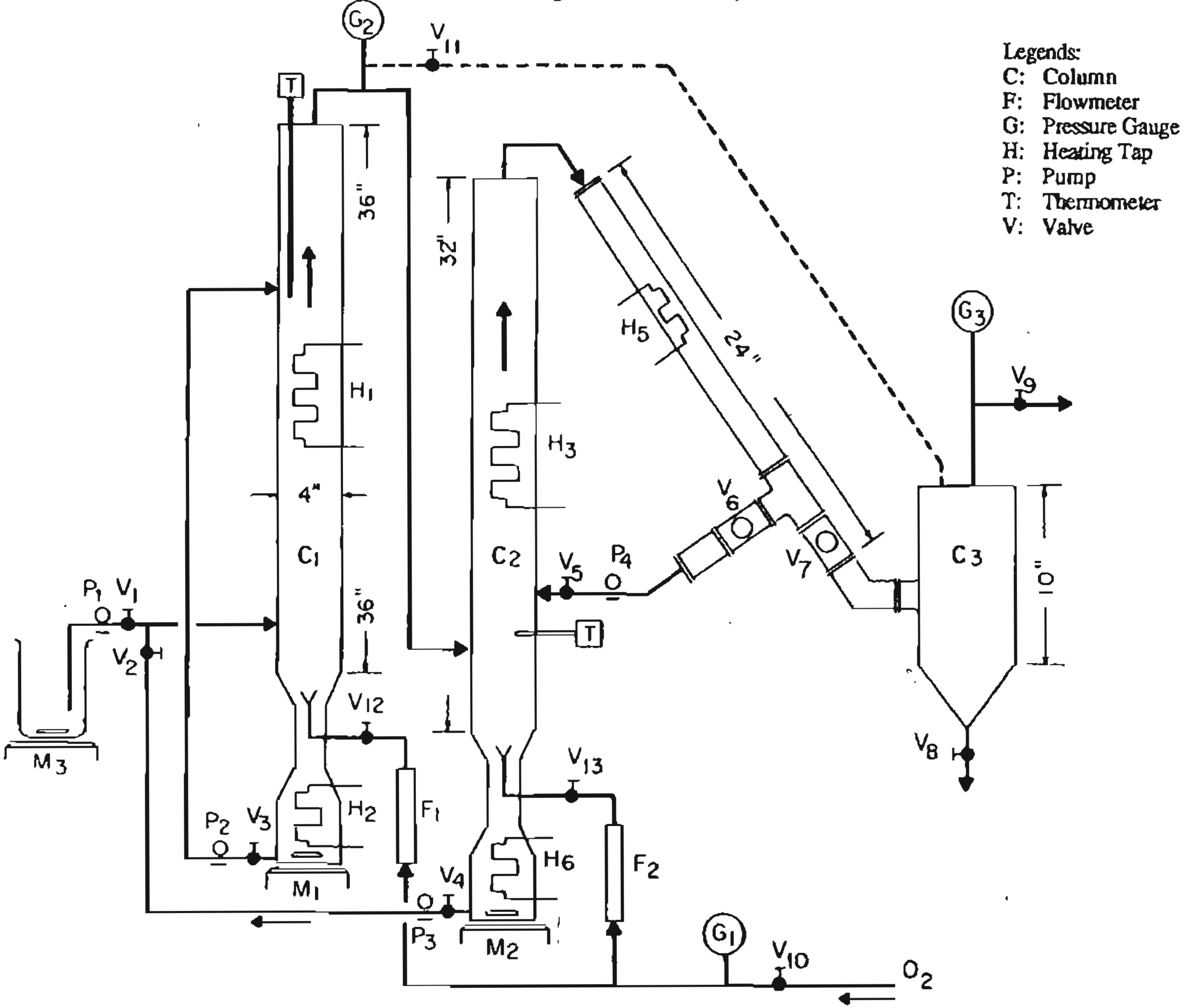
Appendix 7

Design of reactive medias injector.



Appendix 8

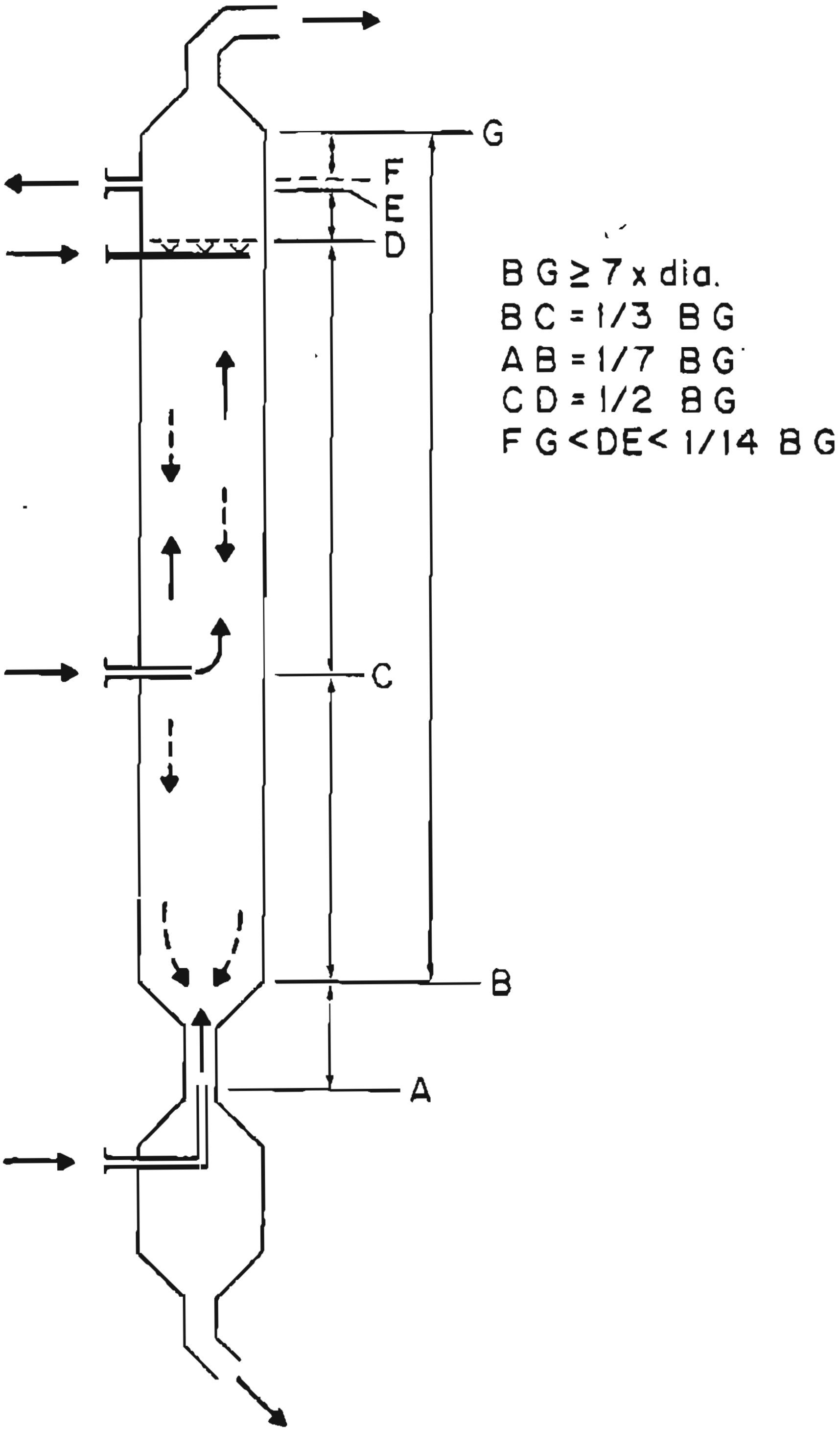
Actual configuration of laboratory installation



Legends:
C: Column
F: Flowmeter
G: Pressure Gauge
H: Heating Tap
P: Pump
T: Thermometer
V: Valve

Appendix 9

Detail design of a leaching/flotation column.



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