HYDROMETALLURGY

OF THE DELTA SULFIDE ORES

First Stage Report

Submitted To:

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By

F. Letowski and Kuo-Tung Chou (Authors)
P.D. Rao (Principal Investigator)

Mineral Industry Research Laboratory
School of Mineral Engineering
University of Alaska - Fairbanks
Fairbanks, Alaska 99775-1180

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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.

1. INTRODUCTION

Most nonconventional hydrometallurgical methods of the processing of complex sulfide ores are based on metals extraction from bulk flotation concentrates [1-11]. 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 1,a) must be applied [12,13].
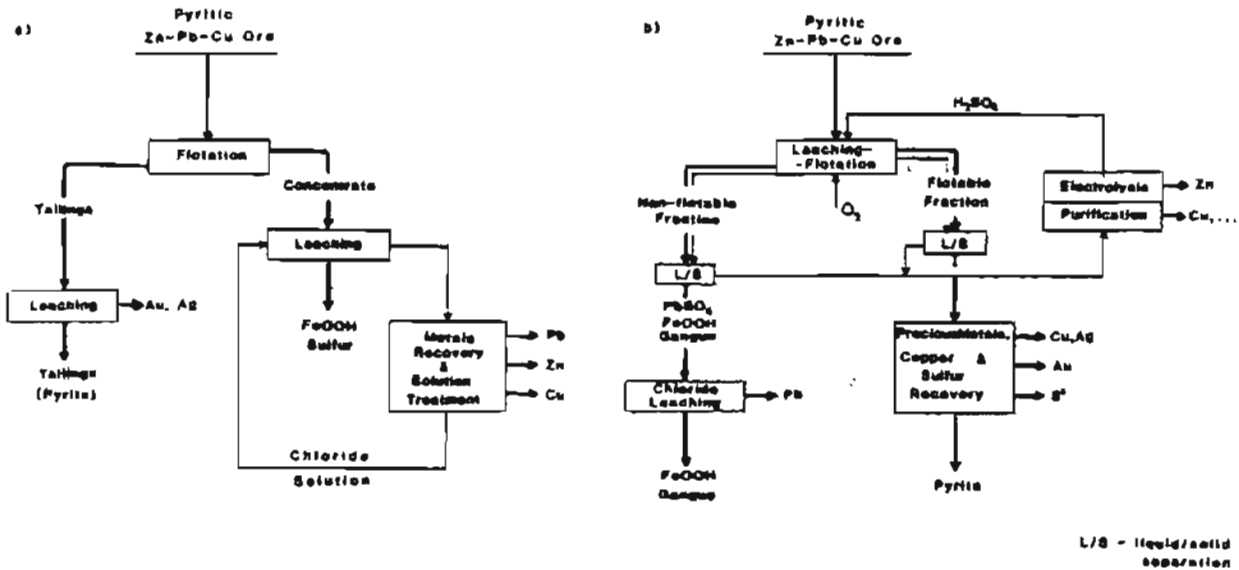

Figure 1   Hydrometallurgy of complex sulfide ores (gold and silver are associated with pyritic matrix):
    a)   Classical concept of hydrometallurgical processing of concentrate (example of chloride leaching)
    b)   Leaching-Flotation processing of ore (example of sulfate leaching).

Just such a situation occurs with the pyritic deposit of complex sulfide ores found near Tok, Alaska [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 [15] allows for:

-     selective extraction of zinc as soluble zinc sulfate;

$$ZnS(s) + Fe_2(SO_4)_3(aq) = ZnSO_4(aq) + 2FeSO_4(aq) + S°(s) \tag{1}$$
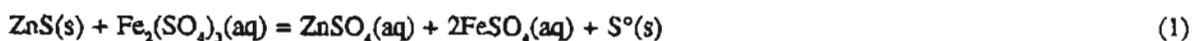
-     separation of insoluble lead sulfate, formed during galena oxidation by ferric sulfate solution, in the non-flotable fraction:

$$PbS(s) + Fe_2(SO_4)_3(aq) = PbSO_4(s) + 2FeSO_4(aq) + S°(s) \tag{2}$$

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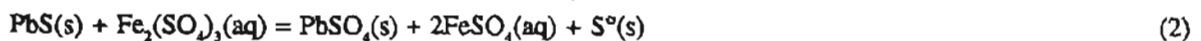
- separation of other unreacted sulfides and sulfur in the flotable fraction;

- 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:

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

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 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. [16]. Fugleberg et al. [17] describes the direct leaching and flotation of a black schist ore (Ni, Zn, Cu, Co sulfides). Wakamatsu et al. [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. [19] presents a paper on oxidative leaching and flotation of nickeliferous 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. CHEMICAL CHARACTERISTICS OF ORE

Six bulk samples of ore were collected from the Delta Massive Sulfide belt [14]. The concentration of metals and sulfur in the samples is presented in Table 1.

The chemical characteristic of the ore samples is presented in Table 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 differ slightly from the mineralogical description of the ore samples presented previously in the Research Grant Proposal [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 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. Contents of sulfides and other components in the ore samples

Sample		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). 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) 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. For the sample #1 (LPU) and #2 (LPL) the loss of weight is a function of the following order:

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

The higher dissolution of components 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 3 is a supplementary illustration of chemical properties of raw material.
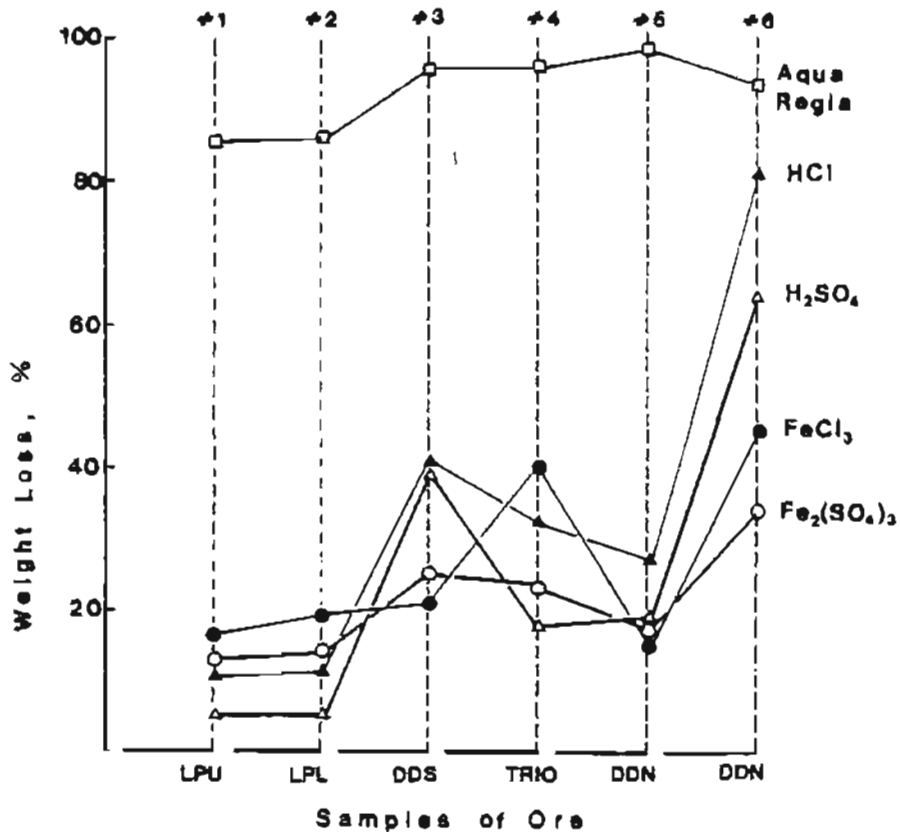

Figure 2 Loss of weight of the ore samples during digestion in different solutions. Test conditions - see Table 3.

Table 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

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);

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- 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 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 3.
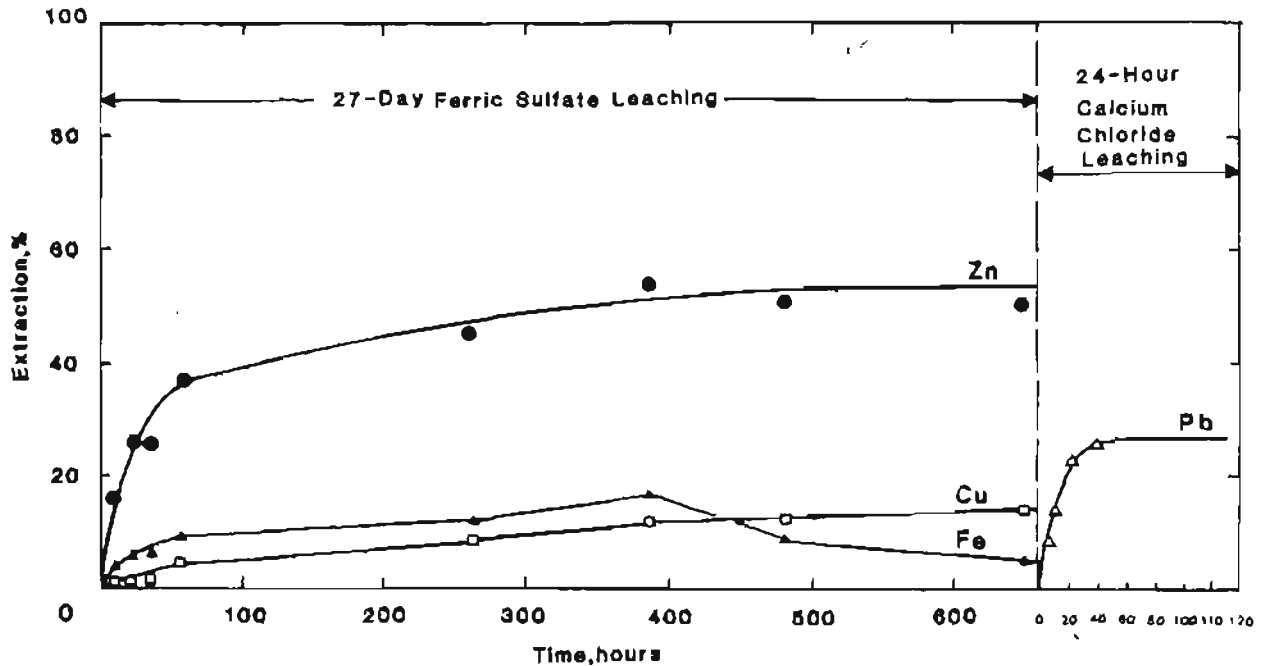

Figure 3   Extraction of metals in the column-leaching test in ferric sulfate - sulfuric acid solution and in calcium chloride - hydrochloric acid solution at temp. 20-22°C; - ● zinc, □ - copper, ▲ - iron, △ - lead. (Other conditions in the text.)

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 4 and specific conditions of these leaching tests are collected in Table 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 5 and in Table 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 6-12.
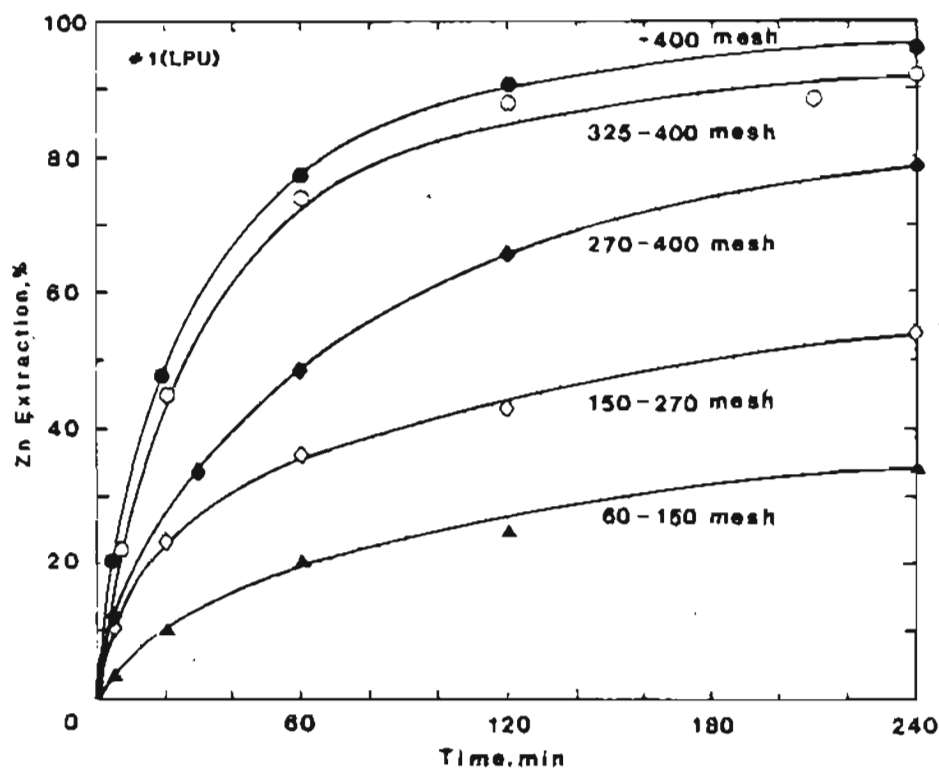
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Figure 4 Effect of size fraction of the ore on zinc extraction. Ore sample #1 (LPU). Conditions of leaching - see Table 4.

Table 4. Leaching conditions of different fractions of ore sample #L.
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] | | | | Loss of weight (%) |
		Fe[2] (g/L)	Zn (g/L)	Cu (g/L)	H$_2$SO$_4$ (%)	
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
270-400	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. 31)
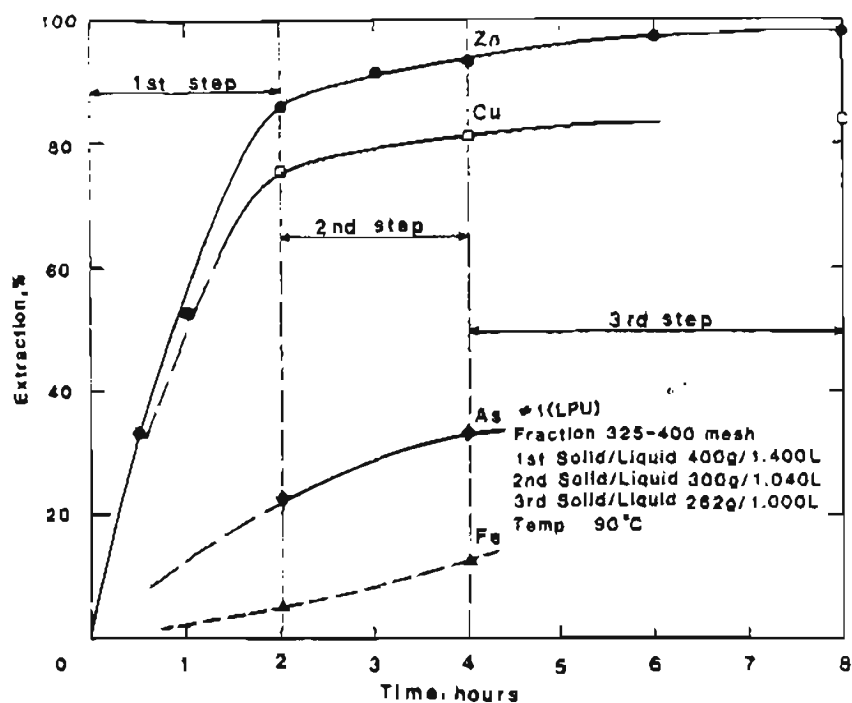2) Total iron concentration, with $[Fe^{2+}] < 10\%$ of total iron

Figure 5 Metals extraction during 3-step ferric sulfate leaching of the fine fraction of ore sample #1: ● - zinc, □ - copper, ◆ - arsenic, ▲ - iron.

Table 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. 5.

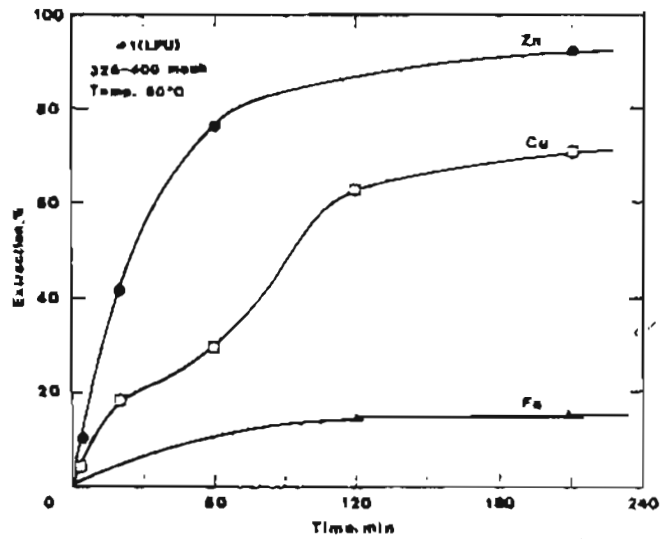| Step of Leaching		Concentrations (g/L)				Extraction (%)				Loss of weight %
		Fe^{3+}	Fe^{2+}	Zn	Cu	Zn	Cu	As	Fe	
1st	Initial*	79.2	42.8	24.1	0.82					
	Final	40.7	88.3	40.5	1.74	86.3	75	23	5	14.62
2nd	Initial*	79.2	42.8	24.1	0.82					
	Final	77.0	52.2	25.7	0.92	93.2	81	33	12	20.6
3rd	Initial*	129.6	—	—	1.18					
	Final	126	~6	1.3	1.20	96.0	82	nd	nd	26.3

*   in 1% H_2SO_4 solution

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Figure 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%.
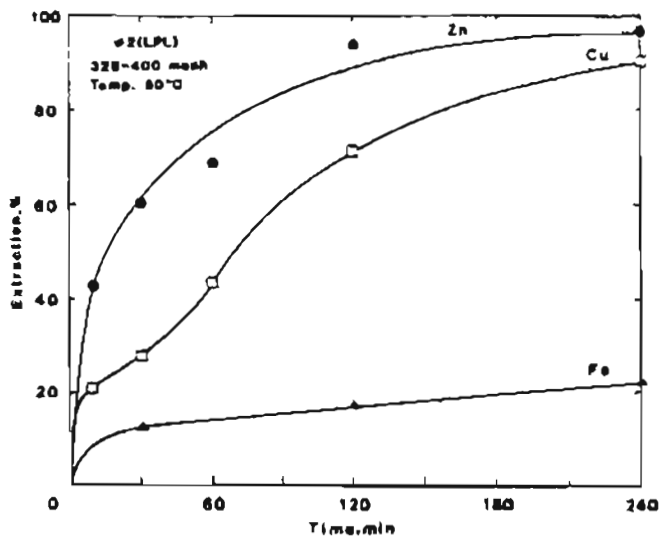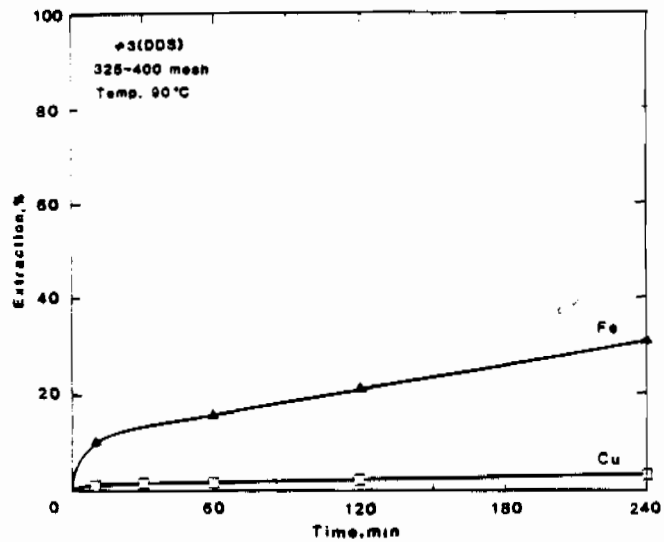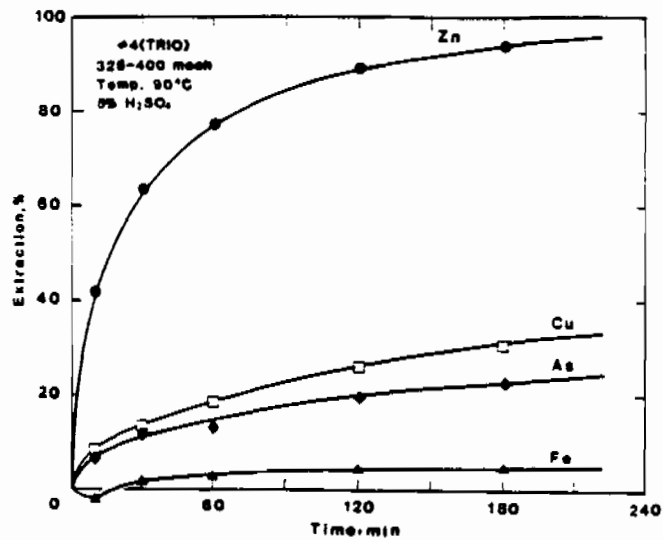

Figure 7   Ferric sulfate leaching of ore sample #2; solid/liquid = 50 g/0.7 L; initial concentration: Fe^{3+} 40.9g/L, Fe^{2+} 26.7g/L, Zn 13.45g/L, Cu 0.38g/L, H_2SO_4 1%. Loss of the sample weight during leaching 20.56%.

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Figure 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 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%.

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Figure 10 Ferric sulfate leaching of ore sample #4; solid/liquid = 50 g/0.7 L; initial concentration: Fe^{3+} 106.0g/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 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 16.0%.
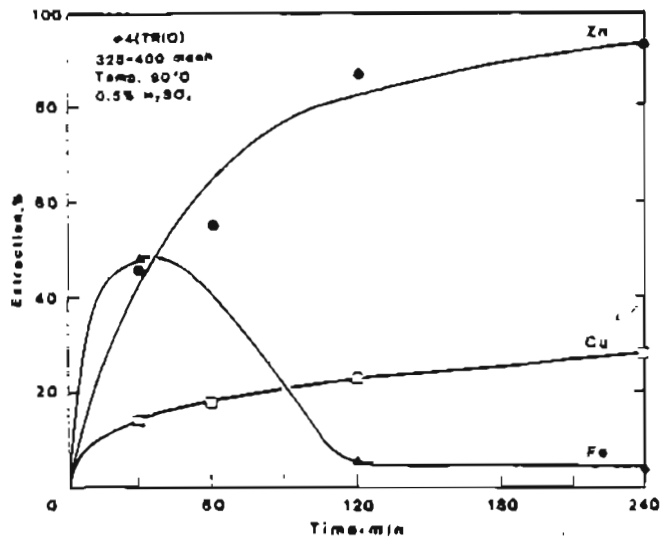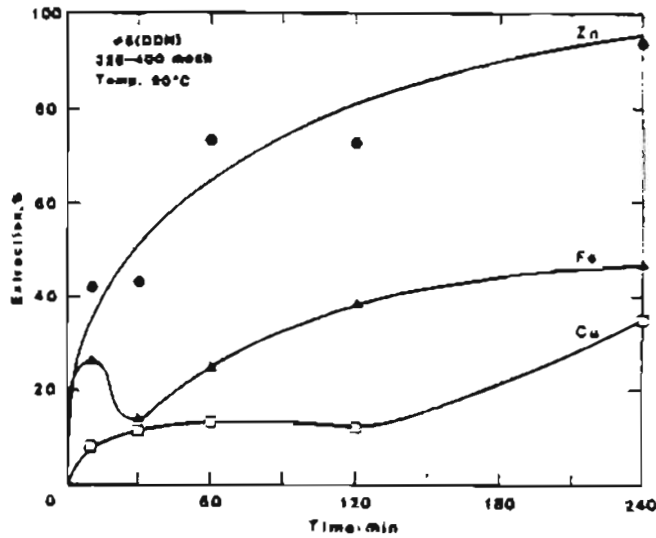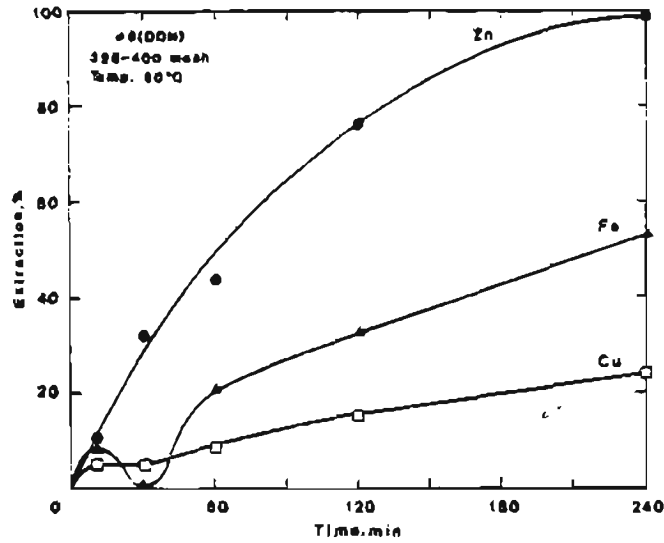
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Figure 12   Ferric sulfate leaching of ore sample #6; solid/liquid = 50 g/0.7L; initial concentration: Fe³⁺ 113.8g/L, Fe²⁺ 30.4g/L, Zn 16.6g/L, Cu 0.57g/L, H₂SO₄ 1%. Loss of sample weight during leaching 34.8%.

Pure ferric sulfate solution in 5% sulfuric acid was applied as a leaching agent only in the tests carried out on sample #4 (Figure 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 13).
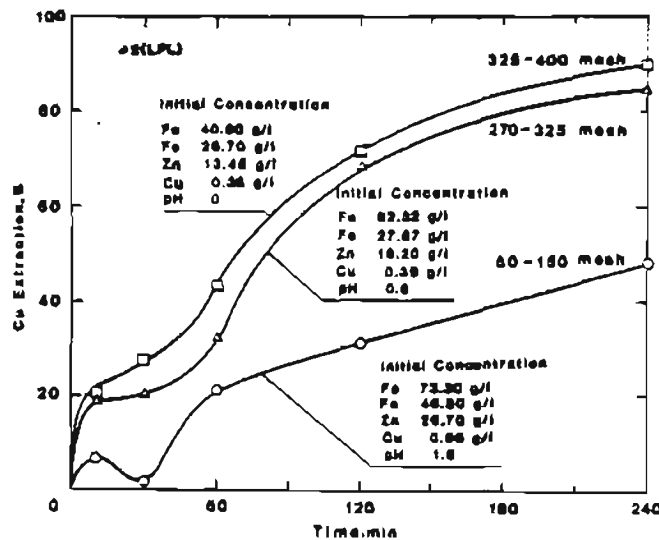

Figure 13   Ferric sulfate leaching of ore sample #2. Effect of iron(III) concentration and pH of leaching solution on copper extraction from 3 different size fractions of the ore at 90°C. Solid/liquid = 50 g/0.7L

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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 11 and 12). Another cause of iron precipitation during the leaching of sample #4 might be its high arsenopyrite - FeAsS concentration (Figures 9 and 10). Arsenates of iron(II) and iron(III) can be easily precipitated from low acidity solutions (Figure 10).

In the case of sample #3, high concentration of iron sulfide FeS (see Table 2), caused fast and total reduction of ferric sulfate long before leaching was completed. Under the test conditions (Figure 9) only fifty percent of the FeS was decomposed due to the lack of leaching agent.

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 (see p. 7). 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 14-19).

Metals extraction and loss of weight of the samples after 4 hours of leaching is compared in Table 6.

Two stage leaching tests were performed on sample #1 and 2 (Figures 14 and 15). Results indicate that prolongation of leaching time for an extra 2-4 hours raises the yield of metals extraction.
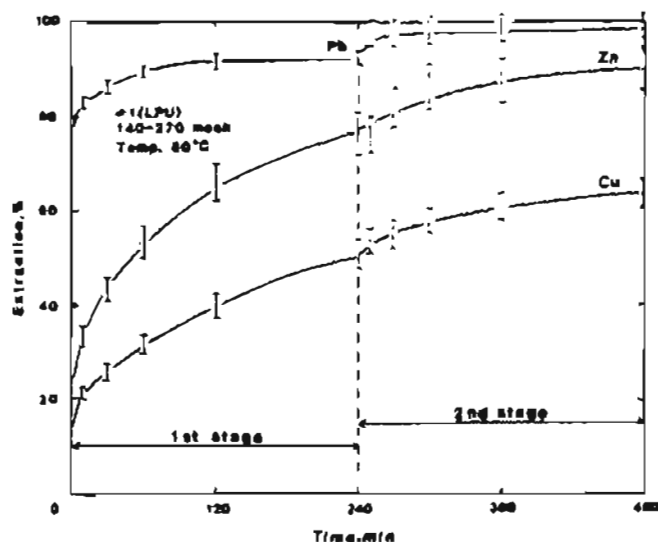
Figure 14   2-stage ferric chloride leaching of ore sample #1; solid/liquid = 75 g/0.6L (1st stage) and 56.5 g/0.5L (2nd stage); initial concentrations: [CaCl₂] = 58g/L, [MgCl₂] = 79g/L, [HCl] = 0.4g/L, [Fe³⁺] = 99.8g/L (1st stage) and 64g/L (2nd stage).
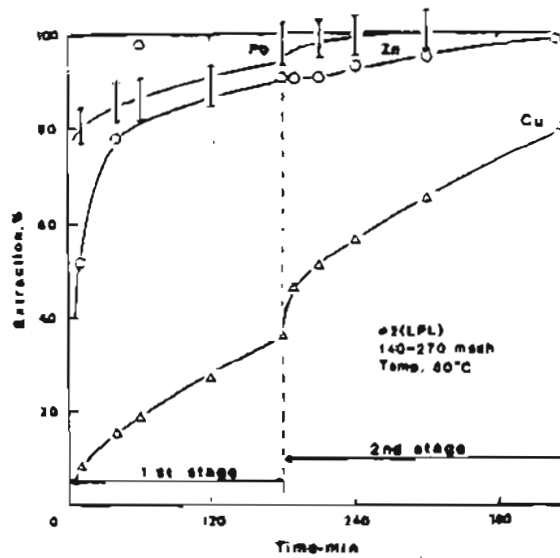
Figure 15   2-stage ferric chloride leaching of ore sample #2; solid/liquid = 55 g/0.6L (1st stage) and 42 g/0.6L (2nd stage); initial concentrations: $[CaCl_2]$ = 58g/L, $[MgCl_2]$ = 79g/L, [HCl] = 0.4g/L, $[Fe^{3+}]$ = 64g/L
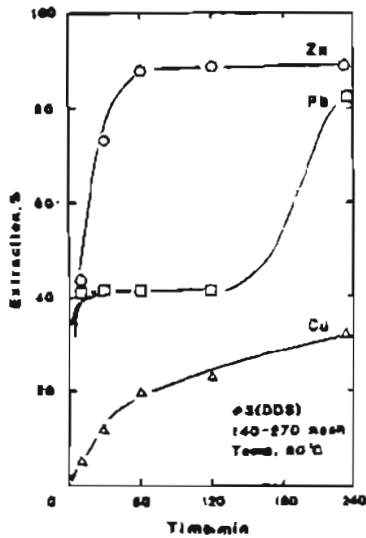
Figure 16   Ferric chloride leaching of ore sample #3;solid/ liquid = 50 g/0.64 L; initial concentrations: $[CaCl_2]$=58g/L, $[MgCl_2]$=79g/L, $[Fe^{2+}]$=90g/L, [HCl] = 4g/L .

Figure 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, $[Fe^{2+}]$=90g/L, [HCl] = 4g/L.

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Figure 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 .
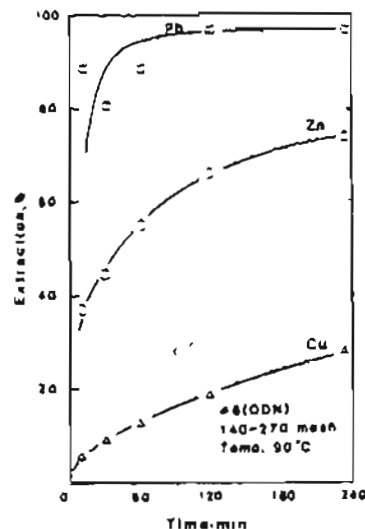
Figure 19 Ferric chloride leaching of ore sample #6;solid/ liquid = 20 g/0.6 L; initial concentrations: [CaCl$_2$]=58g/L, [MgCl$_2$]=79g/L, [Fe^{3+}]=94g/L, [HCl] = 4g/L .

Table 6. Metals extraction and loss of the samples weight after 4 hours of leaching. Fraction 140-270 mesh. Other conditions: see figures 14-19.

Sample	Metals Extraction (%)					Loss of weight (%)
	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

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The results of lead extraction from sample #3 differ from that in other cases (Figure 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 1).

Iron extraction is very low or some part of iron precipitates from solution at low acid concentration (Table 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 6). Some regularity with copper extraction is observed.

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 Chapter 2. The quantitative compositions of the samples wererepresented in Tables 1 and 2 and the leachability of the samples in ferric sulfate solution is described in Chapter 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 Chapters 3 and 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 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 21.
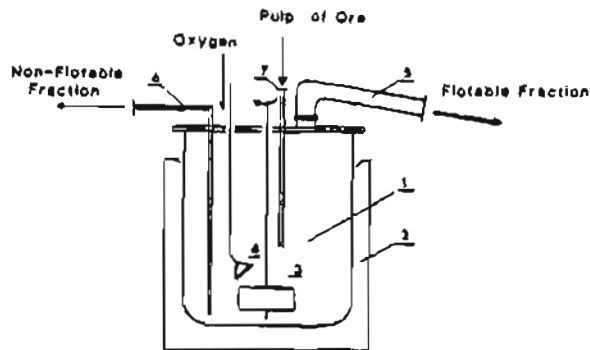
Figure 20   Laboratory reactor for leaching-flotation tests:
1. Glass reactor
2. Heater
3. Stirrer
4. Gas dispersion tube (medium porosity)
5. Outlet of foam (flotable fraction)
6. Outlet of non-flotable fraction
7. Inlet of ore pulp

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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 22). The 3rd and 4th L-F tests were followed
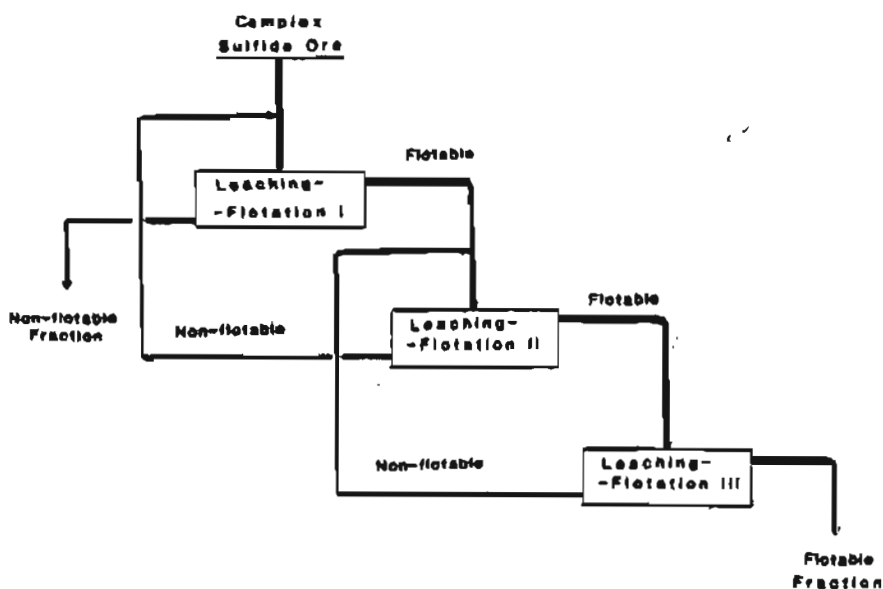
Figure 21   Simplified flowsheet of 3-step leaching-flotation test.
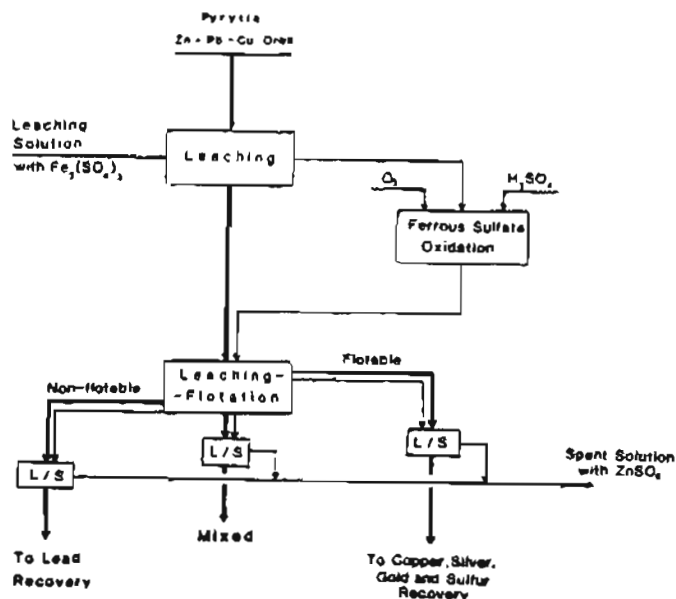
Figure 22   Arrangement of the 1st, 2nd and 5th L-F tests. Leaching-flotation steps follow initial sulfate leaching step.

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by sulfate leaching of the flotable fractions and by chloride leaching of the nonflotable fractions (Figure 23).

General conditions of the leaching-flotation tests are presented in Table 7.

The 1st and 5th experiments were performed with small solid samples in the one, 1L volume unit (Figure 20). The flotation products were cleaned in additional flotation steps, according to schematic flowsheet shown in Figure 24. The intermediary fractions were collected together as a "MIXED" fraction.

Results and other conditions of the tests are summarized in Tables 8 and 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.
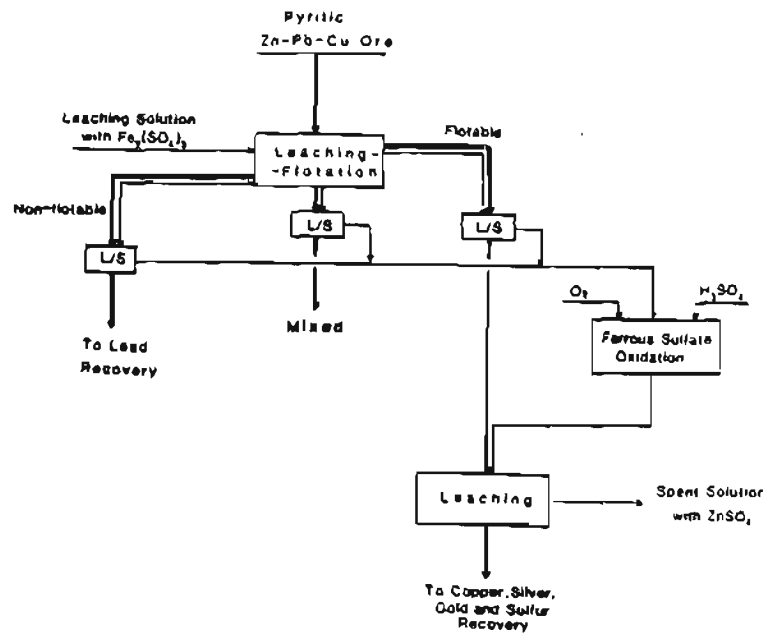
Figure 23 Arrangement of the 3rd and 4th L-F test. Sulfate leaching follows leaching-flotation step.
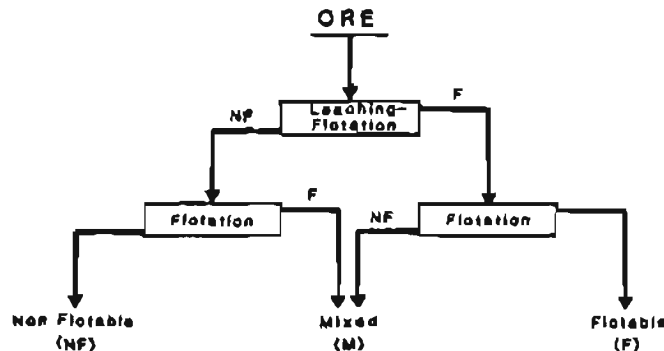
Figure 24 Scheme of the leaching-flotation batch experiments.

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Table 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	140-375	140-270	325-400
Total volume of solution (L)		0.83)	2.8	3.0	3.33	1.84)
	Fe^{3+}	45.3	74.7	70.0	84.4	20.0
Initial concentration (g/L) and pH in solution	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. 22
    B - according to scheme in Fig. 23
    1 - bath process, according to Fig. 24
    2 - 3-step continuous process, according to Fig. 21

Table 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	30.45	2.04	105ppm	nd
	NF	14.63	0.06	14.89	0.06	0.2	–	93.4ppm	–
	M	8.94	0.08	4.74	0.02	9.2	1.7	92.0ppm	nd
	F	68.46	2.45	1.33	0.33	43.2	7.19	176.4ppm	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	32.25	–	92.60ppm	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 (%).

		Zinc	Lead	Copper	Iron	Sulfur	Silver	Gold
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 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 9. Leaching flotation test of sample #4 (TRIO)

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

| | Specification | Fraction Distribu-tion, % | Concentration (%) | | | | | Conc. (ppm) | |
			Zinc	Lead	Copper	Iron	Sulfur[2]	Silver	Gold
4th Experiment	Ore	100	7.50	7.30	1.35	25.03	–	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	3.12	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)

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		56.7/92.75)	–	81.3[6]	8.4	–	nd	–

Notes 2-6 as in Table 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 8 and 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 25 and 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 6.

The flotable fraction from the 3rd experiment (Tables 7 and 8) was leached with the solution from the L-F step, after the solution had been regenerated under elevated oxygen pressure (see p. 30 and 31). The resulting zinc and copper extractions

Ore Sample #1(LPU)
150.45 g   Ag 92.6 ppm (100%)
           Au 3.004 ppm (100%)
① Sulfate Leaching
132.04 g   Ag 105. ppm (99.6%)
  -        Au 3.42 ppm (100%)
② Leaching & Flotation
NF 19.84 g   Ag 100. ppm (14.2%)   Au 0.17 ppm (8.6%)
F 110.08 g   Ag 106. ppm (83.7%)   Au 4.09 ppm (99.5%)
③ Leaching & Flotation
Heavy 11.84 g   Ag 137. ppm (11.8%)   Au 0.17 ppm (0.4%)
White 8.00 g   Ag 48. ppm (2.6%)   Au —
④ Leaching & Flotation
NF 57.60 g   Ag 89. ppm (36.8%)   Au 3.8 ppm (48.5%)
F 52.48 g   Ag 125. ppm (47.1%)   Au 4.39 ppm (51.0%)
⑤ Leaching & Flotation
NF 4.16 g   Ag 155. ppm (4.83%)   Au 2.16 ppm (2.60%)
F 52.24 g   Ag 85.62 ppm (32.1%)   Au 4.13 ppm (47.8%)
⑥ Leaching & Flotation
NF 2.45 g   Ag 88. ppm (1.5%)   Au 2. ppm (1.1%)
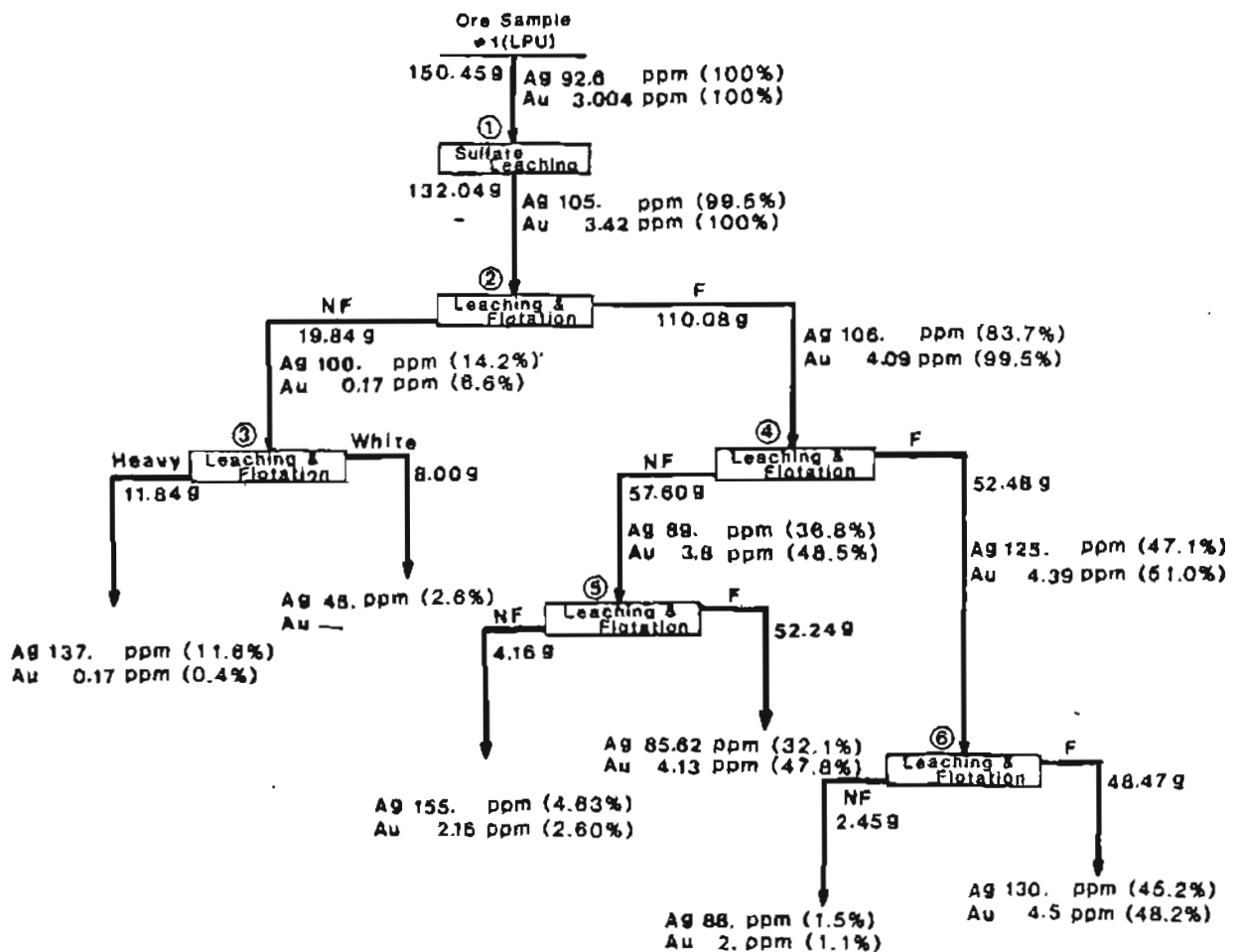F 48.47 g   Ag 130. ppm (46.2%)   Au 4.5 ppm (48.2%)

Figure 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 8.

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are presented together in Figure 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 27 by the dashed lines. After two hours 98.5% of total zinc and 64% of total copper were recovered.
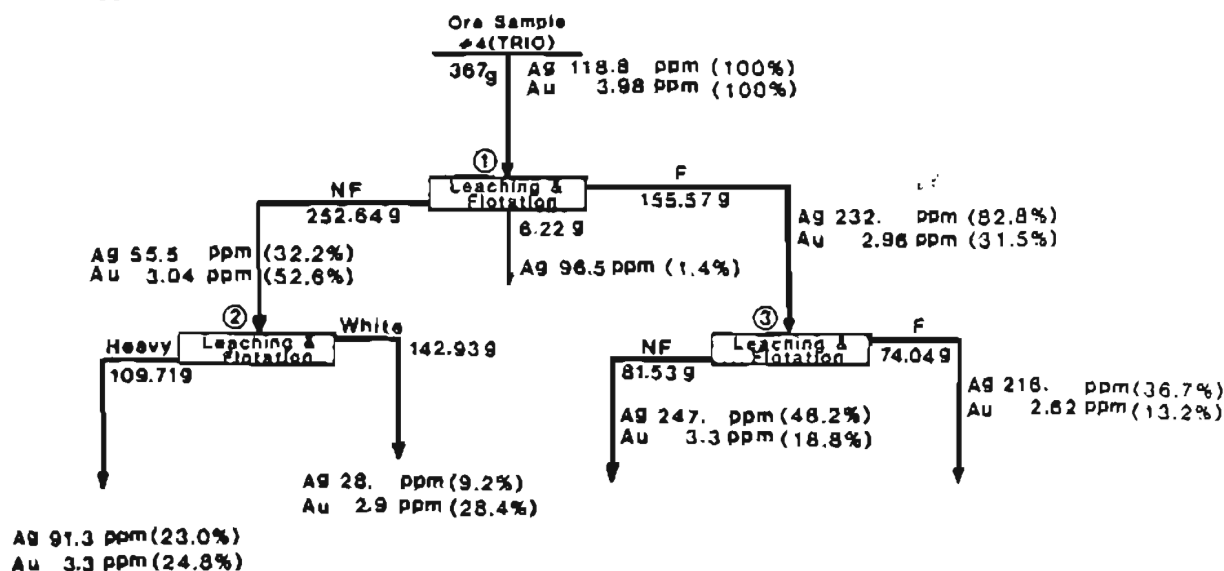

Figure 26 Multistage leaching-flotation test. Silver and gold concentrations (ppm) and distribution (%). Other metal distribution in 1st L-F step - see 4th experiment in Table 9.
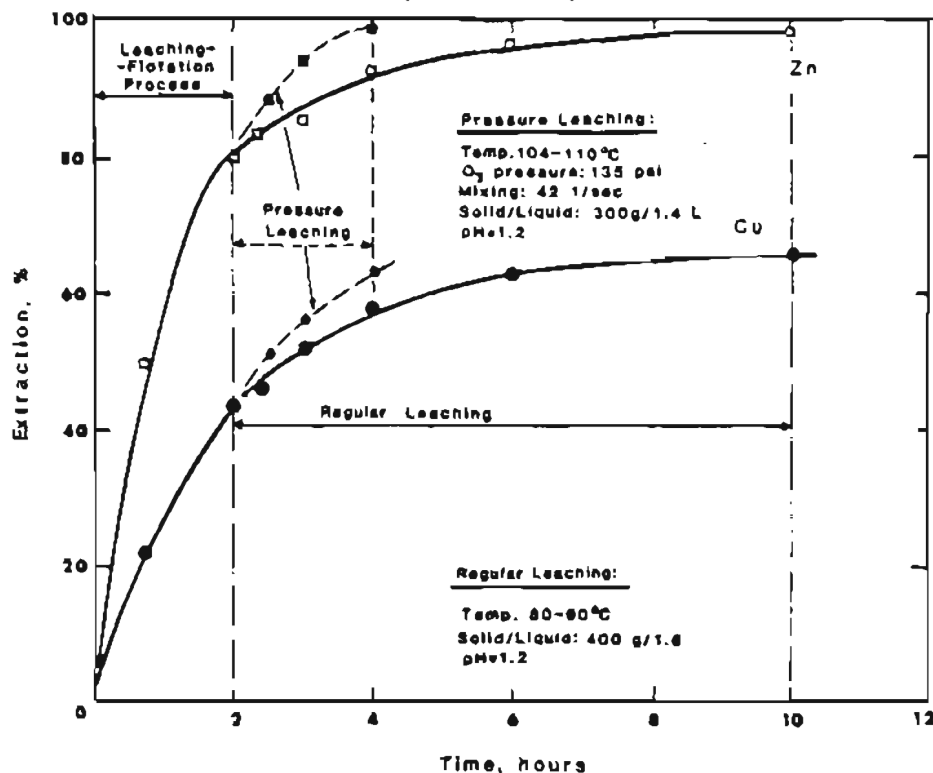

Figure 27 Zinc and copper extraction during leaching-flotation and leaching tests. Dashed line: pressure leaching test (other conditions - see text and Tables 7 and 8).

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The nonflotable fraction from the 4th experiment (Tables 7 and 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 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 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 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 28).
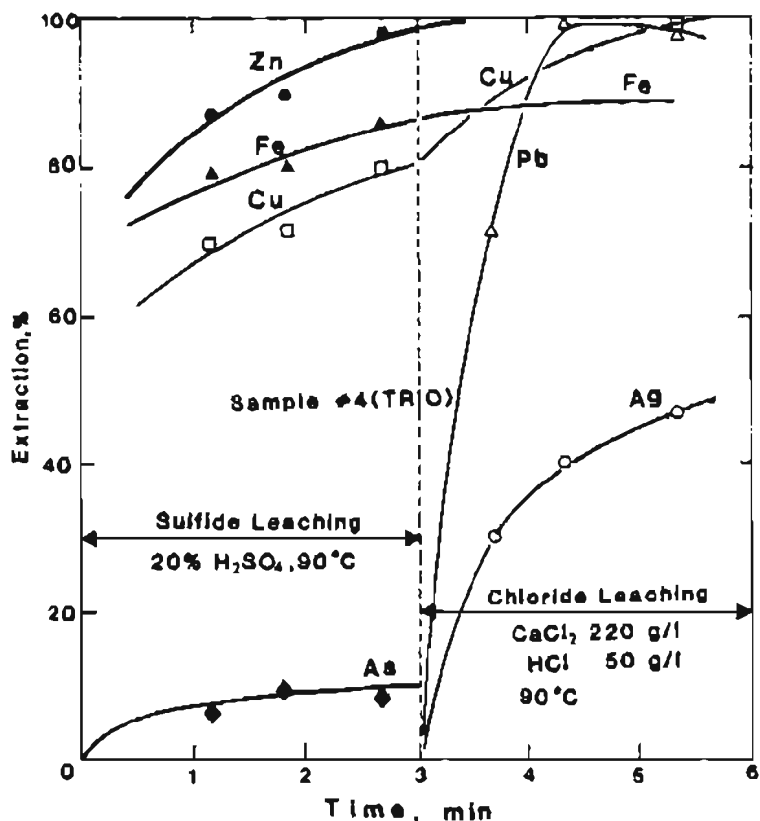

Figure 28   Metal extraction from "white" non-flotable fraction during sulfate and chloride leaching tests. Ore sample #4 (TRIO) after 4th L-F experiment. Solid/liquid = 40g/0.7L. Initial contents of metals in solid: Zn 0.4%, Pb 9.7%, Cu 0.1%, Fe 22.4%, As 6.3%, Ca 5.7%, Ag 28 ppm, Au 2.9 ppm.

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 easy 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 $CaSO_4 \cdot 2H_2O$:

$$PbSO_{4(s)} + Ca^{2+} + 4Cl^- + 2H_2O = PbCl_4^{2-} + CaSO_4 \cdot 2H_2O_{(s)} \tag{4}$$
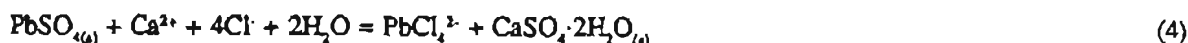
Lead extraction, by calcium chloride solution, from the "white" and the "heavy" nonflotable fractions is presented in Figure 29. Both fractions were separated from the bulk nonflotable fraction obtained from sample #1 during the 3rd L-F experiment (Table 8 and Figure 25). Reaction (4) is very fast and 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 9 and Figure 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 (p. 13-14) 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 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 9 and Figure 26) are presented in Figure 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 32 and 33, and of sample #4 in Figure 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.
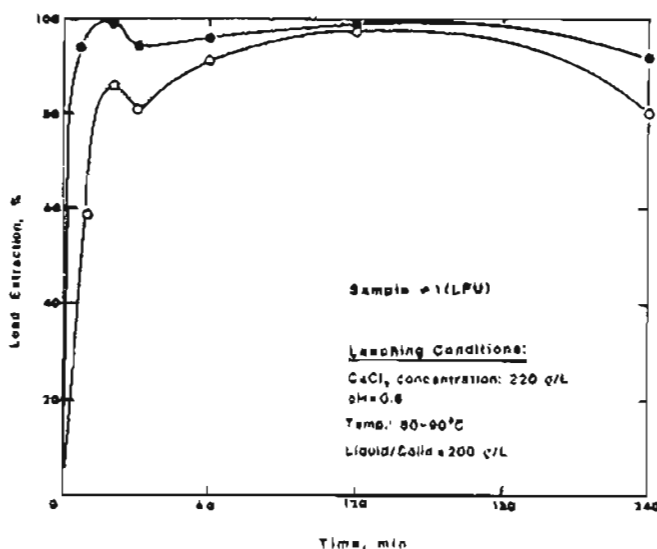

Figure 29   Lead extraction by calcium chloride solution from two non-flotable fractions: ● - "white" fraction, o - "heavy" fraction.

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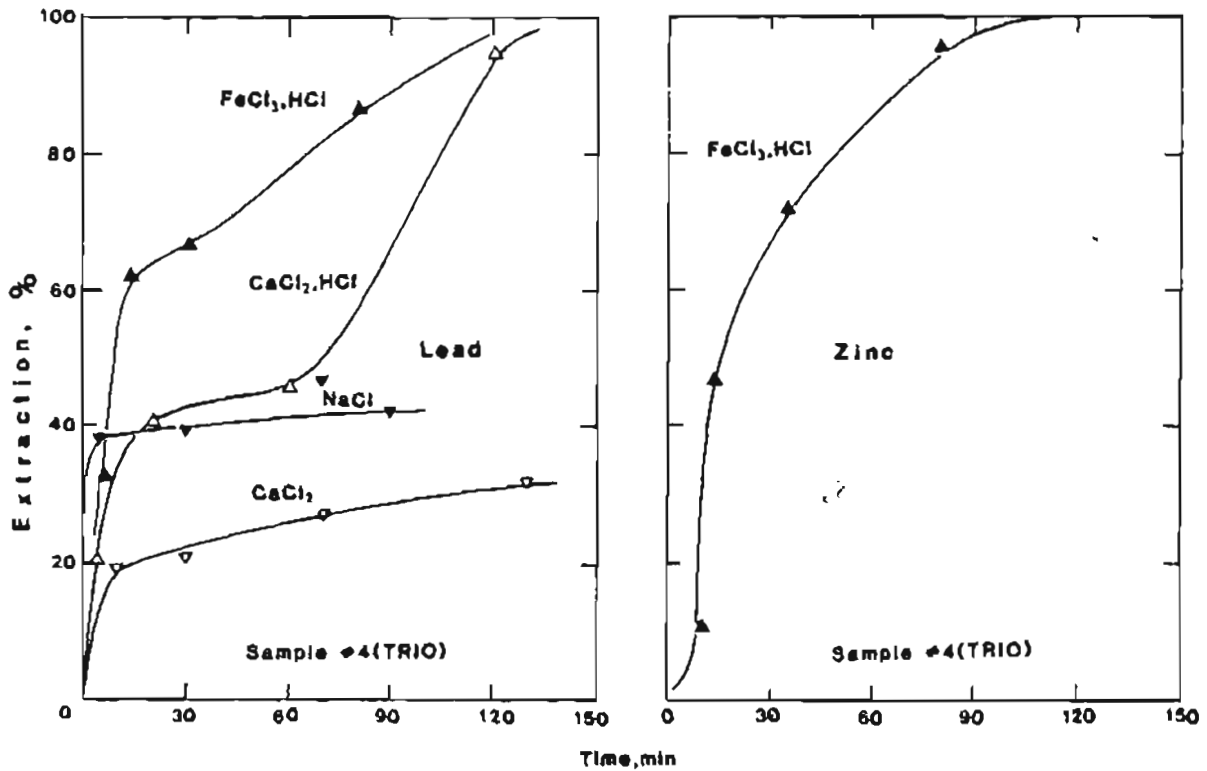
Figure 30 Lead and zinc extraction from "white" nonflotable fraction after 4th L-F experiment (Table 9 and Figure 26), during chloride leaching tests. Liquid/solid = 10g/0.3L Temp. 90°C. a) lead extraction in: sodium chloride - 234g/L, calcium chloride - 220g/L, calcium chloride - 166g/L, with hydrochloric 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.
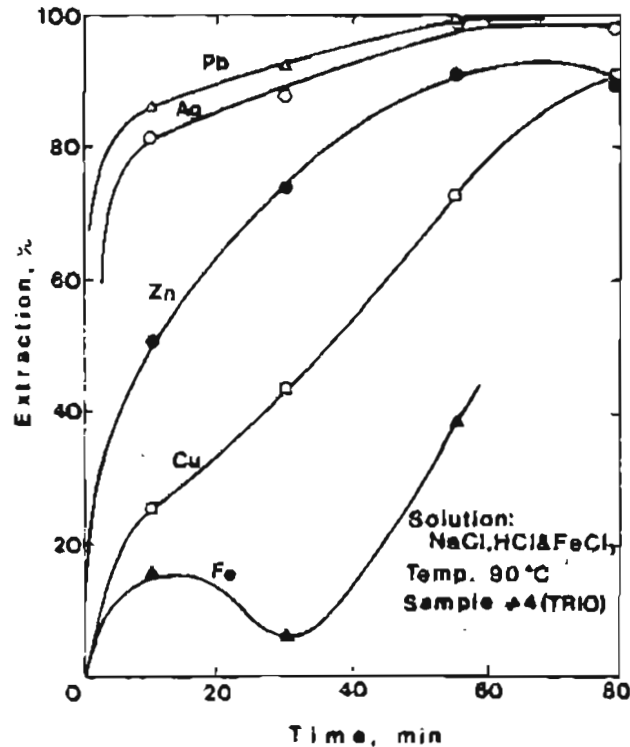
Figure 31 Ferric chloride leaching of "heavy" nonflotable fraction after 4th L-F experiment (Table 4). Initial metal concentration in solid fraction: Fe 31.75%, Zn 7.35%, Pb 5.84%, Cu 1.29%, As 6.72%, Ag 91.4 ppm, Au 3.26 ppm. S/L = 30g/0.7L Initial composition of solution: NaCl 164g/L, HCl 9g/L, Fe³⁺ 20.2g/L Temp. 90°C.

26
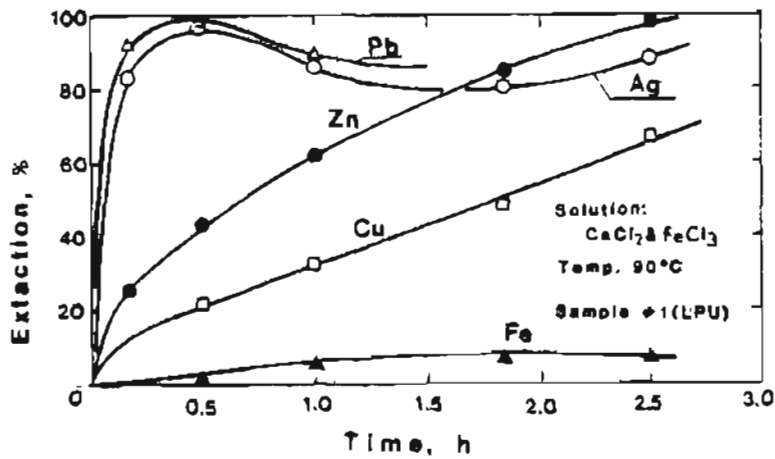
Figure 32 Ferric chloride leaching of flotable fraction after 3rd L-F experiment (Table 8). Initial metals concentration in solid: Fe 35.7%, Zn 0.38%, Pb 1.15%, Cu 0.19%, Ag 96 ppm. S/L=300g/1L. Initial composition of solution: CaCl$_2$ 220g/L, HCl 44g/L, Fe 48g/L, Zn 2.8g/L, Pb 4g/L, Cu 340mg/L, Ag 96mg/L.
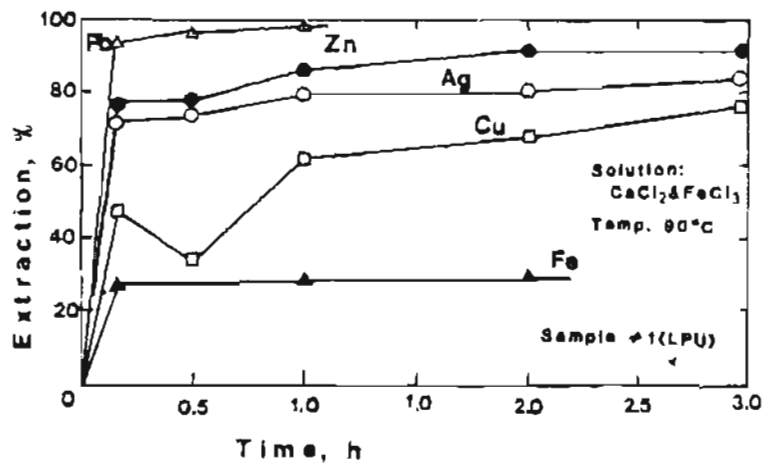
Figure 33 Ferric chloride leaching of flotable fraction after 2nd L-F experiment (Table 8). Initial metals and sulfur concentration in solid: Fe 43.2%, Zn 2.45%, Pb 1.33%, Cu 0.33%, Ag 176ppm, S° 7.2%. S/L = 250g/L. Initial composition of solution: CaCl$_2$ 220g/L, Fe^{3+} 74g/L, pH 0.7.
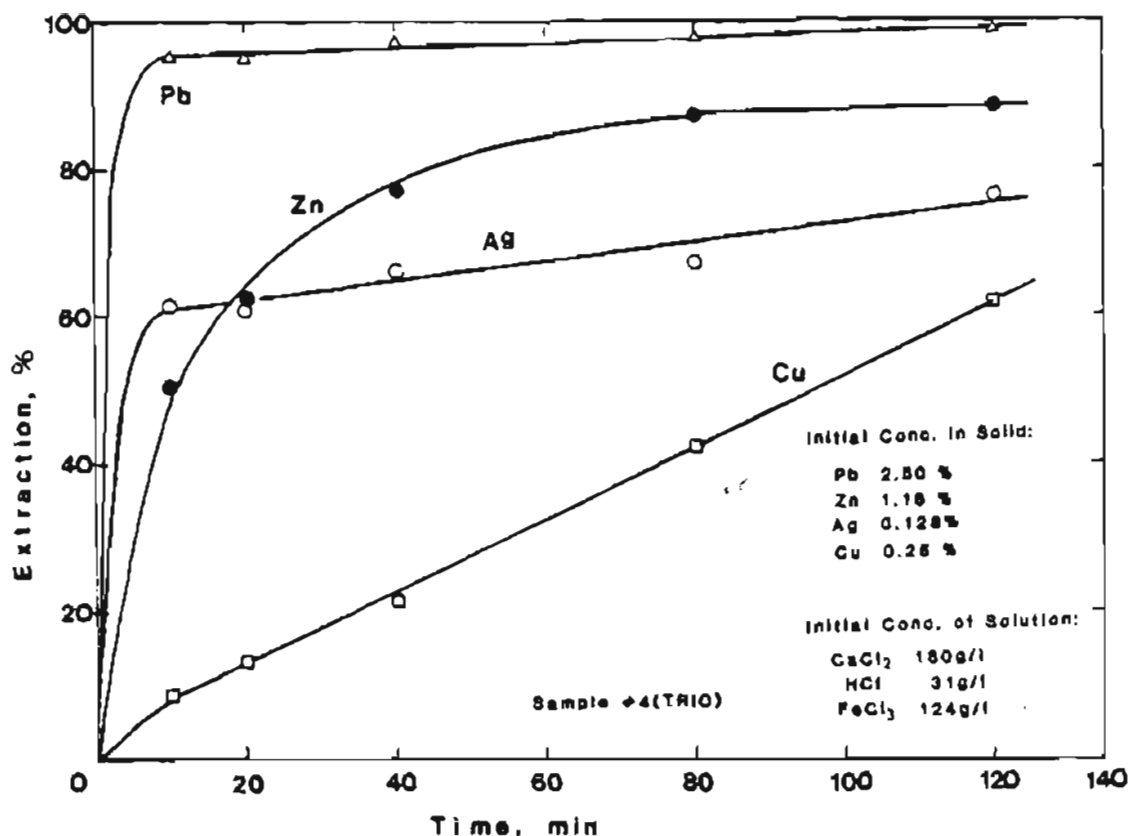
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Figure 34 Ferric chloride leaching of the flotable fraction after 5th L-F experiment (Table 9). S/L = 50g/0.7L pH 0.2 Temp. 90°C.

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 10 to actual sulfur yield from sulfate leaching and leaching-flotation tests (Tables 8 and 9). As indicated in Table 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.

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(SO₄)3] = 25 g/L, [H₂SO₄] = 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 11.

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Table 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 8 and 9; only for ore samples #1 and #4
nd   not determined

Table 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%

9. IRON OXIDATION BY OXYGEN

Iron oxidation of spent leach solutions accomplishes three goals:

- regeneration of the leach solution:

$$2Fe^{2+} + 1/2\ O_2 + 2H^+ = 2Fe^{3+} + H_2O \tag{5}$$

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

$$2FeCl_3 + 3CaO + H_2O = 2FeOOH + 3CaCl_2 \tag{6}$$
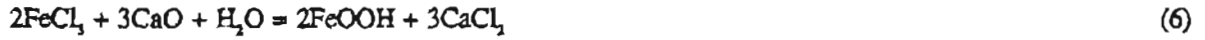
- purification of zinc sulfate solution prior to electrolysis:

$$2FeSO_4 + 1/2\ O_2 + 3H_2O = 2FeOOH + 2H_2SO_4 \tag{7}$$

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.

$$6Fe^{2+} + 3/2\ O_2 + H_2O = 2FeOOH + 4Fe^{3+} \tag{8}$$

The kinetics of such an oxidation are shown in Figure 35 and typical conditions are described briefly in Table 12. For the most part, solutions applied in the sulfate leaching and leaching-flotation experiments were regenerated using this technique.
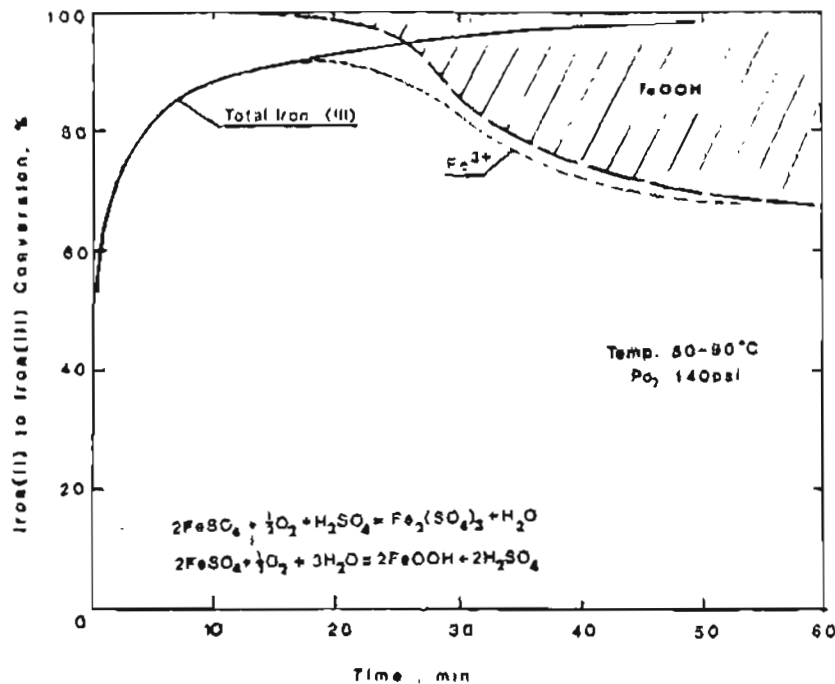

Figure 35 Typical characteristics of ferrous sulfate oxidation by oxygen with partial precipitation of iron as FeOOH.

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Table 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

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 3, 5 and 6.

Zinc   **Extraction**

-    Direct nonoxidative leaching with HCl solution: 81%[1]

-    Direct oxidative leaching with FeCl3 solution (2-step):   95-97%[2]

-    Direct oxidative leaching with Fe2(SO$_4$)$_3$ solution (2-step):   89%
     with a subsequent leaching-flotation step: 96.9%

-    Direct leaching-flotation processing: 79%
     with subsequent leaching by Fe2(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 FeCl₃ solution:	96-97%[2]
-	Leaching of the nonflotable fractions with CaCl₂ + HCl solution: with additional recovery of lead from the flotable fraction during	52-79%
	FeCl₃ leaching (simultaneous with copper and silver recovery:	96-99%

Silver		Extraction
-	Direct oxidative leaching with FeCl₃ solution:	85%[1,2]
-	Leaching of the flotable fraction with FeCl₃ solution: with additional silver recovery from the nonflotable fractions	70-86%[3]
	during CaCl₂ - 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 FeCl₃ leaching of flotable fractions:	71.4%[3,4]
-	Cyanide or thiourea leaching of the solid residue after sulfur extraction: with additional gold recovery from the selected "heavy" nonflotable	88.7%[3,4]
	fraction:	~90-92%[3,5]

Sulfur		Extraction
-	Extraction with xylene from solid residue of the flotable fraction after FeCl₃ 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 FeS₂.

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.

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 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 step during nearly
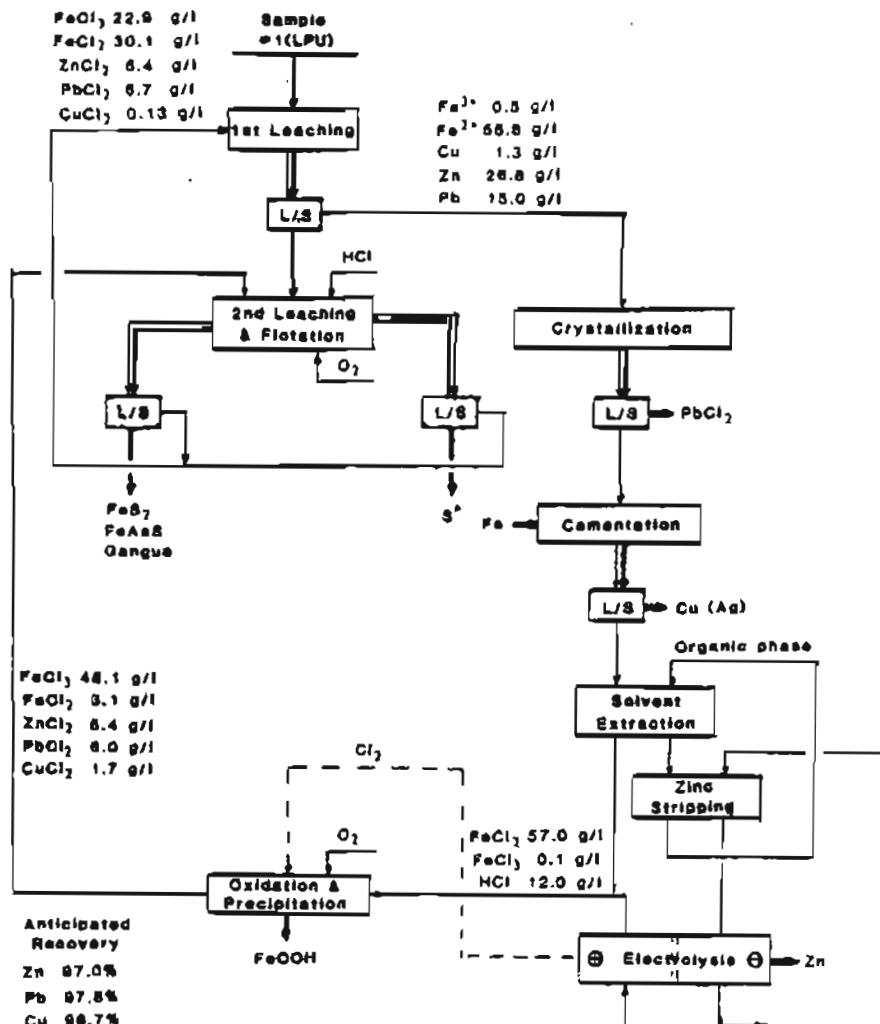

Figure 36 Flowsheet of the ore treatment with direct ferric chloride leaching. Only the main components of solution are indicated.

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 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 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 37 and 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 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 Fig. 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 [21]

Figure 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.
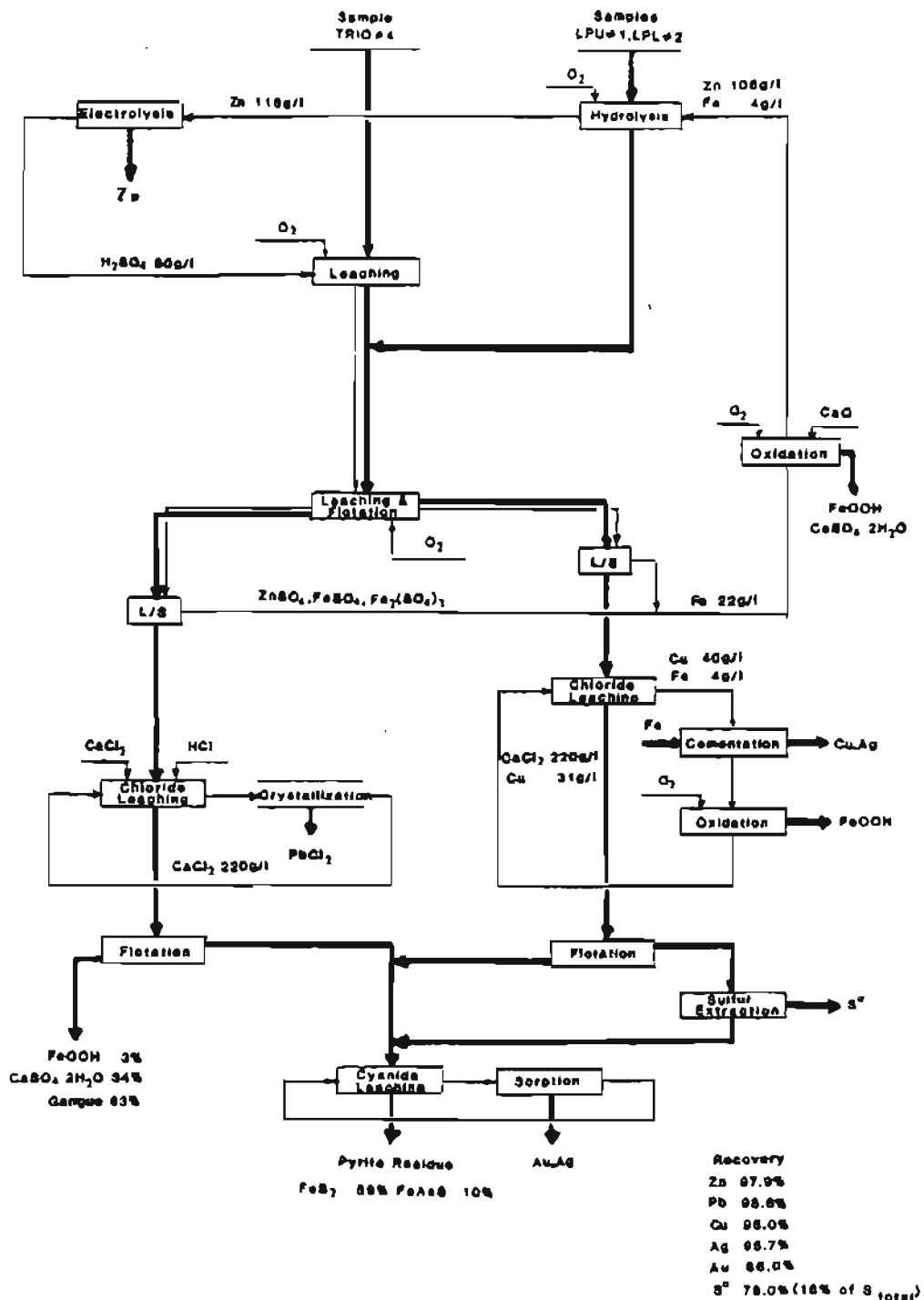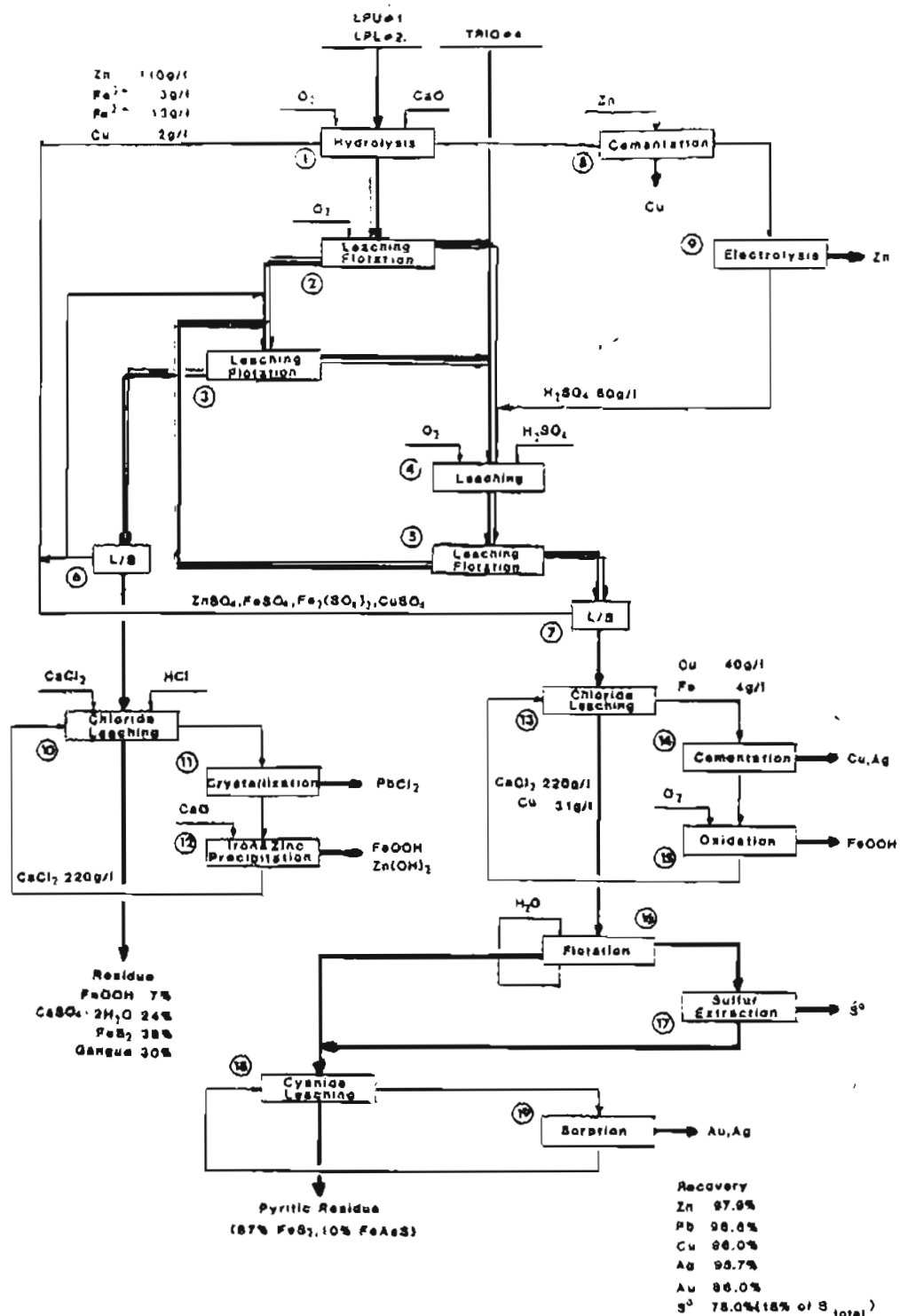
Figure 38 Flowsheet of the 2nd variant of the ore treatment with leaching-flotation steps in ferric sulfate solution. Only the main components of solution are indicated. Numbers in circle correspond to the unit processes numbers in Table 16.

pyritic fractions. The process presented in Figure 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 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 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:

$$FeS + 1/2\ O_2 + H_2SO_4 = FeSO_4 + H_2O + S° \tag{9}$$

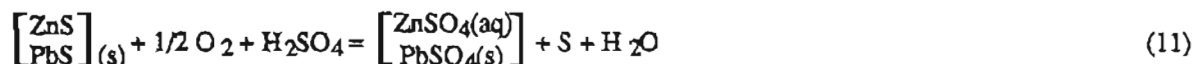$$2FeSO_4 + 1/2\ O_2 + H_2SO_4 = Fe_2(SO_4)_3 + H_2O \tag{10}$$
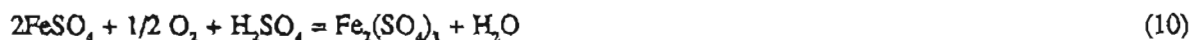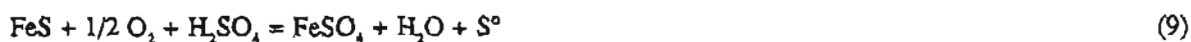
The sulfuric acid consumed in these reactions is supplied by spent electrolyte after zinc electrolysis (Figure 37).

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:

$$FeSO_4 + 1/2\ O_2 + 3H_2O = 2FeOOH + 2H_2SO_4 \tag{7}$$

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:

$$\begin{bmatrix} ZnS \\ PbS \end{bmatrix}_{(s)} + 1/2\ O_2 + H_2SO_4 = \begin{bmatrix} ZnSO_4(aq) \\ PbSO_4(s) \end{bmatrix} + S + H_2O \tag{11}$$

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_4·2H_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 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 38). The removal of excess iron and other components contaminating chloride solutions is also shown in Figure 38. Consumption of reagents and other anticipated data for the treatment of 1 t of mixte ore are presented in Table 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 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. 37
2) After Fig. 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

13. PRELIMINARY ECONOMIC EVALUATION

The cost of the reagents and electricity consumed according to the 1st sulfate flowsheet (Figure 37) is 38.60 $/t of the ore, and 42.55 $/t for the 2nd flowsheet (Figure 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 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.

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 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 38 is shown in Figure 39. The ore (14t/h) is fed simultaneously into a 3-phase reactor (1) and a leaching-flotation multi-

Table 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) Total[2]		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 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. 38 and 39).

Opera-tion No.	Unit Process	Prin-cipal Reaction No.	Conditions and Parameters	Rate of Process[1]	Apparatus type, Materials, Equipment	Study[2] Required	Reference to the Knowledge Level[3]			
							Lab.	Pilot	Indus-try	Other Rmks
1	Hydrolysis	8,9, 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	(21) 22. 23	24 (25)		
2,3	Leaching-Flotation	1,2, 3,5, 7.8	Two steps of L-F process in ferric sulfate solution; Temp. 80-90°C, P_{O_2}=50-100 psi, pH = 1-2	Mod-erate	Continuous,gas/liquid/solid pressure flota-tion column,with centrifugal separa-tion of liquid/solid/oxygen suspension; minimum 4 mixing/flotation units in one column	Lab. Study Eng. Study	15	(26) 27		
4,5	Leaching-Flotation	1,2, 3,10	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 flota-tion column,with centrifugal sep-aration of suspen-sion with higher capacity than for operation 2 & 3, Min. 6 mixing/flo-tation units in one column	Lab. Study Eng Study		(26) 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.			26	known
7	Filtration	—	Coarse flotable fraction of sul-fur and not reac-ted sulfides; pressure 40-90 psi temp. 70-80°C; Separation of oxygen necessary	Mod-erate	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.			26	known

Table 16. (cont.)

Opera-tion No.	Unit Process	Prin-cipal Reaction No.	Conditions and Parameters	Rate of Process[1]	Apparatus type, Materials, Equipment	Study[2] Required	Reference to the Knowledge Level[3]			
							Lab.	Pilot	Indus-try	Other Rmks
8	Cementation	12[4]	Cementation of copper by zinc from purified zinc sulfate solution with solid particles sedimentation	Fast	Standard thickener	Ind. Proj.			27	known
9	Electrolysis	13[5]	Zinc electrolysis; [Zn] from 110 g/L to 60 g/L	Slow	Standard electrolyzers	Ind. Proj.			27	known
10	Calcium chloride leaching	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.		(11)		
11	Crystal-lization		Crystallization about 30% of Pb in form of $PbCl_2$ crystals, by cooling from 80-90 to 50-60°C	Mod-erate	Crystallizer with continuous separations of crystals by cyclone or centrifuge; moderate corrosion by chlorides	Test Lab.			30	
12	Precipi-tation	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.	(21) 22, 23	24 (25)		
13	Ferric chloride leaching	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	Mod-erate	Typical vessel reactors, thickener and belt-filter, strong corrosion by chlorides	Consr. Proj.	7-9	11		
14	Cementa-tion	12[4]	Cementation of copper and silver by iron or scrap	Fast	Column system with fixed bed of iron pellets	Lab. and Eng. Study	27			
15	Oxidation	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.	(21) 22, 23	24 (25)		

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) $Zn + CuSO_4 = ZnSO_4 + Cu$ (12)
5) $ZnSO_4 + H2O = H_2SO_4 + Zn$ (13)
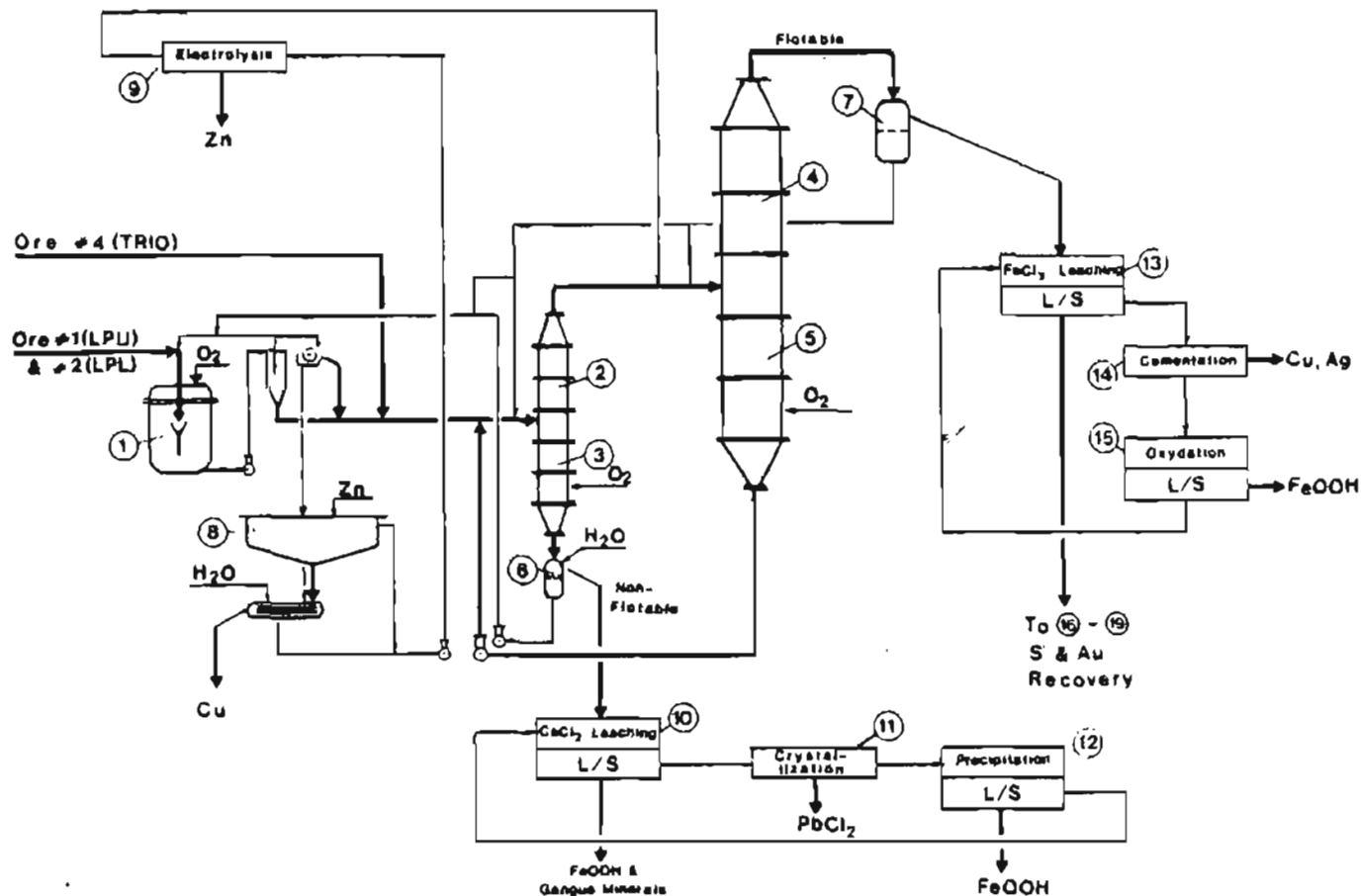6) $CuFeS_2 + 4FeCl_3 = CuCl_2 + 5FeCl_2 + 2S$ (14)

Figure 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 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 m3, 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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