

HYDROMETALLURGY OF THE DELTA SULFIDE ORES

Second Stage Report

Submitted to:

Nerco Minerals Company

by:

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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.

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 (1986) LPU ore-sample. The tests were carried out to confirm results described in the 1st stage report (1986)¹⁾.
2. Fluidized-Bed Leaching and Flotation tests conducted on the new (1987) 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.

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 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.

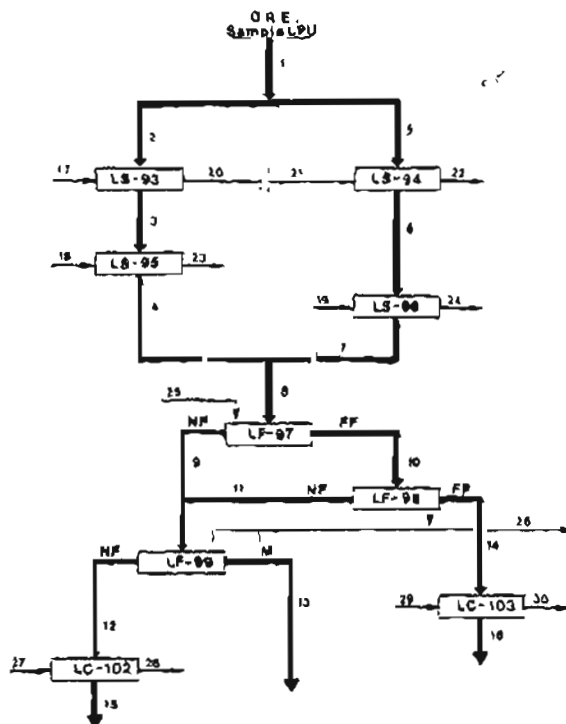


Figure 1 Experiments flowsheet carried out with the old ore sample LPU (1986). LS-93 to LS-96: ferric sulfate leaching under atmospheric pressure; LF-97 to LF-99: 3-step flotation under atmospheric pressure in the ferric sulfate solution; LC-102: calcium chloride leaching; LC-103: ferric chloride leaching; NF - nonfloatable fraction; FF - floatable fraction, M - mixed fraction. The numbers identify flows according to Table 1 and 2.

Three fractions were collected after LF processing: non-flotable (NF), mixed (M) and floatable 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 1. Metal concentration in solutions are shown in Table 2.

Metals extraction at different stages of processing, calculated from the mass balance in solids, is presented in Table 3 and extraction progress during the leaching steps is shown in Figure 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 4.

General results of these tests confirm the data presented earlier in the 1st stage report (1986). Even with only half

Table 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 1.

Specifications		ID No ^{*)}	Weight Grams	Grams in Solids (Ag: milligrams)					
				Cu	Fe	Zn	Pb	Ag	Ca
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	
Ferric Sulfate Solution	2nd Steps of Leaching	5	200	0.76	64.5	13.26	5.66	18.54	
	After LS-94 to LS-96	6	194.84	1.58	60.5	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-Flouable 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	
	Flouable 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 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 2. Leaching-Flotation processing of the LPU (old) ore sample. Concentration and volumes of solutions used in experiments according to flowsheet in Figure 1.

Specifications		ID No ^{*)}	Volume (liters) ¹⁾	Concentration, g/l (Ag: mg/l)						pH
				Cu	Fe	Zn	Pb	Ag	Ca	
In Sulfate Solutions	Leaching solution inletting to LS-93	17	1.60	0.5	33.8	8.2	--	--	--	0.63
	Leaching solution inletting to LS-95	18	1.28	0.5	33.8	8.2	--	--	--	0.63
	Leaching solution inletting 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 inletting to LF-97	25	1.0	0.52	35.7	8.3	--	--	--	0.72
	Solution from LF-97-99 ²⁾	26	(1.5)	(0.44)	(34.7)	(6.4)	--	--	--	n.a.
In Chloride Solutions	Solution inletting to LC-102 ³⁾	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 inletting 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 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 1).

3) Recalculated from experiment carried out on 37.5g NF99 sample to the real weight of flow 12, i.e. 60.63g.

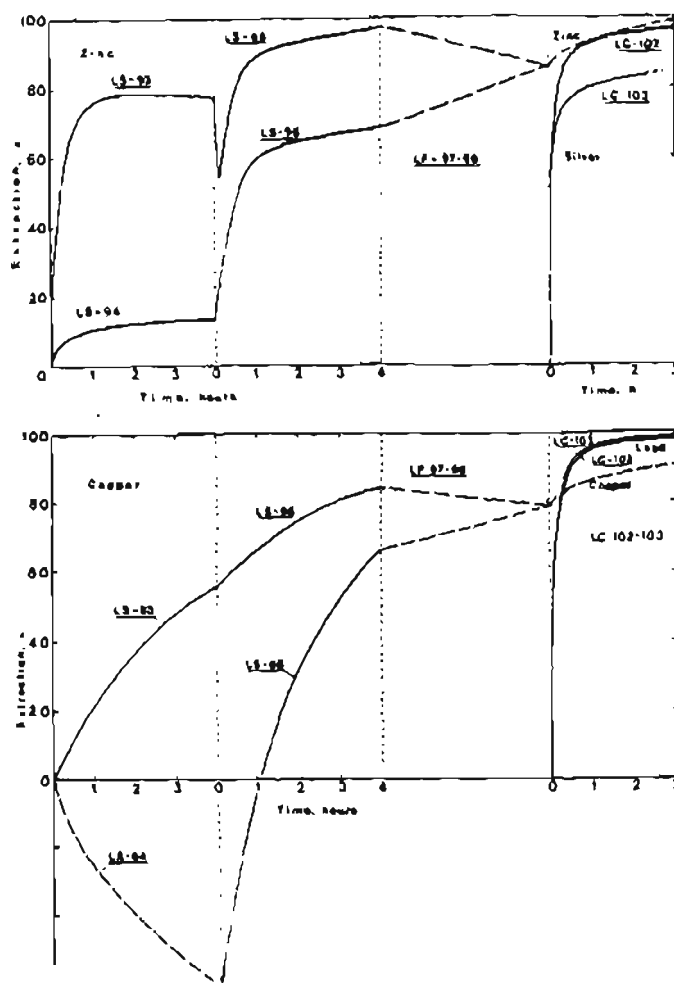


Figure 2 Progress of zinc, copper, lead and silver extraction during experiments carried out according to the flowsheet presented in Figure 1. Temperature 90-95°C.

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). 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). 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), new LPU ore is contacted with the to 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, in spite of drastic diminishing of the oxidation potential, 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 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

Table 3. Metals extraction during Leaching-Flotation processing of the LPU (old) ore sample (375-400 mesh) calculated from metals content in solids, according to the flowsheet in Figure 1.

Specification		Extraction %				
		Cu	Fe	Zn	Pb	Ag
Sulfate	After leaching LS-93	56.57	8.56	76.92	--	--
Leaching	After leaching LS-94	-60.5 ¹⁾	6.20	13.57	--	--
1st Step						
Sulfate	Cumulative after LS-93 and LS-95	84.6	12.96	96.15	--	--
Leaching	Cumulative after LS-94 and LS-96	70.46	16.01	81.56	--	--
2nd Step						
Sulfate	Cumulative after leaching LS-93-LS-95 and Flotation and LF-97-99	79.74	28.40	86.23	--	--
Leaching						
Chloride	From non-flotable (NF) fraction after CaCl ₂ leaching LC-102	14.3	22.4	39.6	98.04	96.32
Leaching	From floatable fraction (FF) after FeCl ₃ leaching LC-103	58.16	-13.3 ²⁾	97.24	89.18	87.43
Sulfate and Chloride Leaching	Total cumulative extraction after chloride leaching	91.3	19.14	99.54	89.96	85.25

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

**2) Calculated as $1 - \frac{((15) + (16))}{((1) - (13))}$; (1), (13), (15) and (16) amount of silver in the flows 1, 13, 15 and 16.

Table 4. Leaching-Flotation processing of LPU (old) ore sample. Metals partition among flotation fractions and solution (in weight percent).

	Weight grams	Per cent				
		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.

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 floatable fraction by ferric chloride leaching, is fast and easy (Figure 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

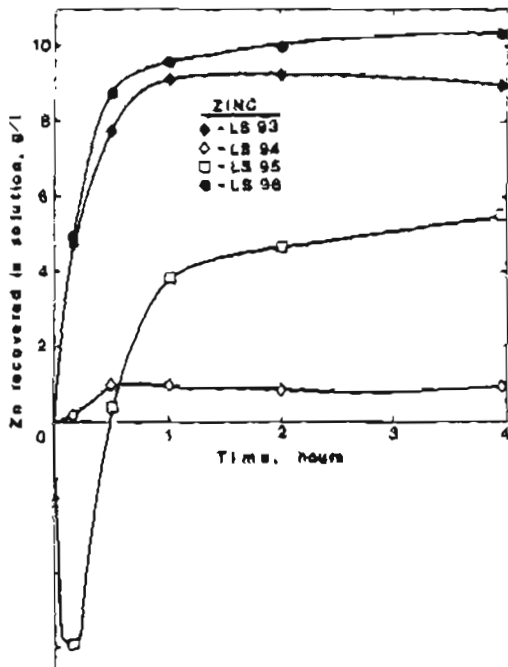


Figure 3. Zinc behavior during the leaching tests LS-93 to LS-96.

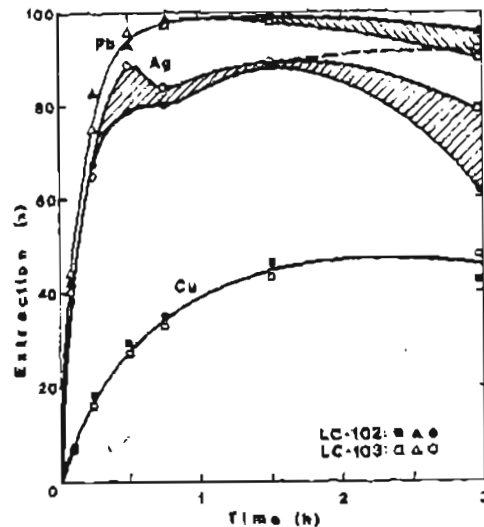


Figure 4. Behavior of silver leaching during the leaching tests LC-101 (CaCl_2 soln.) and LC-103 (FeCl_3 soln.). Temp. 90-95°C, other conditions and results: Table 1 and 2.

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%.
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 floatable fraction, while 74% of lead is collected in the non-floatable fraction.

3. Sulfate Leaching Under Oxygen Pressure

Process description

The laboratory installation built from Corning glass elements and schematically shown in Figure 5 is a mini-copy of the leaching section of the ore treatment plant³ suggested earlier.

The scale of this mini-pilot installation is 1:63,000 and the retention time of ore in the leaching reactor (R₁) 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

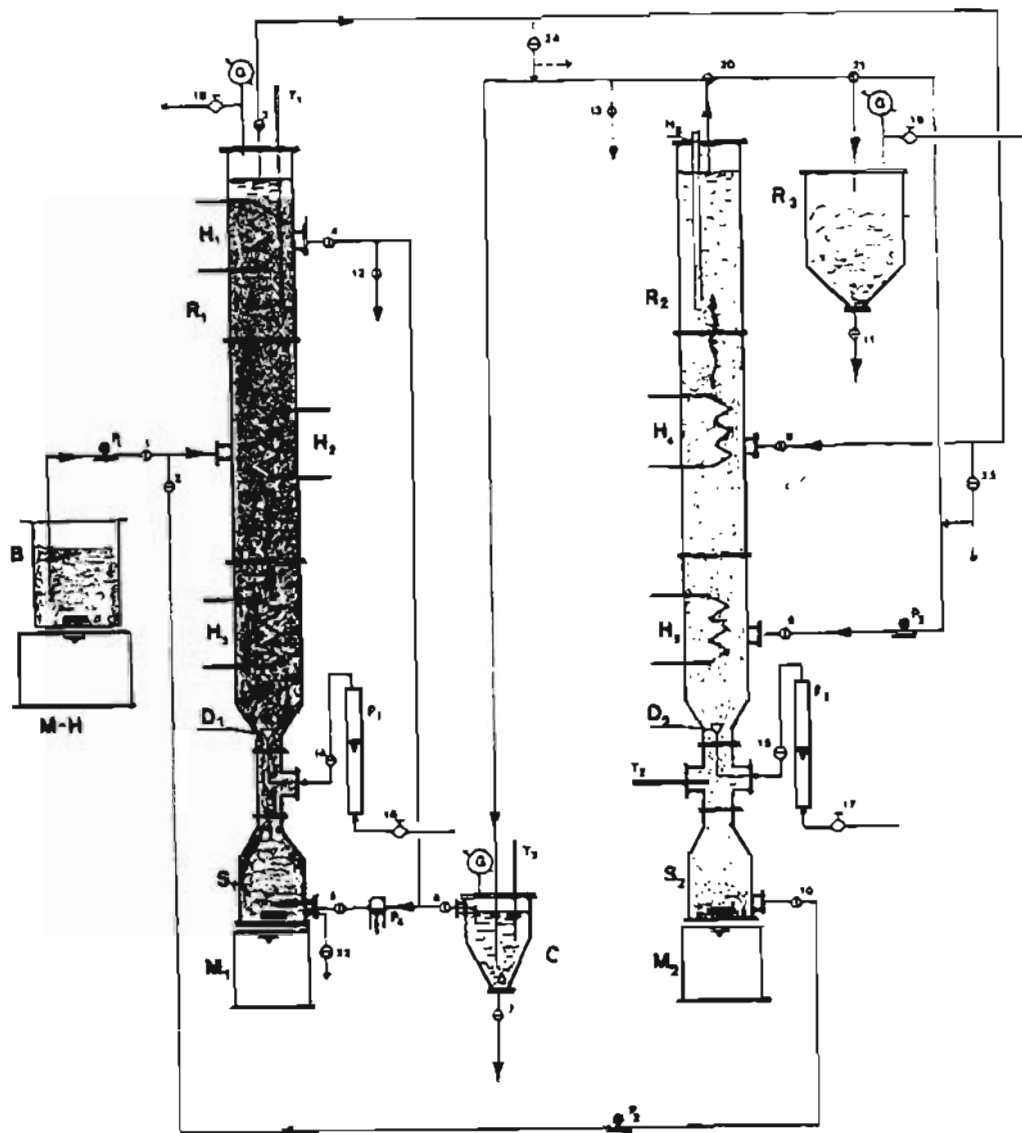


Figure 5. Laboratory Corning-glass installation for the continuous leaching and flotation under elevated pressure of oxygen:

R₁ and R₂ - Column reactors (dia. 4 inch, height 48 inch, max. pressure 50 psi)

R₃ - Pressure liquid/solid separator (150 psi)

S₁ and S₂ - Separators for sedimented fraction of suspension (50 psi)

B - Pulp preparation beaker

C - Pressure crystallizer (100 psi)

D₁ and D₂ - Fritted-glass discs for oxygen dispersion in reactors (60 psi)

F₁ and F₂ - Oxygen flow-meters (150 psi)

G₁-G₂ - Gauges (oxygen, 150 psi)

H₁-H₃ - Heating tapes

H₄ - Immersion heater (in fused quartz tube)

M₁ and M₂ - Magnetic stirrers

M-H - Hot plate with magnetic stirrer

P₁-P₂ - Tubing pumps Masterflex with Norprene tube, adapted to pulp transportation under 50 psi pressure

P₃ - Piston metering pump for solution (150 psi)

T₁-T₂ - 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)

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 glass disc (D) 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_2).
- 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 floatable fraction from the 2nd reactor (R_2) is collected in the separator (S_2). The mixed fraction from the bottom part of the second reactor is recycled through a separator S_1 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 6.

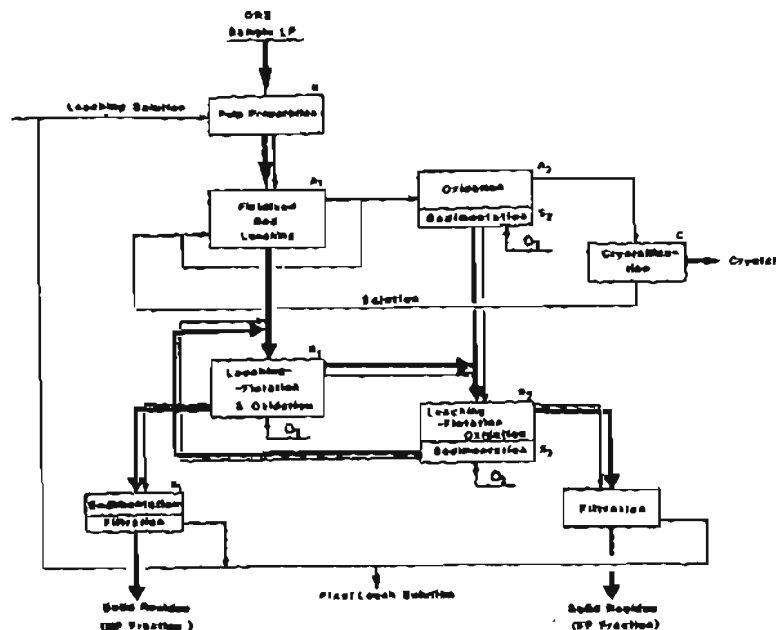


Figure 6. General flowsheets of experiments carried out in pressure installation presented in Figure 5.

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_2). 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.

A schematic flowsheet is presented in Figure 7. Generally, the left branch of the flowsheet, beginning with flow

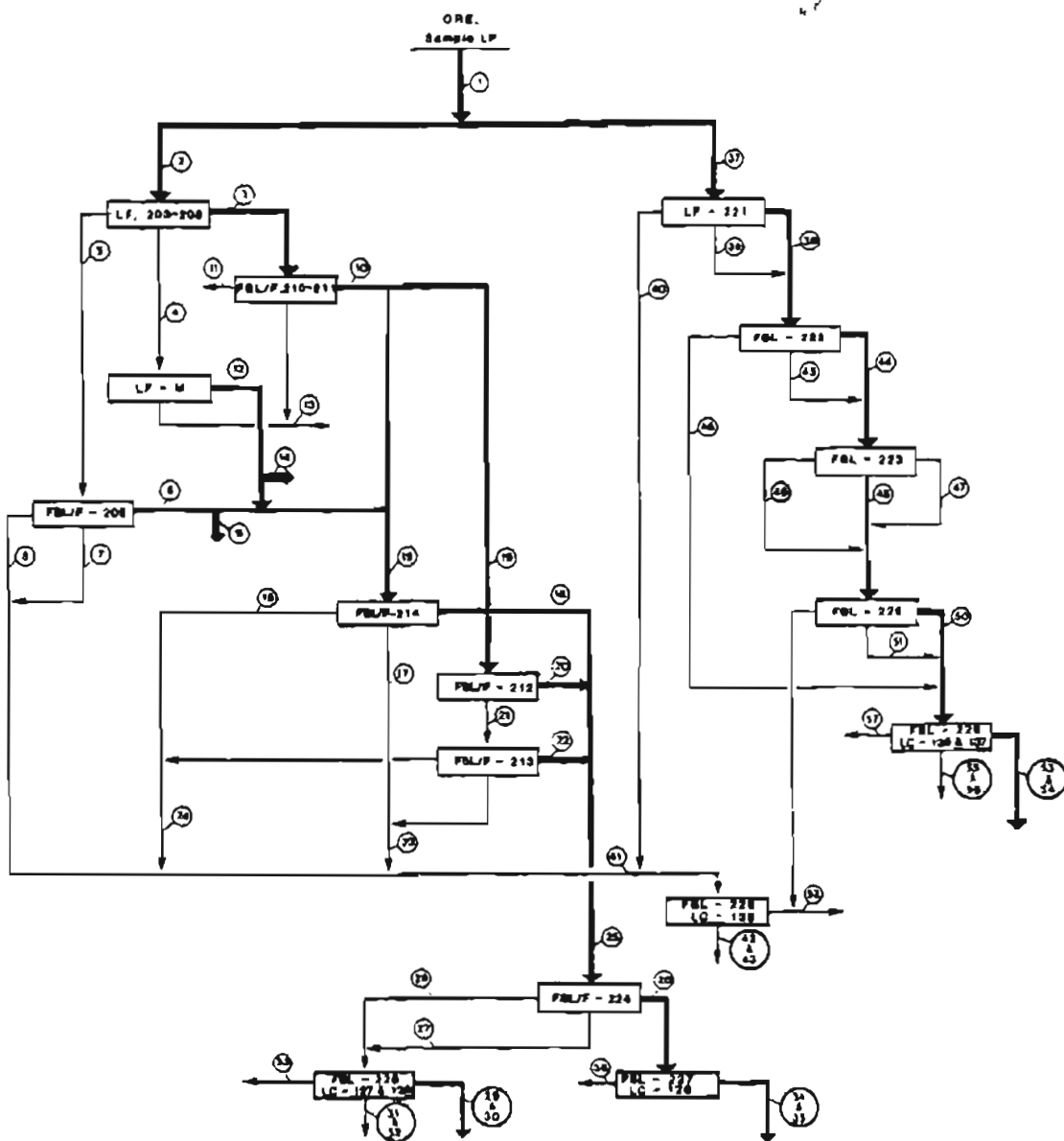


Figure 7. Flowsheet of experiments on Fluidized-Bed Leaching and Flotation in sulfate solution in the laboratory installation (Figure 5). Circled numbers of flows correspond to the identification numbers in Table 6.

#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 7 by coarse lines and the non-flotable, "mixed" or "light" fractions by fine lines. The following symbols are used for the tests identification:

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 5. The runs of experiments performed

Table 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 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 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 8c)
FBL/F 224	1,102.5	146	70	15	See Figure 9
FBL 227	615.3	50 ⁶⁾	90 ⁷⁾	--	Single passing of CaCl ₂ leach solution through fluidized bed (see Figure 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	10	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 6. Values in Table 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 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.

on the ore-sample-flow #2, and on the floatable fractions of the left branch of flowsheet (Figure 7) are shown in Figures 8 and 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_c , 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 8a). 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 problems 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 5. Concentration of ferrous ions, and total iron were analyzed from the samples of solutions. The mass balance in the experiments is

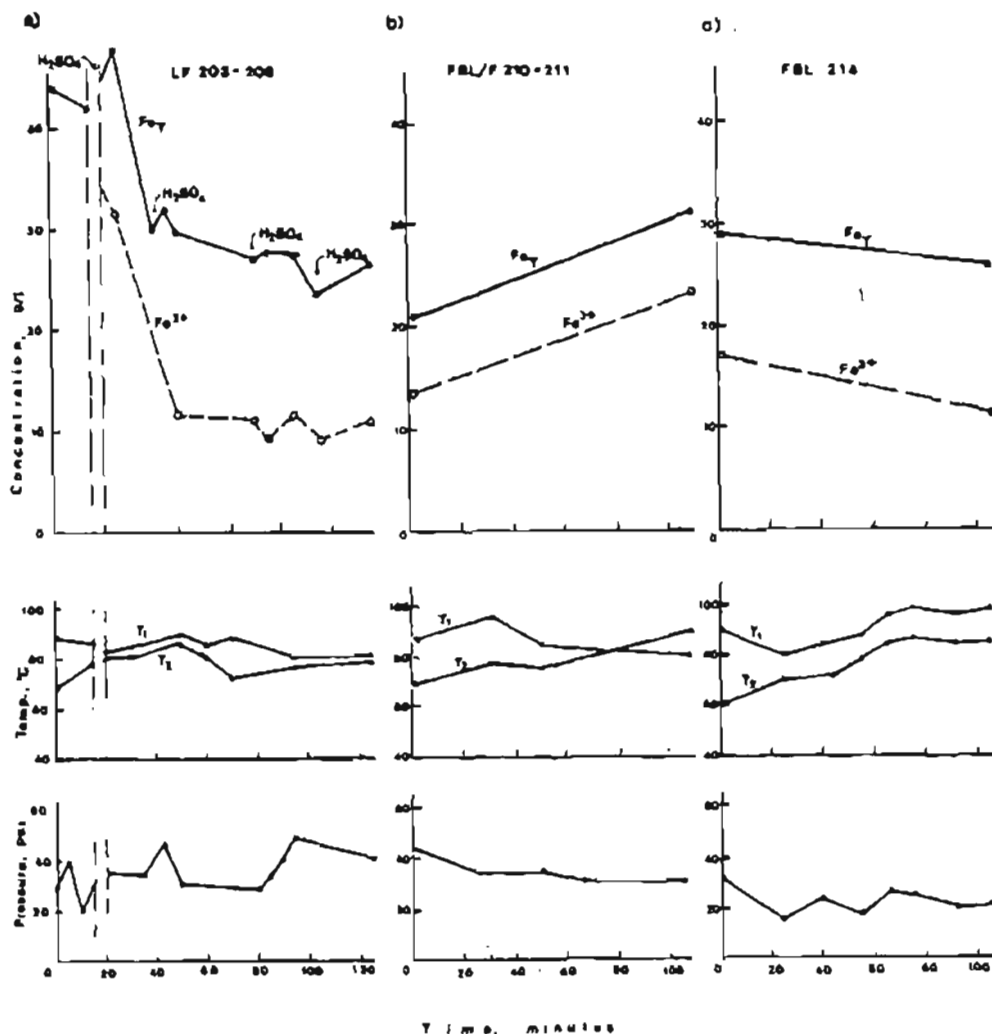


Figure 8. Characteristics of the continuous fluidized-bed sulfate leaching tests described as LF 203-209, FBL/F-210, 211 and FBL-214 (Figure 7 and Table 6). Description in the text.

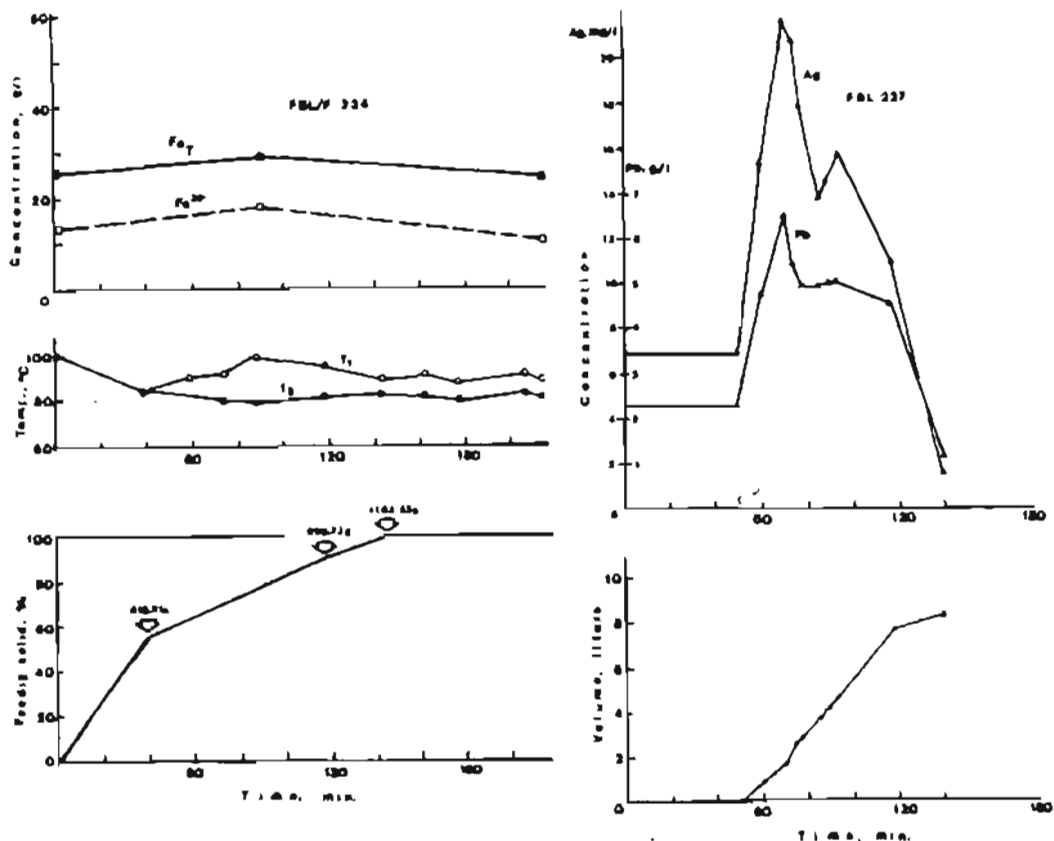


Figure 9. Characteristic of the continuous tests FBL/F-224 in sulfate solution and followed FBL-227 in calcium chloride solution carried out with the flotable fraction from FBL/224.

presented in Table 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 7. They are calculated from the mass balance in Table 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:

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 $MgCl_2$

Table 4. Fluidized-bed leaching and flotation. Mass balance of the experiment in sulfate and chloride solution according to the flowchart in Figure 7. Sample LP, fraction 400 mesh \times 20 μ m.^a

Specifications	ID (No ^o)	Sample Weight (grams)	Concentrations in Solids, grams (Ag, Au: mg)										
			Cu	Pb	Zn	Pb	Ag	Sb	As	Au	Ca	S	
Leaching-Floation (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	34.35	7.45		
	Ore inlet to LF-203-208	2	2,500	7.05	768.	170.0	88.0	217.71	1,380	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.	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.	n.a.		
	Non-Flotable Fractions (NF) from 203-208	5	n.d.	n.a.	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 219	FF from FBL/F 209	6	546.3	1,147	18.8	18.57	11.36	65.81	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	0.55	0.077		
	NF from FBL/F 209	8	192.5	0.068	14.5	1.15	57.31	13.07	0.108	0.38	0.117		
	Sample excluded from processing	9	18.5	0.039		0.64	0.39	2.27	0.004	0.21			
	FF from FBL/F 210-211	10	843.7	2.19	379.9	29.70	10.79	89.94	0.194	10.21	1.305		
	M from FBL/F 210-211: excluded from processing	11	31.0	0.018	11.3	0.82	3.88	4.05	0.005	0.10			
	FF from LP-M	12	260.9	0.57	104.6	8.19	4.96	27.58					
	ZNF from FBL/F 210-211 and LP-M	13	12.37	0.069	1.6	0.09	2.38	1.85	0.024	0.044			
	Sample excluded from processing	14	50.0	0.127	20.0	1.57	1.04	5.29	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 ^b	77.5					
	FF from FBL/F-212	20	145.9	0.262	53.0	2.64	2.63	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	456.1	0.480	163.9	7.50	2.83	46.10	0.174	5.36			
	ZM 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			
ZNF from FBL/F 213 and FBL/F 214	24	46.83	0.077	15.5	1.07	3.59	6.62	0.047	0.04				
Inlet to FBL/F 224	25	1267.9	2.114	464.6	25.16	15.83	143.58	0.562	15.51				
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	3.68				
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	0.05	0.03	2.33					
	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	7.59	1.560	33.00	
H-fraction after FBL-227 from LC-128	35	595.7	0.578	188.5	1.12	0.37	21.63						
Crystals from cooling system FBL-227	36	3.4	-	-	-	-	-	-	-	-	-		
FBL-221 in sulfate solution	Ore inlet to LC-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	ZNF from 209 and 212-214	41	483.7	0.402	111.5	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-226 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	5.42	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	1.50	2.71	6.49	0.051	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	0.78	22.32	0.123	5.13			
	M-fraction from FBL-226	51	47.2		15.7	0.53	0.08	1.35					
	E crystals from FBL-226 & 226	52	42.3	0.0004	0.02	0.003	0.19	0.04	0.002	-		1.90	
FBL-229 in CaCl ₂ -LC-137 in FeCl ₃	H-fraction from FBL-229	53	460.5	1.019	148.3	10.23	3.27	23.31	0.092	3.82	1.082	22.38	
	H-fraction after FBL-229 from LC-136	54	505.1	0.252	96.9	0.43	0.27	11.37					
	L-fraction from FBL-229	55	68.5	0.070	22.1	0.90	0.55	2.68	0.015	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	3.9	-	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

^a Metals concentrations in the LP net 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%

^b Identical flow-numbers according to the flowchart in Figure 7.

Initial concentrations of the solutions:

a) Sulfate solution: Zn 21-35 g/L, Cu 1-2 g/L, Fe₂ 23.8-28.1 g/L, H₂SO₄ 5% w.t.

b) Calcium chloride solution: CaCl₂ 200 g/L, HCl 1.2% w.t.

c) Ferric chloride solution: Fe³⁺ 20-22.2 g/L, CaCl₂ 47 g/L, MgCl₂ 68 g/L, HCl 2% w.t.

Table 7. Metals extraction during fluidized-bed leaching and flotation in sulfate and chloride solutions calculated from metals content in solids (see Table 6 and Figure 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	--
	Cumulative 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 CaCl₂ solution
- 3) As above with additional 60 min in FeCl₃ solution
- 4) 370 min in sulfate solution and 60 min in CaCl₂ solution
- 5) As above with additional 60 min in FeCl₃ solution
- 6) Average from 2) and 4)
- 7) Average from 3), 5), and simultaneous leaching of NF fractions in: CaCl₂ solution (FBL-225) - 60 min, and in FeCl₃ 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.

and 100 ml of 36% HCl per liter. The solution used for leaching samples FBL 228 also contained 6.4 g/l Zn as ZnCl₂ and 3.3 g/l Pb as PbCl₂.

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 6 and 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 to another. One probable reason of such a silver behavior is its slow dissolution in the sulfate solution as silver sulfate (Ag₂SO₄).

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 8. The kinetics of leaching for more typical samples is shown in Figures 10 and 11. General conclusions after sulfate leaching are:

Table 8. Results of control chloride leaching of lead, silver and antimony (experimental conditions - see text).

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-flouable fraction

M - mixed fraction

FF - flouable fraction

n.d. not determined

1) Numbers of flows from Figure 7

2) Yield in the carried out test (not cumulative extraction degree)

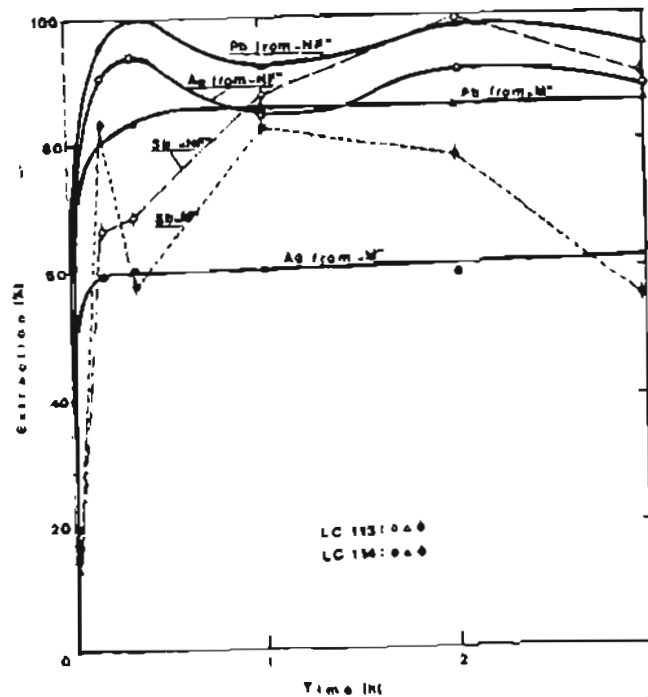


Figure 10. Leachability of lead, silver and antimony from nonflotable (LC-113) and mixed (LC-114) fractions after FBL/F-209 in calcium chloride solution. For other conditions see text.

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.
2. Slow reoxidation of ferrous ions under oxygen pressure of 20-30 psi and low temperature (80-85° C) caused

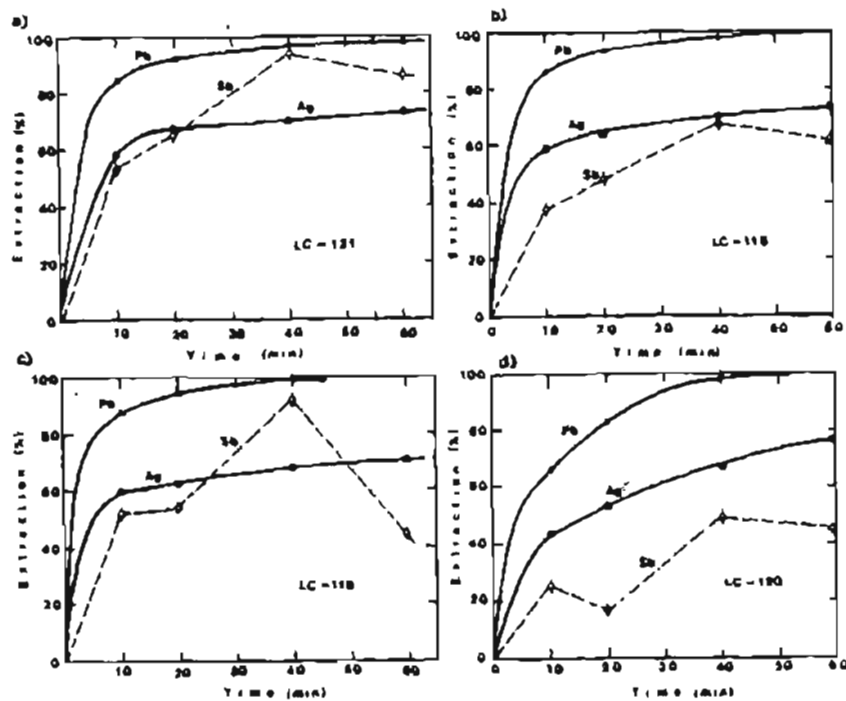


Figure 11. Leachability of lead, silver and antimony from different fractions after FBL 212 to 214 in calcium chloride solution:
 a) from mixed fractions after FBL 213 and 214 (LC-121)
 b) from floatable fraction after FBL 212 (LC-120)
 c) from floatable fraction after FBL 213 (LC-119)
 d) from floatable fraction after FBL 214 (LC-120)

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 the 1st stage report³ and in Section 2 of this report. 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 Fe³⁺/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 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 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 8). The extraction of lead, silver and in some cases, antimony from different samples is schematically shown in Figure 12. It is evident that not more than about 30% of the total silver is dispersed in the non-soluble pyritic matrix.

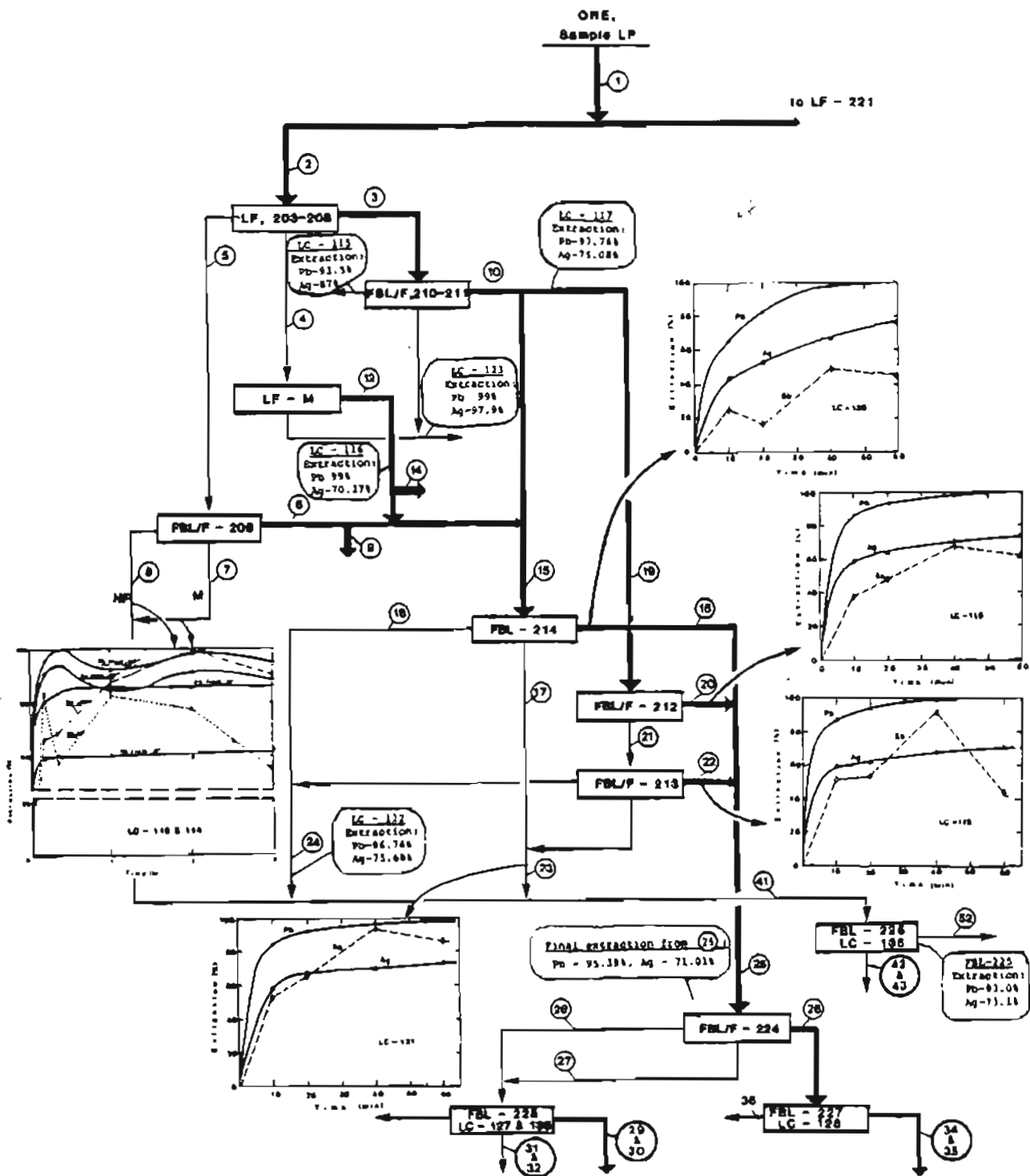


Figure 12. Leachability of lead, silver and antimony from solid semi-products at different steps of treatment of the flow (2) (left branch of the flowsheet in Figure 9).

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 both atmospheric and increased pressures. For this reason leaching by FeCl_2 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 13 in the mini-pilot laboratory installation shown in Figure 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) 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).

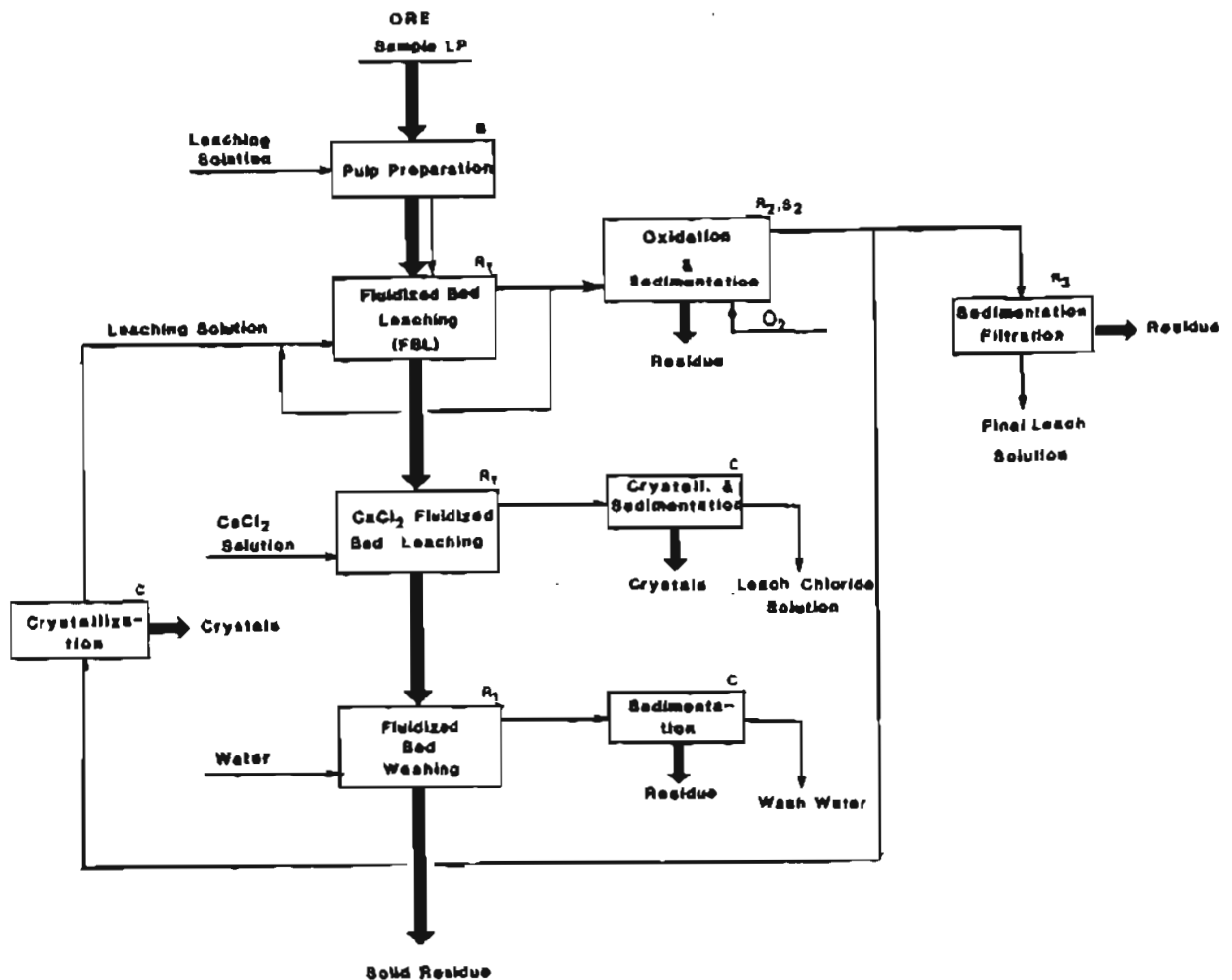


Figure 13. General flowsheet of experiments carried out in chloride solutions in the pressure installation presented in Figure 5.

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 second reactor (R₂). When leaching was finished the calcium chloride solution had been fed continuously to the 1st reactor, through the valve (12) and the pump (P₂) 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 (R₃) and then outside the installation. The spent CaCl₂ wash solution was transported, bypassing the 2nd reactor, directly to the crystallizer and then outside the installation.

Fluidized-bed calcium chloride (CaCl₂) 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 CaCl₂ washing. A schematic flowsheet of the two experiments is presented in Figure 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

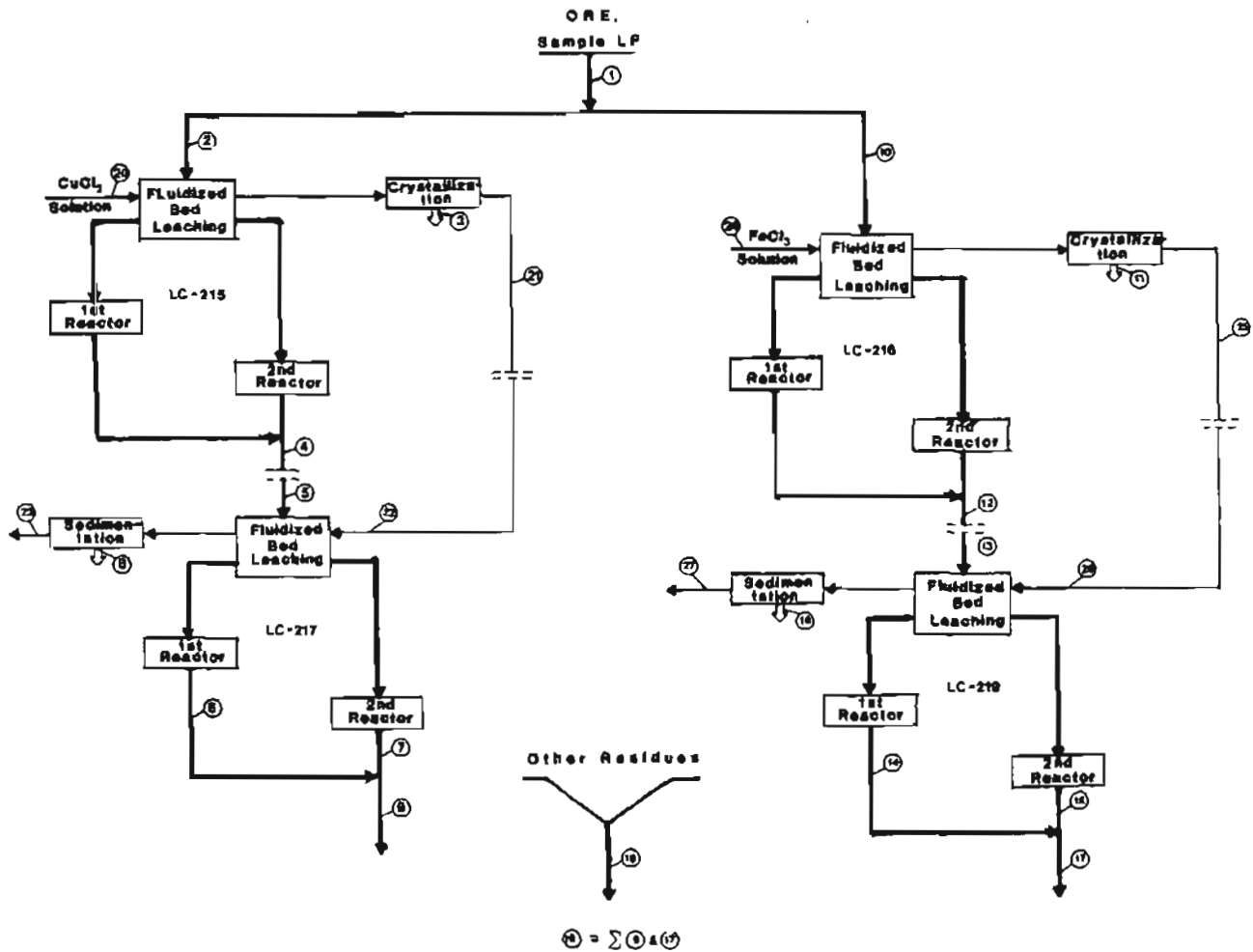


Figure 14. Flowsheet of experiments on the Fluidized-Bed Leaching in cupric and ferric chloride solutions in the laboratory installation (Figure 5). Circled numbers of flows correspond to the identification numbers in the Table 9 and 10.

ore-samples, 700 g each of the fraction 400 mesh x 20 μm , were leached according to the above procedure (Figures 13 and 14). The tests were carried out in the following steady state conditions:

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 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:

CuCl₂ leaching: 1st step: 150 ml

2nd step: 70 ml

FeCl₃ leaching: 1st step: 150 ml

2nd step: 100 ml

Liquid/solid ratio in the 1st reactor:

CuCl₂ leaching: 1st step: 1.75 l/kg

2nd step: 2.08 l/kg

FeCl₃ leaching: 1st step: 2.00 l/kg

2nd step: 2.70 l/kg

Other conditions and data are presented in Tables 9 and 10 - the mass balances of metals in solid and in solution.

Results of the leaching tests are presented in Table 11.

Table 9. Fluidized-bed leaching. Mass balance of metals content in solids during cupric- and ferric-chloride leaching according to the flowsheet in Figure 13.

Specifications		ID No*	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	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
	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	Inlet to LC-216	10	700	1,974	215.2	47.6	24.64	60.96	0.441	6.78	1,407
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.
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 13.

Table 10. Fluidized-bed leaching. Mass balance of metals content in solutions during cupric- and ferric-chloride leaching according to the flowsheet in Figure 13.

Specifications	ID No ^{a)}	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.

^{a)} Identification numbers correspond to the flow numbers in Figure 13.

^{**} Including wash-waters.

Table 11. Metals extraction during fluidized bed leaching in chloride solutions, calculated from metals content in solids (see Table 9 and Figure 13).

Specifications	Leaching Time (min)	Extraction, %							
		Cu	Fe	Zn	Pb	Ag	Sb	As	
CuCl ₂ Leaching	Conditioned at 60°C ¹⁾	15	-13.7 ²⁾	1.8	2.6	40.2	30.7	1.8	n.a.
	Conditioned at 95°C ³⁾	37	-2.4 ²⁾	2.7	11.3	73.0	40.3	25.9	n.a.
	After LC-215 ⁴⁾	123	27.8	-26.1 ²⁾	64.2	98.2	59.0	59.2	n.a.
	After LC-217 ⁵⁾	273	76.9	1.7	95.5	97.6	82.8	75.2	28.2
FeCl ₃ Leaching	After LC-216 ⁶⁾	120	32.8	-4.5 ²⁾	72.9	97.4	42.4	26.8	5.1
	After LC-219 ⁷⁾	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 O₂ 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; O₂ pressure: 16±2 psi; S/L (1st reactor): 0.48 kg/L.

6) Temp: 1st reactor 95°C; 2nd reactor 75°C; average O₂ pressure 20 psi; S/L (1st reactor): 0.50 kg/L.

7) Temp: 1st reactor 92°C; 2nd reactor 90°C; average O₂ 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. Extraction of copper and silver is higher in the cupric than in the ferric chloride solution. Copper extraction attains 76.9% and 46.7% in CuCl₂ and FeCl₃ 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 Cu²⁺/Cu⁺ than Fe³⁺/Fe²⁺;
- 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 12. A kinetic characteristic of the leaching test LC-125 is shown in Figure 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 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 20 μm , 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

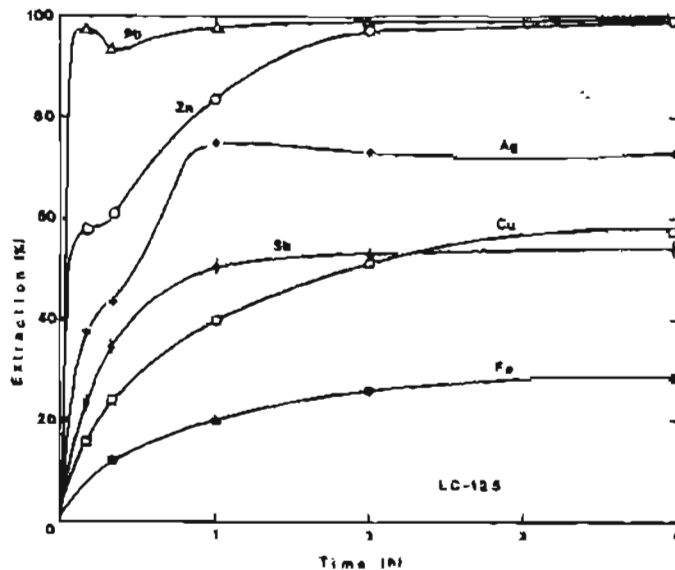


Figure 15. Extraction of metals during leaching of the LP ore sample with zinc chloride/ferric chloride solution. Experimental conditions see Table 12.

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 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 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.

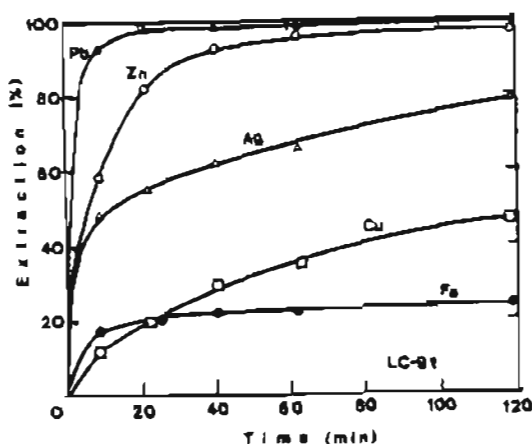


Figure 16. Kinetic of leaching in ferric chloride-aluminum chloride system. Sample LP, fraction 200-270 mesh. Solution concentration: $[Fe] = 30 \text{ g/l}$; $[Al] = 27 \text{ g/l}$, $[Cl] = 5.6 \text{ mol/l}$; $[HCl] = 18 \text{ g/l}$, liquid/solid ratio = 0.7 l/50 g, temp. 95°C .

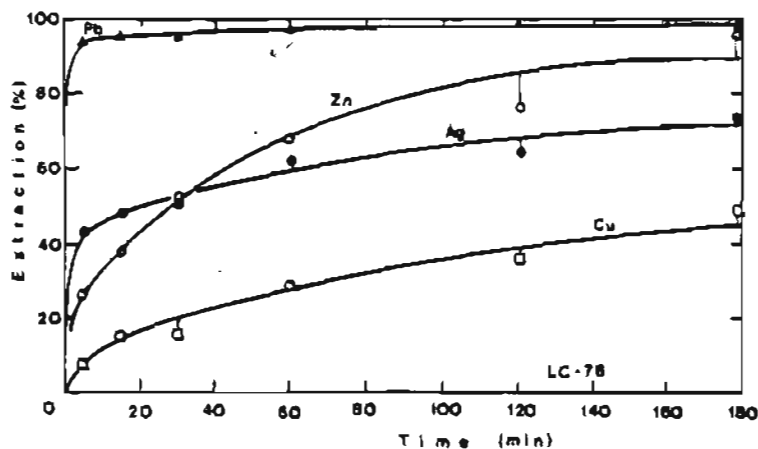


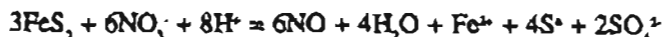
Figure 17. Kinetic of leaching in ferric sulfate-aluminum chloride system. Sample LPU (old) fraction 325-400 mesh. Solution concentration: $[Fe] = 60 \text{ g/l}$, $[Cu] = 1.7 \text{ g/l}$, $[Al] = 40 \text{ g/l}$, $[SO_4^{2-}] = 1.60 \text{ mol/l}$, $[Cl^-] = 3.5 \text{ mol/l}$, temp. 95°C , liquid/solid ratio = 0.7 l/50 g.

6. Sulfur and Gold Extraction from Residues after FBL Processing

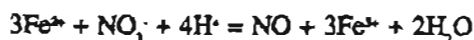
Gold extraction from the residues after Fluidized-Bed sulfate processing was investigated in a function of the pyritic matrix decomposition. For this purpose the solid residues were leached in ferric sulfate solution with continuous addition of small quantities of nitric acid. In this condition sulfidic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



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



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



Results of tests on the gold recovery as a function of the pyritic matrix destruction are presented in Table 13. The heavy floatable fraction of the sample LP, after sulfate processing and fluidized-bed calcium chloride washing FBL 227 (Figure 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 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.

Table 13. Gold recovery from treated ore in function of the pyritic matrix destruction by "nitrate" leaching. Sample LP; heavy, floatable fraction after FBL227 (flow 34 in Figure 7). Gold concentration in the sample 2.51 ppm.

Solid Sample Specification	Loss of weight (%)	Concentration of metals and sulfur after leaching							Degree of pyrite decomposition (%)	Liquid/solid Ratio l/g	Cyanide Leaching Change of pH during leaching (pH)	Gold extraction (%)***	Silver extraction (%)
		Cu (%)	Fe (%)	Zn (%)	Pb (ppm)	Ag (ppm)	S (%)						
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	69.0/73.4	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: $[\text{Fe}_2(\text{SO}_4)_3] = 0.12 \text{ mol/L}$; $[\text{H}_2\text{SO}_4] = 1.35 \text{ mol/L}$; 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: $[\text{Fe}_2(\text{SO}_4)_3] = 0.12 \text{ mol/L}$; $[\text{H}_2\text{SO}_4] = 1/35 \text{ mol/L}$; 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: $[\text{Fe}_2(\text{SO}_4)_3] = 0.19 \text{ mol/L}$ $[\text{HNO}_3] = 2.8 \text{ mol/L}$; Leaching time - 18 min; Initial L/S ratio = 0.275 L/73.2g. Cyanide Leaching: $[\text{NaCN}] = 1\text{g/L}$ $[\text{NaOH}] = 1\text{g/L}$; Leaching time = 48 h.

*) Calculated from balance

**) Low accuracy ±10%

***) Analytical result from two digested solid samples.

n.d. - not determined

A relatively strong increase in the gold recovery with the pyritic matrix destruction (Table 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 (1st Stage Report, 1986).

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 13 is attainable after 16 to 26 hours. The fluidized-bed system should be tested for the cyanidation process also.

7. Summary and Conclusions

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:

Concentration in ore	LPU (old, 1985 sample)		LP (new, 1986 sample)	
		Zn	6.63%	
	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 14. These results should be analyzed carefully because of the different experimental systems that were used.

Table 14. Metals extraction from Delta ore (sample LP) in the investigated leaching systems.

No.	Leaching System	Kind of Processing	Time of Processing (h)	Cumulative Extraction, %						
				Cu	Fe	Zn	Pb	Ag	Sb	As
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 - cumulative extraction after partial destruction (~63%) of pyritic matrix (see Table 13)

1d - cumulative extraction after cyanide leaching (see Table 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: 200-275 mesh; No. 6: 325-400 mesh.

* After 2h of leaching; 97%

** Low accuracy ± 15%

Nevertheless, visible superiority of the silver extraction in CuCl_2 solution, the total and fast zinc extraction in $\text{ZnCl}_2/\text{FeCl}_2$ 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.

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	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	2.97
Ag_2S	7.2-7.4	CuS	4.6-4.8	ZnCl_2	2.91
PbSO_4	6.2-6.35	CuFeS	4.1-4.3	SiO_2	2.65
FeAsS	6.1-6.8	ZnS	3.9-4.1	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	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 being developed by the author since 1983 and described in a nonpublished research proposal (Feb. 1987).

The details of the FBL-reactor (not the research installation) will be described in a patent application.

7.3. FBL-Process application in the sulfate system.

The proposed flowsheet of processing is schematically shown in Figure 18. The principal elements are similar to the flowsheet for the second variant of ore treatment presented in the 1st Stage Report¹. According to the current version, the sulfate leaching steps are conducted in three 3-phase (solid-liquid-gaseous) reactors (Figure 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 floatable fraction with non-reacted sulfides and sulfur; 2nd, a light nonfloatable 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 floatable fraction. The suspension of the non-flotable particles is directed to the 2nd reactor.

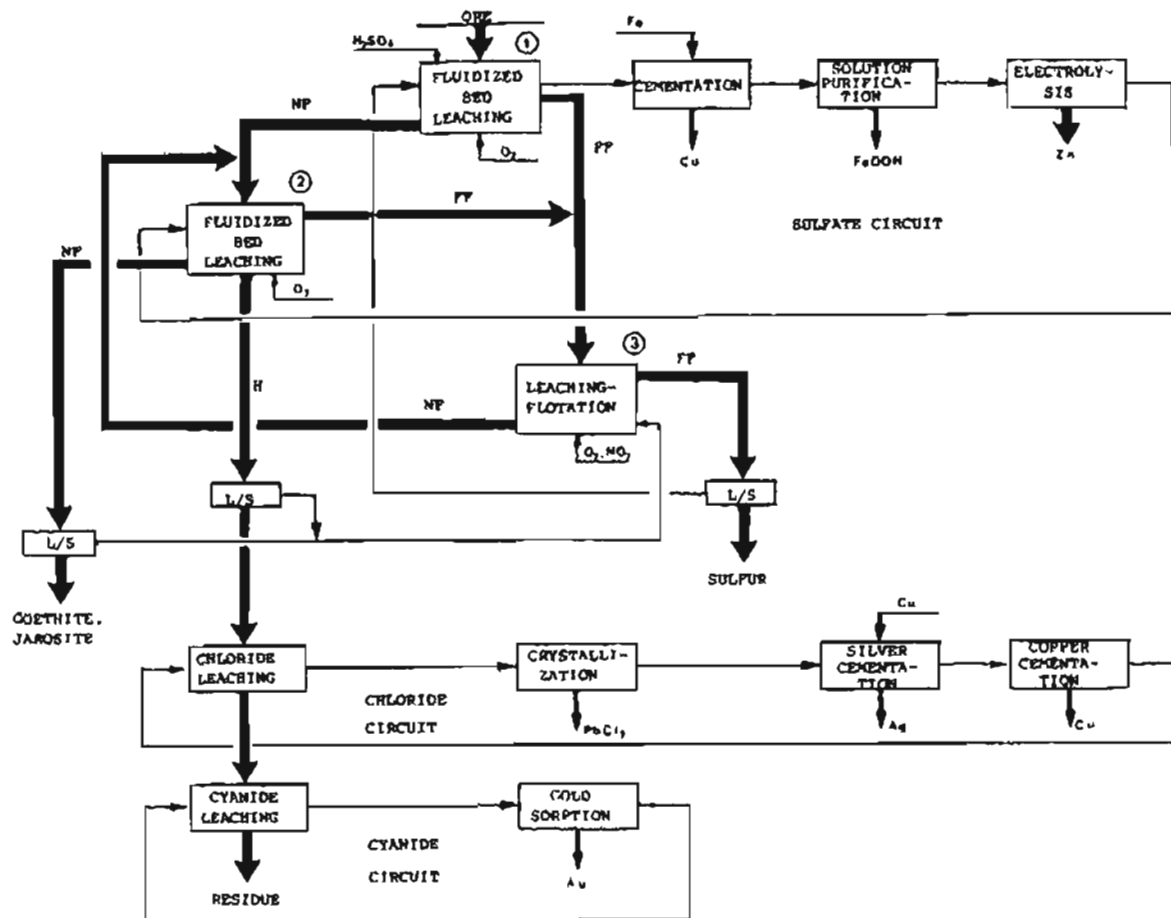
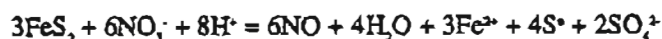


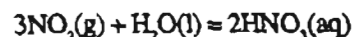
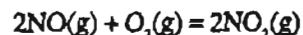
Figure 18. Simplified flowsheet of the Fluidized-Bed and Flotation Processing in the sulfate solution.

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:



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:



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 nonfloatable 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 nonfloatable 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.

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.

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 MIRC as one of the best (Table 14). The following unexpected laboratory results were obtained:

- LP ore leaching by solution with initial concentrations: 170g/l Zn (354.6 g/l ZnCl₂), 20g/l Fe (58 g/l FeCl₃), and 30g/l HCl in the typical conditions (Table 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 ZnCl₂ solubility is very high - 48 moles ZnCl₂ 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 ZnCl₂ has a freezing point of -62°C. Viscosity of the ZnCl₂ concentrated solution is many times higher than that of water. Specific gravity of concentrated solutions attains 2.5. The solution with 6 mol/l ZnCl₂ has pH = 1.

The concentrated solution of ZnCl₂ is an excellent electrolyte for the electrolysis processes. Maximum conductivity at 25°C has the ZnCl₂ solution containing 170 g/l Zn. This value is two times higher than ZnSO₄ 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/m², and 75% efficient for 2,200 A/m².

Other electrolysis conditions in the ZnCl₂ concentrated solution are compared in Table 15 with actually known zinc chloride electrolytic cells in which compact, dendrite-free zinc cathodes are electrowon.

Table 15. Comparison of Zinc Electrolysis Conditions from Zinc Chloride Solutions, for Three Known Processes.

	Thomas and Fray - Cambridge Univ. England ¹⁾	Technicas-Reunidas Proces ²⁾	CANMET Process ³⁾
Zinc concentration in solution 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 ₄ Cl (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.

It is worth mentioning that at a temperature of 9.6°C (49°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 ZnCl₂ 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/m² (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 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.

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