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ABBREVIATIONS AND ACRONYMS

EIP	European Innovation Partnership on Raw Materials
WP	Workpackage

1. INTRODUCTION

INTMET is focused on a sustainable and efficient beneficiation of polymetallic, complex and low grade ores including tailings and wastes. The concept is to produce bulk concentrates or middling concentrates that will be efficiently treated through tailored leaching technology approach to produce added value refined metal (commodities) like Cu, Zn and other metals and critical materials (e.g. Au, Ag, In, Co). This novel hydrometallurgical process has the potential to treat existing complex or low grade concentrates from current operating mines, opening the way to a new and profitable mining business model. Effluents originated in the process will be reused and recycled, maximizing the recovering of dissolved metals. Besides, a very innovative hydroprocessing to valorize sulphur (producing fertilizers) and recover iron from pyrite secondary raw materials will be developed.

INTMET falls under the PolymetOre (EIP-RM Awarded Commitment) umbrella aiming to develop a sustainable and efficient solution to process polymetallic, complex and low grade ores to allow exploitation of resources that are unviable today by conventional routes due to their complexity or low grade. These valuable resources are abundant in some European mining regions in Spain, Portugal, Poland, Serbia, Sweden, Greece, etc. INTMET includes different innovative technologies to increase raw materials efficiency in EU mining business, allowing at the end unlocking a substantial volume of difficult ores that are currently unviable to treat through conventional ways.

An important part of the project is to develop the technological concept for bulk concentrate processing producing metals with high recovery at low cost and using an environmental friendly approach (workpackage 2 of the INTMET Project). For that reason is necessary to define the proper route to produce above mentioned concentrate (nowadays only marketable sulphides concentrates are available in mineral processing industry: Cu concentrate, Zn concentrate & Pb concentrate). Tasks 2.1 & 2.2 of the project deal with improvement of technology for comminution and flotation to define the most suitable process to produce a bulk concentrate. And Task 2.3 consist on the work required to arrange a Flotation Pilot Plant that will produce the sample material for further testing in the different workpackages of the project (WP3 atmospheric leaching- WP4 Pressure leaching – WP5 Bio-leaching). Finally in Task 2.4 the adequate concentrate samples will be produced.

The following text present the main results obtained during the works performed in Task 2.1, 2.2 & 2.4:

- Task 2.1: Energy efficient comminution technology and equipment.
- Task 2.2: Reagents for enhanced flotation process.
- Task 2.4: Flotation pilot plant operation and concentrates production.

2. ENERGY EFFICIENT COMMINUTION TECHNOLOGY AND EQUIPMENT

2.1 TECHNOLOGY: MICROWAVE ASSISTED GRINDING

Microwave energy is a form of electromagnetic radiation, between infrared and radio frequency. Its frequency ranges from 300 MHz to 300 GHz corresponding to a wavelength range from 1 mm to 1 m. Nowadays microwaves have extensive application on the fields of communication and domestic heating purpose.

Microwave radiation heats dielectric materials such as water. This phenomenon lies in the ability of the electric field of microwaves to polarize the charge of the dielectric material, and when polarization cannot accommodate the rapid change of direction of the electric field.

According to their interaction with microwave, three categories of materials had been described (Haque 1999). Dielectrics materials are defined as absorbers of microwaves energy. Metals reflect microwaves, thus they do not heat under microwave radiation. Such materials are classed as conductors, and are often used as waveguides within microwaves generator and oven. Transparent materials also do not heat for they transmit microwave radiation.

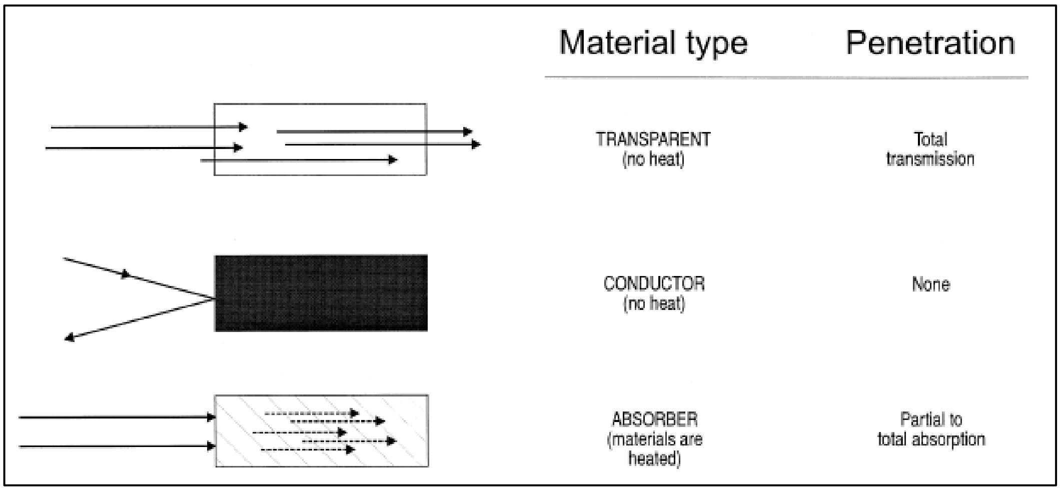

FIGURE 1 - INTERACTION OF MICROWAVE WITH MATERIALS (FROM HAQUE, 1999).

Two factors are often used to express the dielectric response of material under microwave radiation:

- The dielectric constant Ɛ’ measures the ability of a material to store microwave energy.
- The dielectric loss factor Ɛ” measures the ability of a material to dissipate the stored energy into heat.

Poly-metallic ores can be seen as non-homogenous materials regarding dielectrics properties for their minerals are either transparent (e.g. quartz, barite) or either absorber materials (e.g. pyrite, chalcopyrite, galena).

Over the past decades, microwaves had been considered regarding different applications such as, heating drying, reduction of oxide minerals, leaching, roasting / smelting, microwave assisted grinding, extractive metallurgy and microwave treatment of coal (Kingman and Rowson 1998; Haque 1999; Thostenson and Chou 1999; Al-Harahsheh and Kingman 2004).

We will further develop this review with results regarding microwave-assisted grinding.

Walkiewicz, Kazonich, and McGill 1988

Naturally occurring minerals were tested to determine their receptivity to microwave radiation (Table 1).

Mineral	Chemical composition	Temperature max. reached (°C)	Time of exposure (min)
Albite	$NaAlSi_3O_8$	69	7
Chalcocite	Cu_2S	746	7
Chalcopyrite	$CuFeS_2$	920	1
Galena	PbS	956	7
Marble	$CaCO_3$	74	4,25
Pyrite	FeS_2	1019	6,75
Pyrrhotite	$Fe_{1-x}S$	886	1,75
Quartz	SiO_2	79	7
Sphalerite	ZnS	88	7

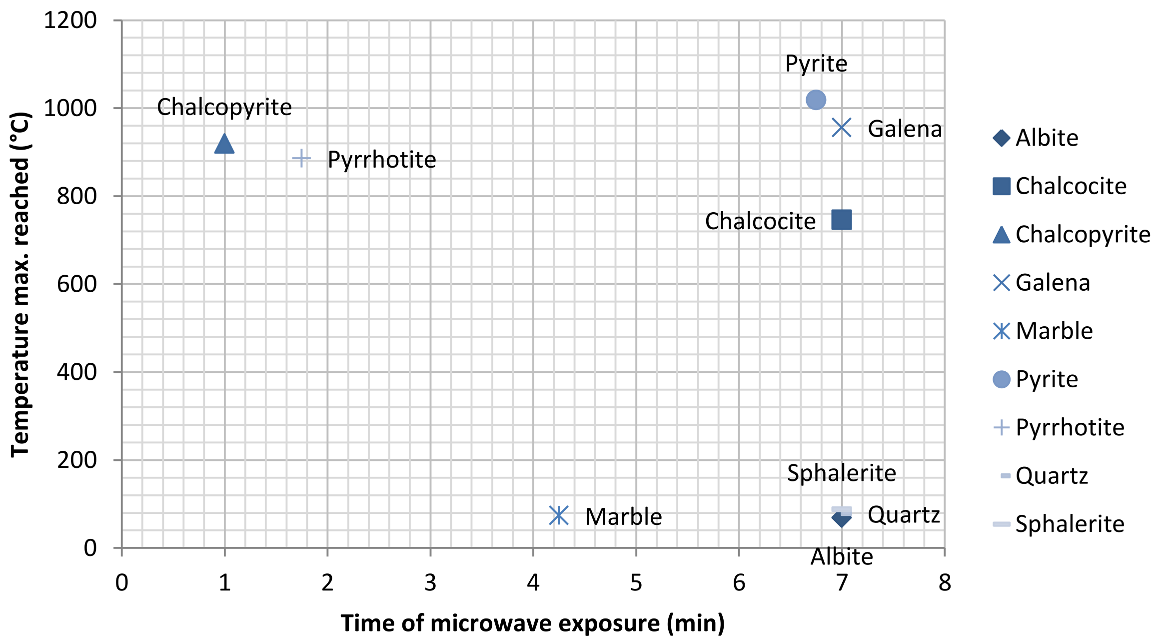

TABLE 1 - NATURALLY OCCURING MINERALS TESTED UNDER MICROWAVE RADIATION (ADAPTED FROM WALKIEWICZ ET AL 1988).

Microwaves selectively heat some minerals such as sulfides but not common gangue mineral (e.g. quartz, marble, and albite). However, sphalerite represents a particular case for it barely heat under microwave radiation in the regard of the others sulfides tested. Selective heating of ore mineral within the rock is then possible.

Rapid heating of ore minerals in a microwave transparent gangue was shown to generate thermal stress, thus creating fractures at mineral grain boundaries. They concluded this would significantly affect grinding energy requirement and liberation properties.

Walkiewicz, Clark, and McGill 1991

The U.S. Bureau of Mines conducted studies to use rapid microwave heating on iron ore samples of 350 g to generate stress-fractures in batch operations at 3 kW.

Fracturing along grain boundaries and throughout the gangue matrix was observed. Moreover, standard bond grindability tests showed that microwave heating reduced the work index of iron ore by 10 to 24%.

They also reported that it may not be necessary to heat an ore at high temperature for stress forces generated by heating depend also on the heating rate. Results showed that even at low temperatures, stress fracturing occurred considering the decrease in work index (TABLE 2 - results of microwave treatment upon iron ore samples (adapted from Walkiewicz et al. 1991).

Sample temperature (°C)	Grindability (g per mill revolution)	Work Index (kWh/st)	Microwave radiation time (s)	Microwave power (kW)	***Microwave energy* (kWh/t)***
As received	1,62	13,15	-	-	***-***
127	1,69	12,7	5,6	3	***13,3***
144	1,71	12,58	7,3	3	***17,4***
197	1,93	11,39	11,7	3	***27,9***
252	1,95	11,3	15,4	3	***36,7***
880	2,07	10,76	210	3	***500,0***
****additional data calculated from operating parameters***					

TABLE 2 - RESULTS OF MICROWAVE TREATMENT UPON IRON ORE SAMPLES (ADAPTED FROM WALKIEWICZ ET AL. 1991).

In spite of the reduction of the work index, the input of microwave energy was systematically greater than the sample work index. Indeed, the minimum microwave energy level tested here (13.3 kWh/t) is close to the work index (13.15 kWh/st ≈ 14.50 kWh/t). Therefore, an amount of 13.3 kWh/t of microwave energy only reduced the work index by 13.15 – 12.7 = 0.45 kWh/st ≈ 0.50 kWh/t. Efficiency of such process is then quite low: 0.50/13.3 = 3.73%.

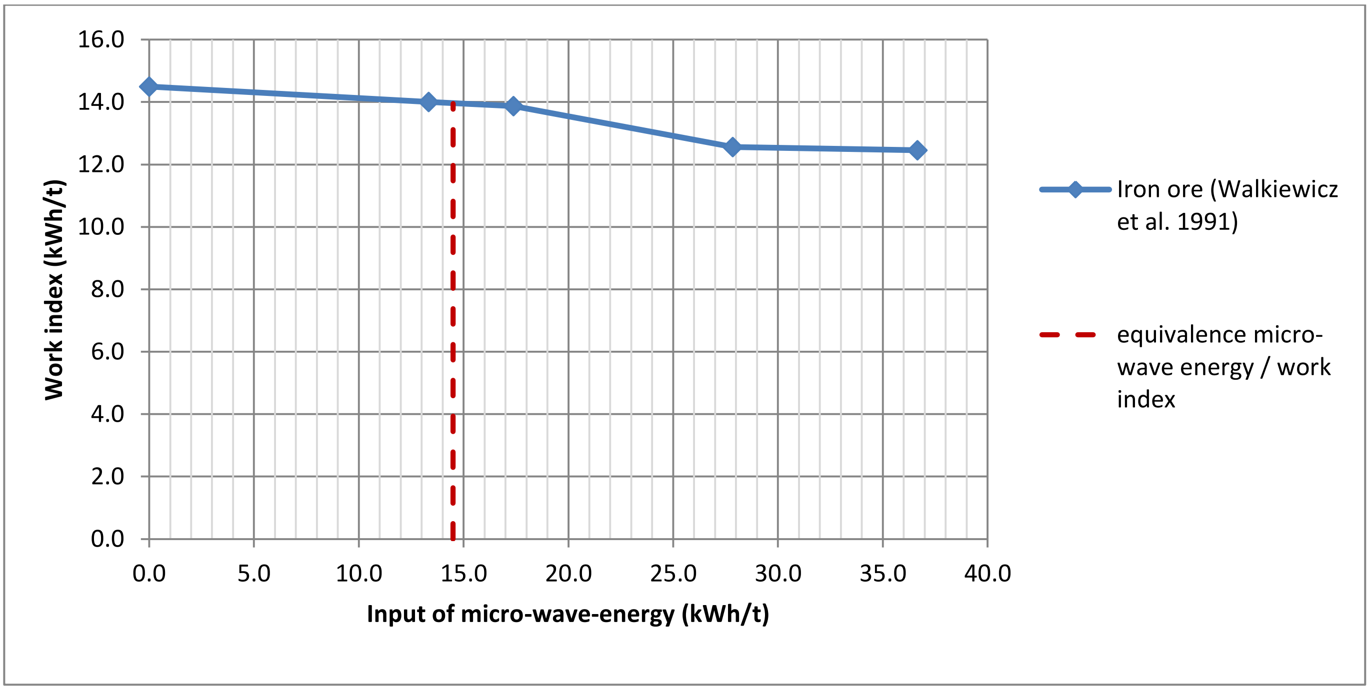

FIGURE 2 - EVOLUTION OF THE WORK INDEX OF IRON ORE SAMPLES WITH INCREASING INPUT MICRO-WAVE ENERGY (WALKIEWICZ ET AL. 1991).

Walkiewicz concluded that microwaving to improve the grindability of iron ores was not cost effective regarding energy saving alone. More parameters have to be taken into account considering downstream process such as wear, recycled flow-rates, separation efficiency through concentration grade and metal recovery.

Salsman et al. 1996

They study the feasibility of using short-pulse microwave energy as a pretreatment step in comminution.

Their simulation indicated that short and intense burst of microwave radiation will selectively heat ore minerals such as pyrite, but not the surrounding gangue material (e.g. calcite). Indeed, stress fractures depending on the heating rate, it seems then attractive to reach a high gradient of temperature between sulfides and gangue in order to maximize the fracturing and thus decrease the grindability of the ore.

Experimental studies of mixtures of crushed sulfides minerals and quartz showed that the energy absorbed is in direct proportion with the mass of chalcopyrite (see Figure 3).

Heating is also influenced by the particle size, more energy absorbed with increasing particle diameter (Figure 3).

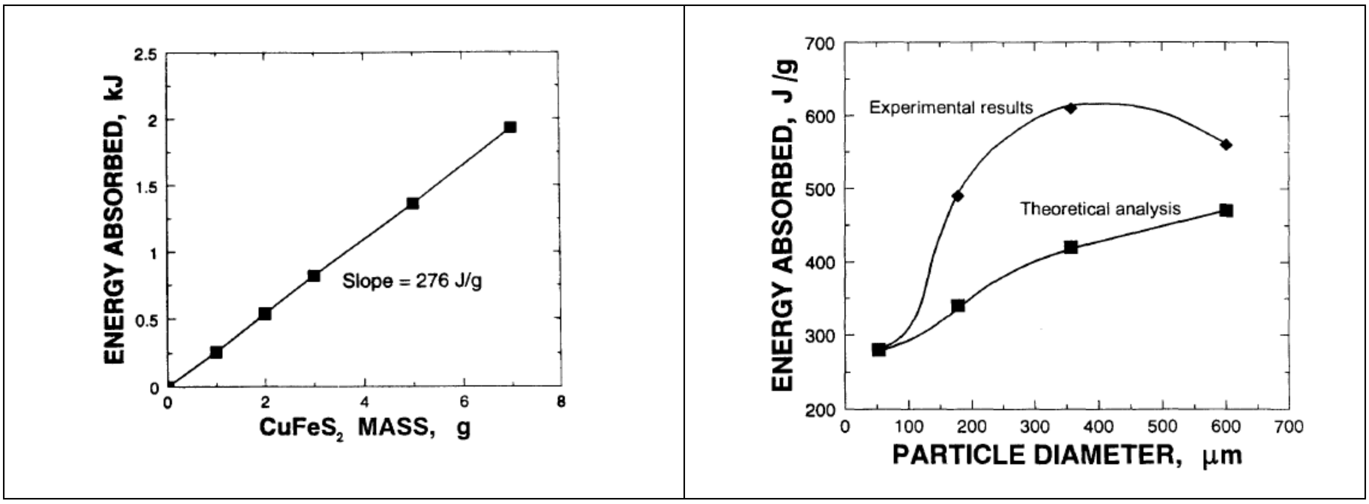

FIGURE 3 - [LEFT] ENERGY ABSORBED IN A QUARTZ/CHALCOPYRITE MIXTURE AS A FUNCTION OF WEIGHT PERCENT OF CHALCOPYRITE [RIGHT] MICROWAVE ENERGY ABSORBED PER GRAM OF CHALCOPYRITE AS A FUNCTION OF PARTICLE SIZE (EXTRACTED FROM SALSMAN ET AL. 1996).

Kingman and Rowson 1998

They presented a review of the possibilities for future utilization of microwaves regarding treatment of minerals. Different applications were considered, including microwave assisted grinding. They concluded that further work was needed involving higher power levels and shorter exposure times. Indeed, microwave assisted grinding have to get through a decrease of energy input into the ore and thus to tend towards economically viable solutions.

Haque 1999

The results obtained on earlier work upon applied microwave energy to the heating minerals and inorganic products. Such work provides valuable information regarding the ability of minerals to heat under microwave radiation.

He reported from Chen et al. (Chen et al. 1984) two groups of minerals depending on their ability to heat under microwave radiation:

- No or very little heat was generated and the mineral properties remained essentially unchanged, where most silicates, carbonates and sulphates fall.
- Heat was generated and the minerals were either thermally stable or decomposed rapidly into a different product, where most sulfides, sulfosalts and arsenides fall.

However, this classification is limited for the behaviour of minerals to microwave radiation depends also on their composition. For example, he reported that when Fe substitutes for Zn in sphalerite, the resulting high iron sphalerite becomes microwave responsive.

Kingman, Voster, and Rowson 2000; Vorster, Rowson, and Kingman 2001

They investigated the influence of microwave radiation and quantified the decrease in work index with exposure time on different ores:

- A massive Norwegian ilmenite ore;
- A massive sulfide from Portugal (Neves Corvo) : composed mainly of chalocopyrite, pyrite, with lesser amount of sphalerite, galena, arsenopyrite and gangue (ferroan dolomite and quartz);
- A highly refractory gold ore from Papua New Guinea;
- A carbonatite from South Africa.

They prepared representative 500 g batch samples for test works of microwave radiation at 2.6 kW and a frequency of 2.45 GHz, for periods of 10 to 240 seconds.

They also study the heating rate of the main minerals within these ores (Table 3): for example, chalcopyrite, pyrite and galena within Neves Corvo ore. It provides an indication of the mineral responsiveness to microwave radiation.

Time (sec)		**10**	**30**	**60**	**90**	**100**	**120**
Chalcopyrite	$CuFeS_2$	61	98	124	146	148	165
Pyrite	FeS_2	75	134	177	189	197	202
Galena	PbS	211	341	422	436	441	453

TABLE 3 – HEATING RATE OF SULPHIDES MINERALS (FROM KINGMAN ET AL, 2000).

Experimental results showed that microwave treatment had significant effect of reduction of the work index upon the Neves Corvo massive sulphides ore with increasing exposure time, thus with increasing input microwave energy (Figure 4).

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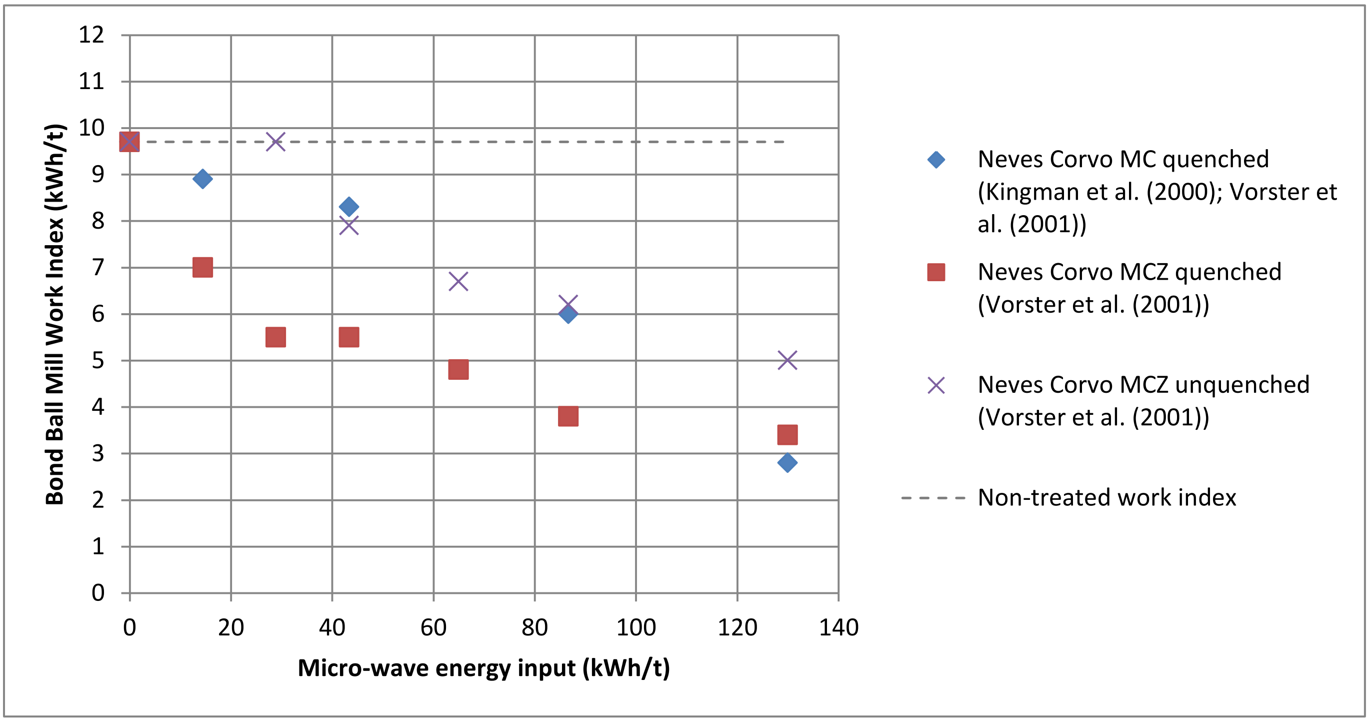


FIGURE 4 - EXPERIMENTAL RESULTS ADAPTED FROM KINGMAN ET AL. (2000) AND VORSTER ET AL. (2001) OF THE MICROWAVE TREATMENT OF NEVES CORVO MC AND MCZ ORES.

They concluded that the increase in grindability after microwave radiation depends on the mineralogy, the particle size and also the dissemination of the minerals into the ore.

The work index was determined using the Berry and Bruce comparative grindability method (Wills and Finch 2016), which requires the use of a reference ore of known Bond work index (see BOND BALL MILL WORK INDEX - COMPARATIVE METHOD).

2.2 EXPERIMENTAL WORKS

2.2.1 ORE CHARACTERIZATION AND PREPARATION

Cobre Las Cruces (Spain)

BRGM received in July 2016 from Cobre Las Cruces (Spain) around 500 kg of run of mine ore, consisting in rocks above 100 mm for the purpose of WP2. The run of mine ore had been crushed with a jaw crusher later.

FIGURE 5 - COBRE LAS CRUCES RUN OF MINE ORE AS RECEIVED AND AFTER JAW CRUSHER.

BOR (Serbia)

BRGM received in July 2016 from BOR (Serbia) around 500 kg of run of mine ore, consisting in rocks above 100 mm for the purpose of WP2. The run of mine ore was crushed with a jaw crusher later.

FIGURE 6 - [LEFT] CRUSHING OPERATION OF THE BOR RUN OF MINE ORE; [RIGHT] BOR RUN OF MINE CRUSHED.

Neves Corvo (Portugal)

BRGM received in August 2016 from Neves Corvo (Portugal) around 500 kg of run of mine ore, consisting in rocks already below 30 mm. As a consequence, no further crushing operation was carried upon Neves Corvo run of mine ore.

FIGURE 7 - [LEFT] RECEPTION OF NEVES CORVO RUN OF MINE; [RIGHT] NEVES CORVO RUN OF MINE AS RECEIVED.

KGHM (Poland)

BRGM received in November 2016 from KGHM (Poland) around 500 kg of run of mine ore, consisting in a mixture of sands and gravels. Due to late shipping, no investigations were carried out regarding KGHM ore.

2.2.1.1 ORE PREPARATION

Prior to conduct any test, particularly before determining the Bond Ball Work Index, each ore had to be divided into representative batches (Figure 8).

FIGURE 8 - [LEFT] BUNDLES OF COBRE LAS CRUCES RUN OF MINE ORE; [RIGHT] BUNDLES OF NEVES CORVO RUN OF MINE ORE.

Figure 9 presents the general scheme followed to constitute for each ore representative batches around 32 kg, and the reduction size conducted in order to feed the Bond Ball Mill and to perform the determination of the work index.

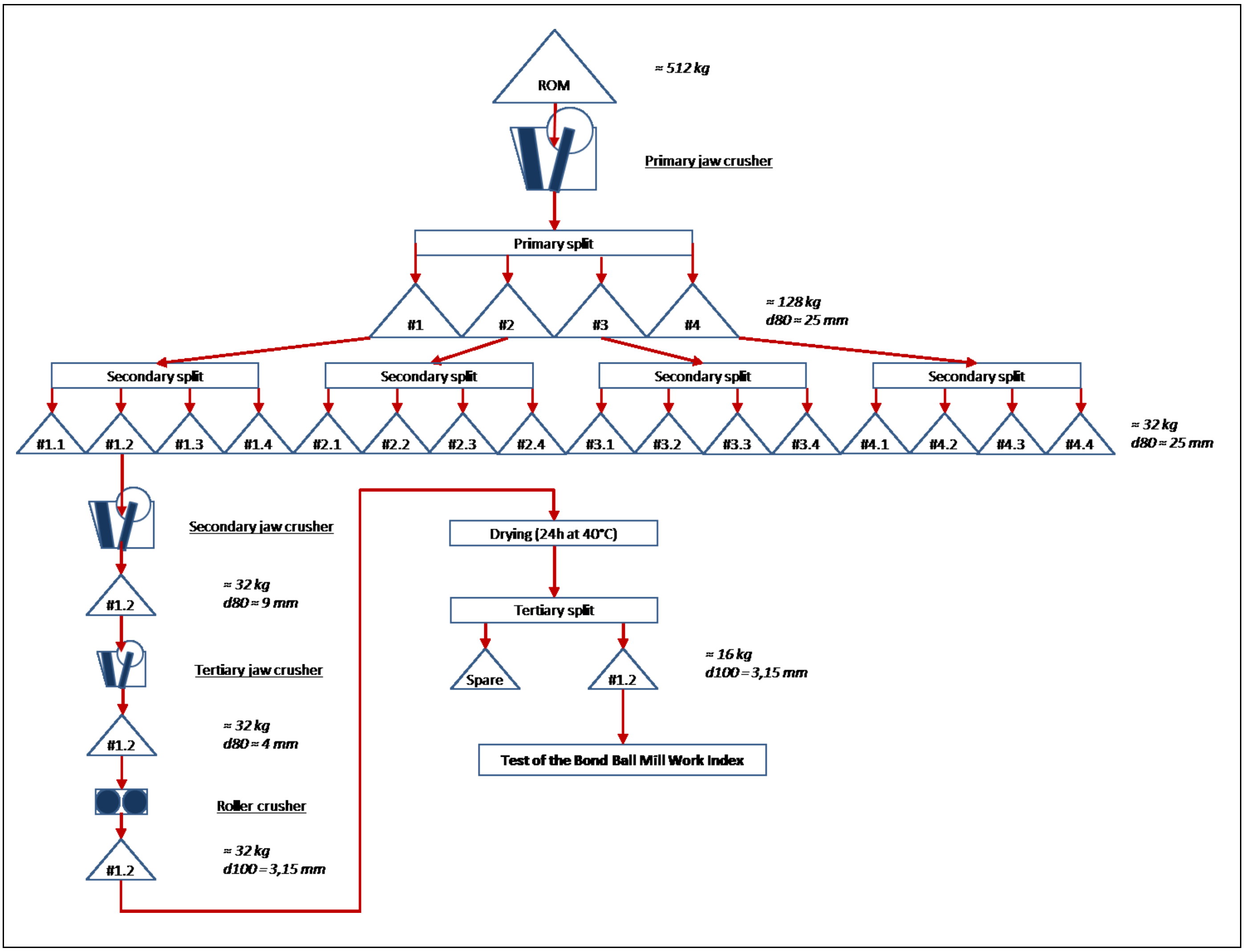


FIGURE 9 - SCHEME OF THE ORE PREPARATION DEDICATED TOWARDS BOND BALL MILL WORK INDEX DETERMINATION.

2.2.1.2 RUN OF MINE ORE CHARACTERIZATION

ICP-MS analysis

ICP-MS analysis had been performed on ground samples of Cobre Las Cruces, Neves Corvo and BOR run of mine ores (Table 4).

	DL[1]	Units	Neves Corvo	Bor	Cobre Las Cruces
Ag (Argent)	0,2	mg/kg	65,5	176	47,8
As (Arsenic)	20	mg/kg	3475	2953	3062
B (Bore)	10	mg/kg	26	11	20
Ba (Baryum)	10	mg/kg	842	80840	1122
Be (Béryllium)	2	mg/kg	< DL	< DL	< DL
Bi (Bismuth)	10	mg/kg	55	17	151
Cd (Cadmium)	2	mg/kg	163	94	51
Ce (Cérium)	10	mg/kg	13	< DL	< DL
Co (Cobalt)	5	mg/kg	209	18	300
Cr (Chrome)	10	mg/kg	18	20	< DL
Cu (Cuivre)	**5**	**mg/kg**	**6442**	**14915**	**8765**
La (Lanthane)	20	mg/kg	< DL	< DL	< DL
Li (Lithium)	10	mg/kg	11	< DL	< DL
Mo (Molybdène)	5	mg/kg	20	75	19
Nb (Niobium)	20	mg/kg	< DL	< DL	< DL
Ni (Nickel)	10	mg/kg	18	69	45
Pb (Plomb)	**10**	**mg/kg**	**15174**	**47280**	**14508**
Sb (Antimoine)	10	mg/kg	519	2080	596
Sn (Etain)	10	mg/kg	486	271	183
Sr (Strontium)	5	mg/kg	45	921	98
V (Vanadium)	10	mg/kg	51	175	12
W (Tungstène)	10	mg/kg	< DL	< DL	< DL
Y (Yttrium)	20	mg/kg	< DL	< DL	< DL
Zn (Zinc)	**5**	**mg/kg**	**65953**	**48680**	**26887**
Zr (Zirconium)	20	mg/kg	26	< DL	35

TABLE 4 - RESULTS OF ICP-MS ANALYSES PERFORMED ON COBRE LAS CRUCES, NEVES CORVO AND BOR RUN OF MINE ORES

DRX analysis

DRX analysis had been performed on ground samples of Cobre Las Cruces, Neves Corvo and BOR run of mine ores.

2.2.2 METHODOLOGY AND EXPERIMENTAL SET-UP

2.2.2.1 EXPERIMENTAL APPROACH

The experimental approach consisted in treating 1 kg of batch ore samples at different input power, and for different exposure time of micro-wave radiation. The total energy input was limited to 30 kWh/t in order to focus the experimental investigation only on an energy input as far as twice the Bond Ball Mill Work index of a given ore.

Once the ore had been micro-wave treated, its Bond Ball Mill Work Index was determined using Bond methodology (Fred C Bond 1961) or using the comparative methodology implemented by Berry and Bruce (Wills and Finch 2016). Moreover, textural and mineralogical characterization had been carried upon treated and non-treated rocks samples using MEB and EDS.

DL: detection limit

Once the ore had been ground in the purpose of the Bond Ball mill work index determination, the ground product was dedicated towards flotation trials in order to evaluate separation efficiency of micro-wave treated product in comparison with non-treated ones.

2.2.2.2 MICROWAVE EQUIPMENT

The microwave device at BRGM is a SAIREM multi-modal micro-wave oven equipped with a magnetron and a generator (see Figure 10). The input micro-wave power can be set between 0.6 and 6 kW, at a frequency of 2.45 GHz. Samples were treated at power levels of 2, 4 and 6 kW. Exposure time of 6 seconds was set for each power level, and exposure time of 12 and 18 seconds was also set at 6 kW of power level. The energy input through these combinations ranges from 3.3 to 30 kWh/t.

Test	Solid mass	Micro-wave frequency	Input power	Exposure time	Energy input calculated
A	1.0 kg	2.45 Ghz	2.0 kW	6 s	3.3 kWh/t
B	1.0 kg	2.45 Ghz	4.0 kW	6 s	6.7 kWh/t
C	1.0 kg	2.45 Ghz	6.0 kW	6 s	10.0 kWh/t
D	1.0 kg	2.45 Ghz	6.0 kW	12 s	20.0 kWh/t
E	1.0 kg	2.45 Ghz	6.0 kW	18 s	30.0 kWh/t

TABLE 5 - OPERATING PARAMETERS OF MICRO-WAVE TREATMENT TESTS.

2.2.2.3 TEMPERATURE MONITORING

For each micro-wave treatment of an ore sample, the temperature had been monitored within four millimetric carved holes in separate stones (see Figure 10). The device used was a fibre optic temperature sensor linked to an external thermometer. The outer jacket of the fibre optic temperature sensors is made out of Teflon (PTFE). The sensor tip is made of a GaAs crystal (gallium arsenide). The probe sensor is completely non-conductive and therefore offers complete immunity to microwave radiation with high temperature operating capability (up to 300 °C).

Starting at a light wave length of 850nm GaAs becomes optical translucent. Since the position of the band gap is temperature dependent, it shifts about 0.4nm/Kelvin. The measurement device contains a light source and a device for the spectral detection of the band gap. This guaranties fast, repeatable and reproducible measurements. Temperature data was recorded every second for the whole duration of each test, including micro-wave radiation and cooling time of the samples.

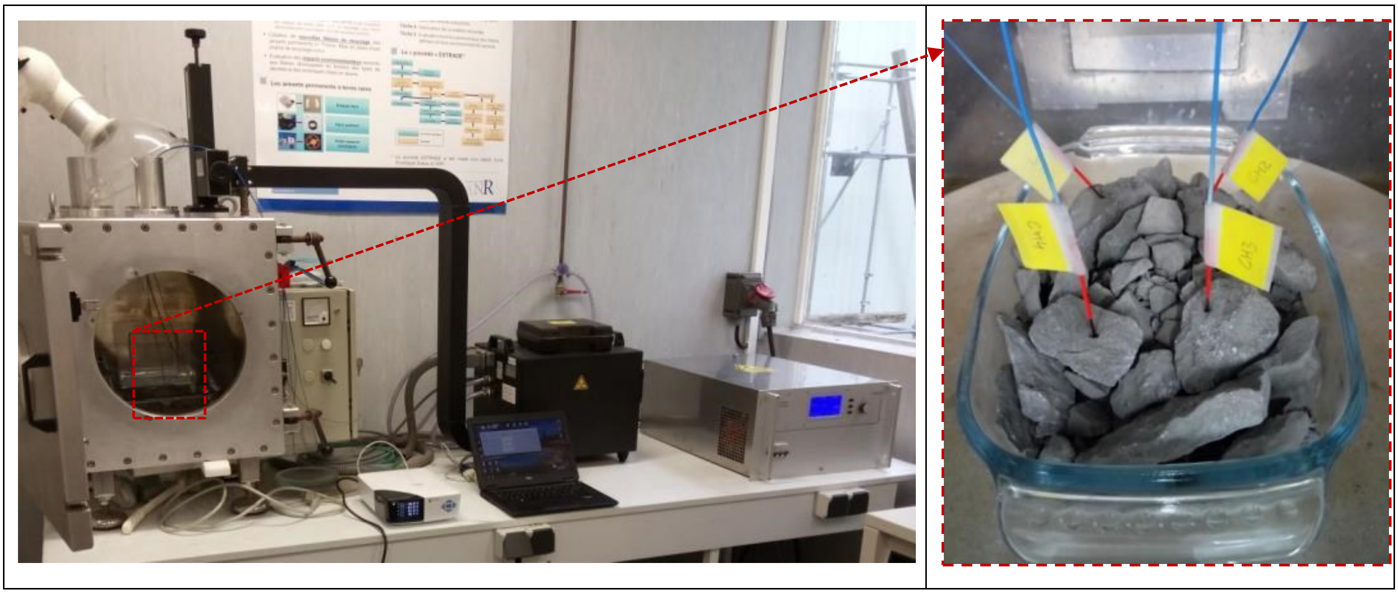


FIGURE 10 - [LEFT] EXPERIMENTAL SET-UP OF WITH THE MICROWAVE OVEN, THE MAGNETRON, THE GENERATOR, AND THE THERMOMETER; [RIGHT] CLOSE LOOK AT THE FIBER OPTIC TEMPERATURE SENSOR WITHIN CARVED HOLES FOR TEMPERATURE MONITORING.

2.2.2.4 TEXTURAL AND MINERALOGICAL CHARACTERIZATION

Textural and qualitative mineral characterization of the treated and non-treated samples had been investigated under Scanning Electron Microscope (SEM) and using Energy Dispersive Spectroscopy (EDS) (see Figure 11).

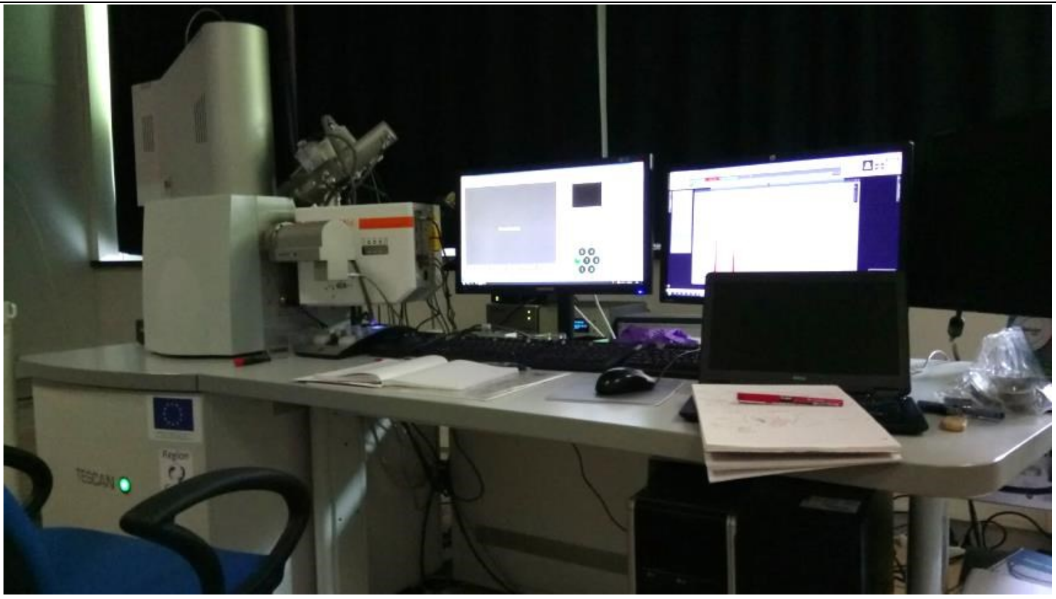


FIGURE 11 - SCANNING ELECTRON MICROSCOPE (SEM) COUPLED WITH AN ENERGY DISPERSIVE SPECTROSCOPY (EDS).

Prior to micro-wave treatment, the samples dedicated to textural investigation under SEM were cut into half. In this way, the other half of each sample micro-wave treated was available for the investigation of its non-treated state.

2.2.2.5 BOND BALL MILL WORK INDEX (BWI)

The Bond Work Index W_i is the most widely used parameter to measure ore hardness (crushability or grindability). Depending on the size class to be characterized, Bond developed different W_i determinations (Fred C Bond 1961):

- Low energy crushing work index (CW_i) or impact work index (IW_i)) for sample larger than 50 mm.
- Rod mill work index (RW_i), for sample prepared to d80 = 12,7 mm.
- Ball mill work index (BW_i), for sample prepared to d100 = 3,36 mm.

Grindability of each run of mine ore from Cobre Las Cruces, Neves Corvo and BOR had been characterized using the Bond Ball Mill Work Index (BW_i). The methodology implemented in this work arises from Bond (Fred C Bond 1961) and is described thereafter. Each value obtained corresponds then to the work index value of each reference ore (i.e. non-treated with micro-wave radiation) used later with the comparative method.

2.2.2.6 PRINCIPLE – BOND METHODOLOGY

The Bond methodology intends to determine the Ball Mill Work index in reproducing with a laboratory scale device a milling operation as close as possible from industrial ones in a close circuit (see Figure 12). It is then necessary to determine laboratory parameters which will lead to the calculation of the Bond Ball Mill Work Index (BW_i).

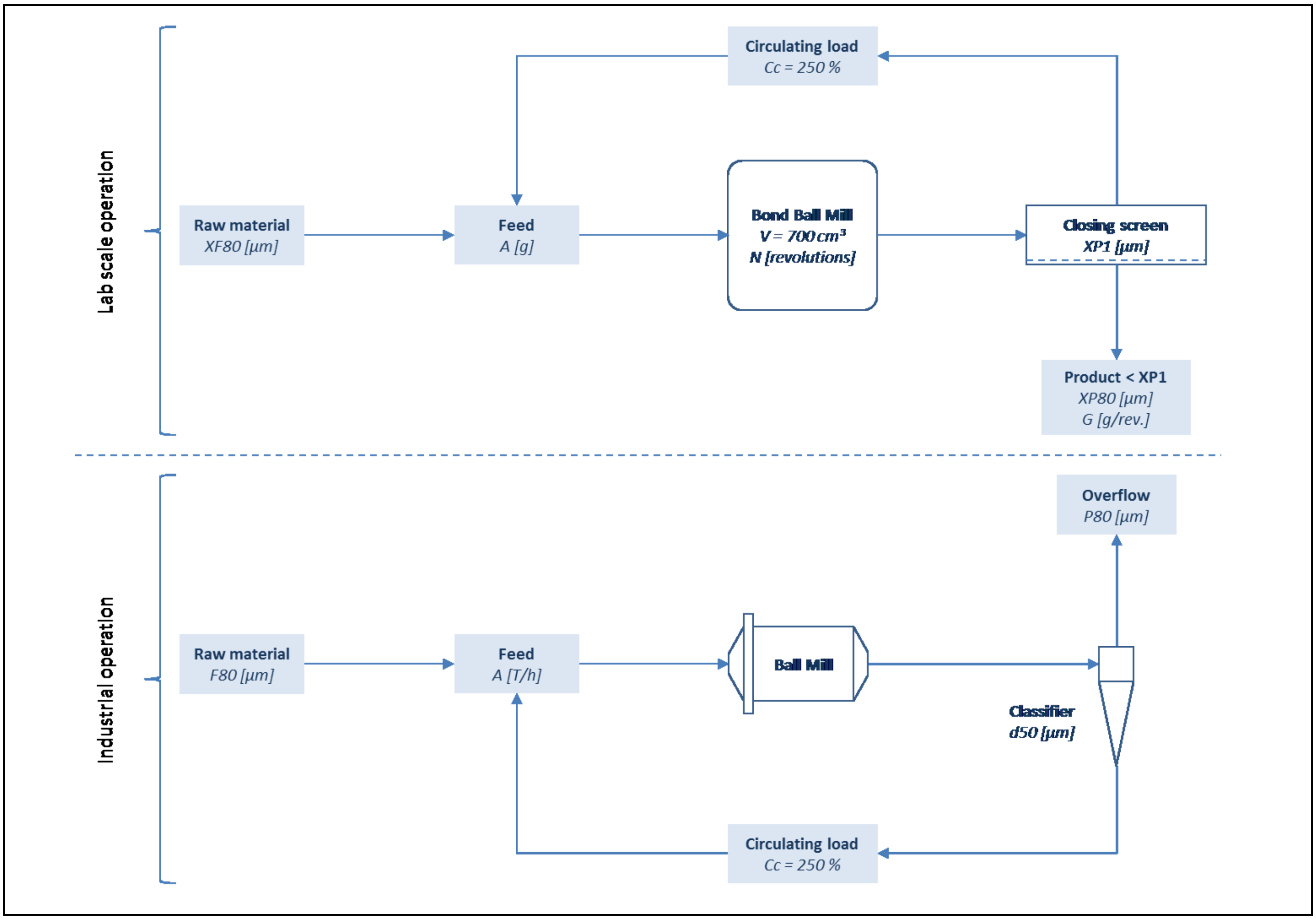


FIGURE 12 - MILLING CIRCUIT: LABORATORY SCALE OPERATION USED FOR BOND METHODOLOGY VS TYPICAL INDUSTRIAL CIRCUIT.

2.2.2.7 BWI CALCULATION

At the end of the test, the Bond Ball Mill Work Index (BW_i) is calculated as follows:

$$\boldsymbol{BW_i} = \frac{44{,}5}{\boldsymbol{XP_1}^{0{,}23} * \boldsymbol{G}^{0{,}82} * \left(\frac{10}{\sqrt{\boldsymbol{XP_{80}}}} - \frac{10}{\sqrt{\boldsymbol{XF_{80}}}}\right)} \qquad kWh/short\ ton$$

EQUATION 1 - BOND BALL MILL WORK INDEX (BWI) EQUATION (FROM BOND, 1965).

With parameters:

- **XP_1**: the mesh size of the reference sieve (microns);
- **G**: the net production of ground product under the mesh size XP_1 (g/revolution);
- **XP_{80}**: the size where 80% passing of the ground product (microns);
- **XF_{80}**: the size where 80% passing of the feed product (microns);

The BW_i as calculated is expressed in kWh/*short ton*. In order get international system units, the factor conversion is as follows: $1\ short\ ton = 0{,}90718\ ton$.

2.2.2.8 BOND BALL MILL WORK INDEX - COMPARATIVE METHODOLOGY

Berry and Bruce (1966) developed a comparative method of determining the hardness of an ore (Wills and Finch 2016).

This method requires the knowledge of a reference ore's work index, and which had been preferentially determined through Bond methodology. Both reference and tested ores are separately ground in identical operating conditions of time, weight and milling load charge. Since the energy input *W* for both ores is equal then the Third Theory of Bond (F.C. Bond 1952) can be written as follows:

$$W = W_{i\,(\boldsymbol{ref})} * \left(\frac{10}{\sqrt{P_{80\,(\boldsymbol{ref})}}} - \frac{10}{\sqrt{F_{80\,(\boldsymbol{ref})}}}\right) = W_{i\,(\boldsymbol{test})} * \left(\frac{10}{\sqrt{P_{80\,(\boldsymbol{test})}}} - \frac{10}{\sqrt{F_{80\,(\boldsymbol{test})}}}\right)$$

EQUATION 2 - EQUATION OF THE THIRD THEORY OF BOND CONSIDERING TWO ORES ("REF" AND "TEST") TO BE GROUND IN IDENTICAL OPERATING CONDITIONS.

Then, in order to compute the work index of the tested ore, we have the following equation:

$$W_{i\,(\boldsymbol{test})} = W_{i\,(\boldsymbol{ref})} * \frac{\left(\frac{10}{\sqrt{P_{80\,(\boldsymbol{ref})}}} - \frac{10}{\sqrt{F_{80\,(\boldsymbol{ref})}}}\right)}{\left(\frac{10}{\sqrt{P_{80\,(\boldsymbol{test})}}} - \frac{10}{\sqrt{F_{80\,(\boldsymbol{test})}}}\right)}$$

EQUATION 3 - EQUATION OF BERRY AND BRUCE (1966) TO DETERMINE THE WORK INDEX OF A TESTED ORE IN COMPARISON TO A REFERENCE ORE.

2.3 RESULTS & CONCLUSIONS

2.3.1 RESULTS OF THE MICROWAVE TREATMENT

2.3.1.1 EVALUATION OF THE ABSORBED ENERGY

Temperature monitoring had been implemented in order to evaluate how much energy is absorbed by the sample under micro-wave radiation. Using the enthalpy equation the energy corresponds to heat for the system is under constant pressure (Equation 4).

$$Q = C_p * m * \Delta T$$

EQUATION 4 – ABSORBED HEAT EQUATION SIMPLIFIED FROM ENTHALPY EQUATION.

Specific heat capacities had been evaluated regarding each ores using their main mineral composition and the specific heat capacities of each mineral (Waples and Waples 2004) (see Table 6).

Ore	Heat capacity Cp (at 20°C)*	CLC	Neves Corvo	BOR
Mineral	J/kg/K	wt%	wt%	wt%
Arsenopyrite	400	0.67	0.88	0.01
Chalcopyrite	534	3.42	2.40	0.04
Covellite	513	-	-	0.04
Galena	210	1.95	1.86	7.57
Pyrite	510	64.11	59.32	45.15
Sphalerite	471	5.36	12.59	7.71
Quartz	740	13.95	14.8	11.11
Barite	540	1.66	-	25.26
Cassiterite	375	-	0.11	-
	Total	*91.12*	*91.98*	*96.89*
Composite Ore Specific Heat Capacity		**537.12**	**535.06**	**517.65**

TABLE 6 - EVALUATION OF EACH ORE SPECIFIC HEAT CAPACITY (*MINERALS SPECIFIC HEAT CAPACITIES EXTRACTED FROM D.W. WAPLES AND J.S WAPLES, 2004).

2.3.1.2 MICROWAVE TREATMENT: TEMPERATURE MONITORING

Cobre Las Cruces

The temperature had been systematically monitored during and after micro-wave radiation in order to record the maximum temperature (T_{max}) reached by the sample due to heat conductivity and temperature homogenization within the sample as illustrated by Figure 13.

In order to apply Equation 4, ΔT had been calculated as the difference between T_{max} and the initial temperature of the sample T_0.

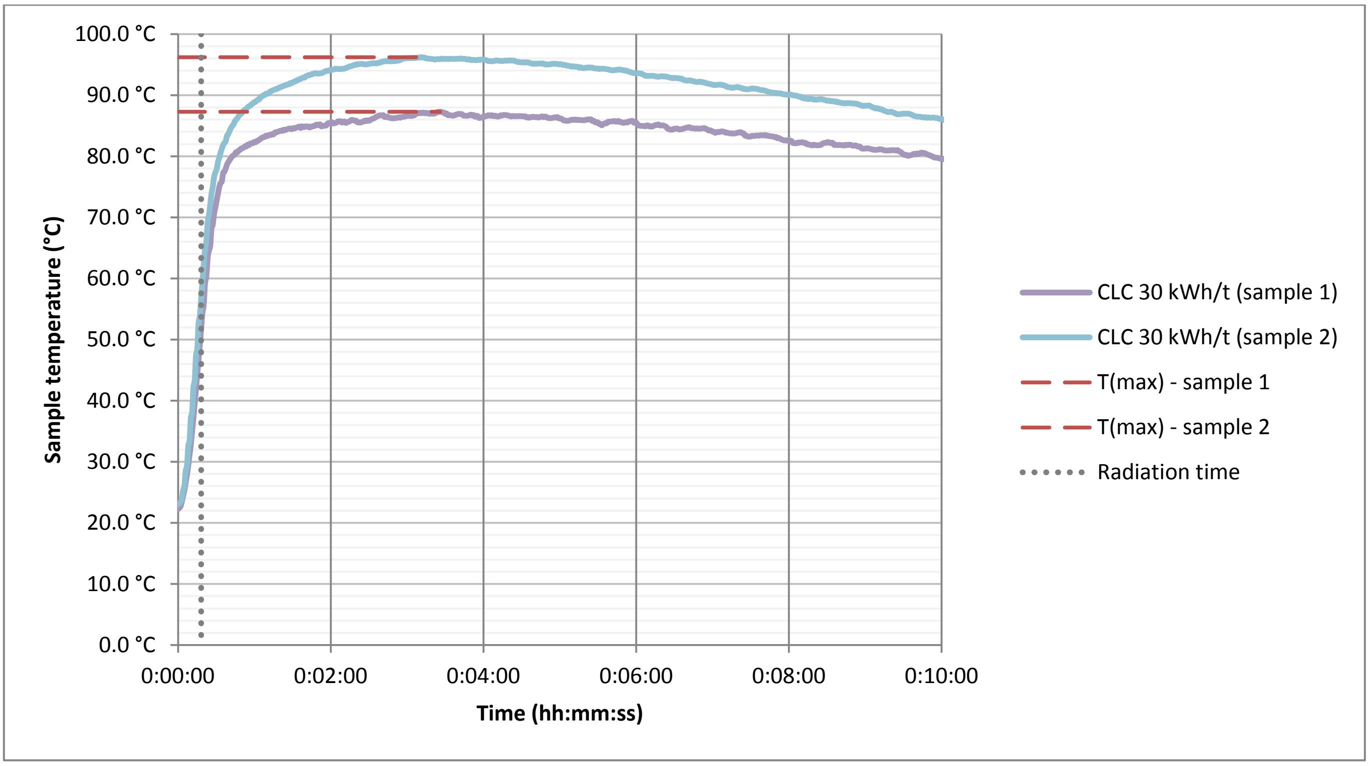


FIGURE 13 – TEMPERATURE MONITORING CLC SAMPLES MICRO-WAVE TREATED AT 30 KWH/T (RADIATION TIME: 18 SEC).

In the case of the CLC samples microwave treated at 30 kWh/t, the results are presented below (Table 7).

Test	Solid mass (kg)	Micro-wave energy input (kWh/t)	T_0 (°C)	T_{max} (°C)	ΔT (°C or K)	C_p (J/K/kg)	Heat absorbed (J)
E (CLC - test 1)	1.0	30.0	22.2	87.3	65.1	537,12	34940
E (CLC - test 2)	1.0	30.0	23.0	96.2	73.2	537,12	39290

TABLE 7 - EVALUATION OF THE HEAT ABSORBED REGARDING CLC SAMPLES MICROWAVE TREATED AT 30 KWH/T.

Table 7 presents then the results obtained on a comparative chart between the input micro-wave energy and the heat absorbed in kWh/t by CLC samples.

For each test undertaken, the absorbed energy as heat within the samples represents a constant-likely percentage between 29.3% and 43.5% of the micro-wave input energy (see Figure 15).

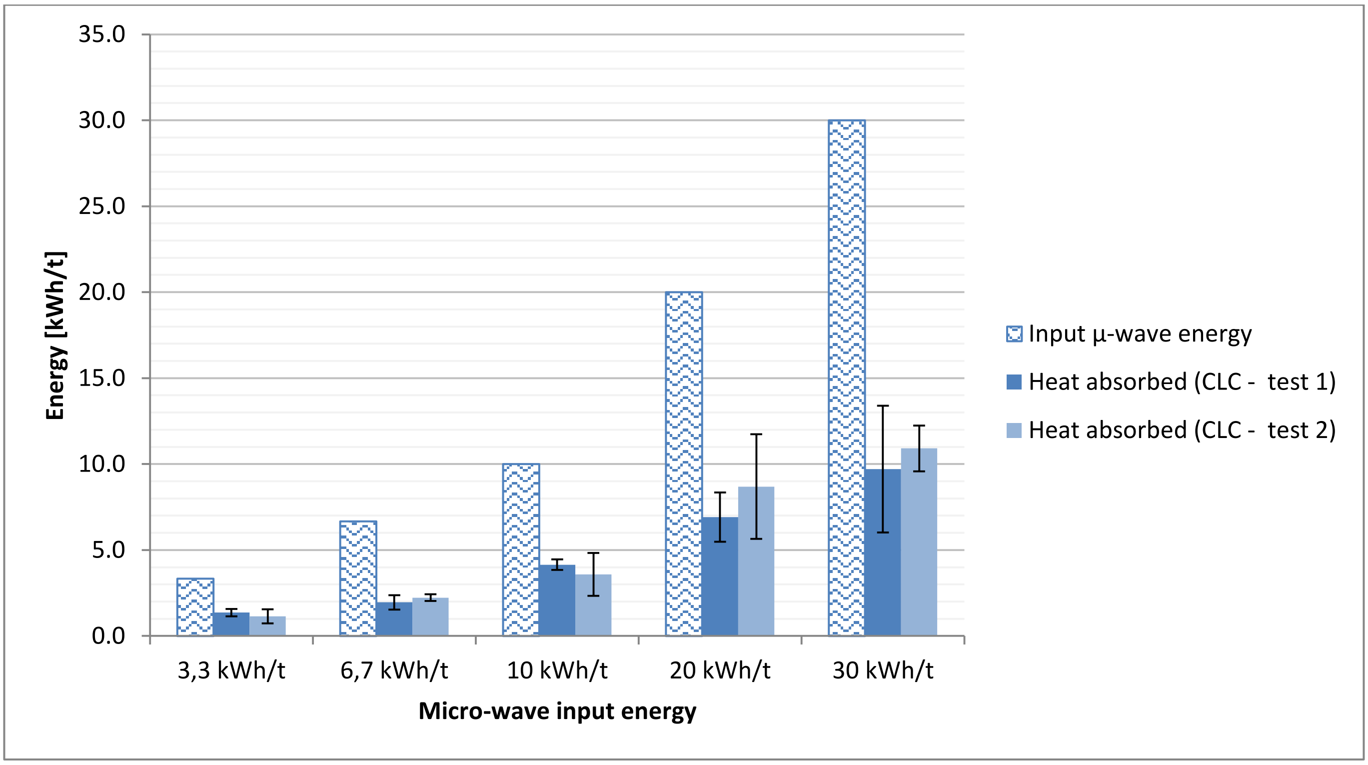


FIGURE 14 - CHART OF INPUT MICROWAVE ENERGY AND HEAT ABSORBED BY CLC SAMPLES.

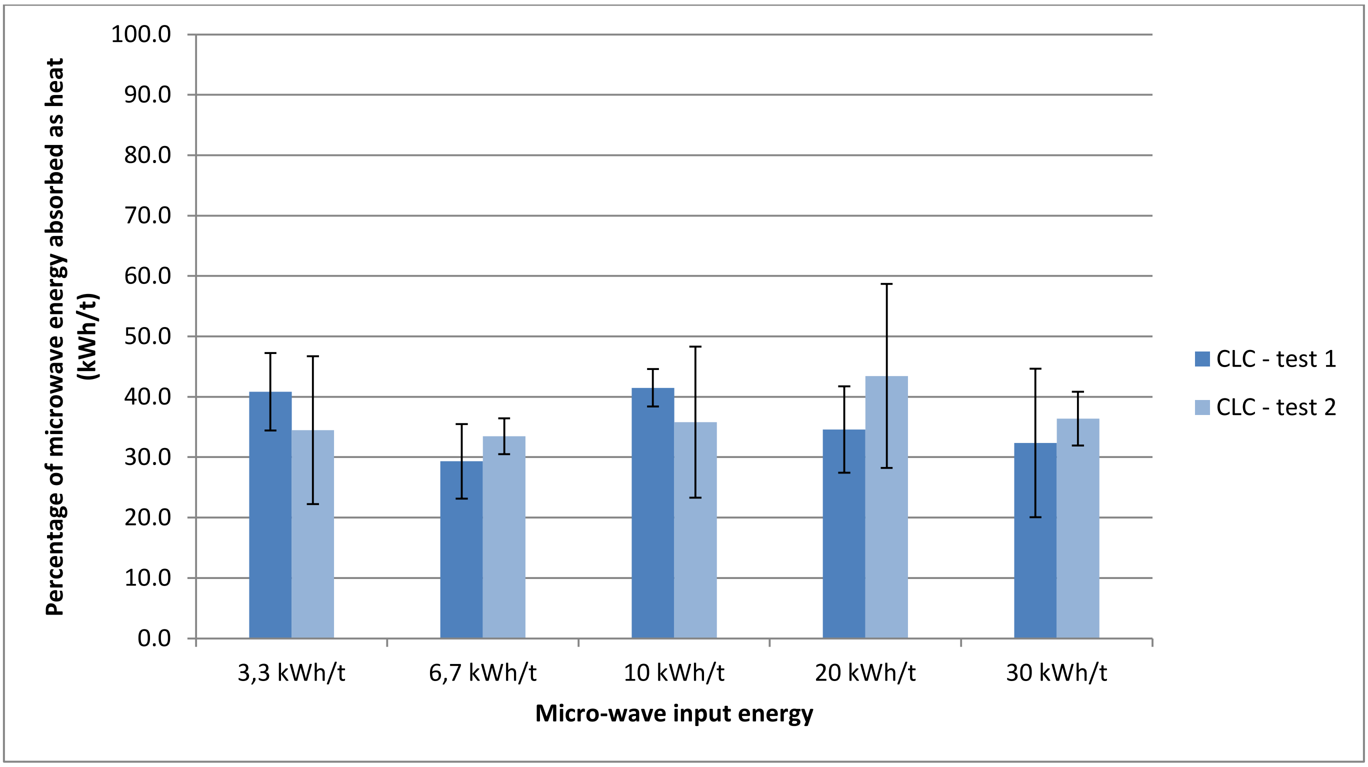


FIGURE 15 - PERCENTAGE OF ENERGY ABSORBED AS HEAT REGARDING THE MICROWAVE TREATMENT OF CLC SAMPLES.

Neves Corvo

Figure 16 presents the results obtained on a comparative chart between the input micro-wave energy and the heat absorbed by Neves Corvo samples. For each test undertaken, the absorbed energy as heat within the samples represents a percentage between 40.8% and 73.3% (see Figure 17). However most of the calculated energy absorbed represented around 50% of the micro-wave input energy.

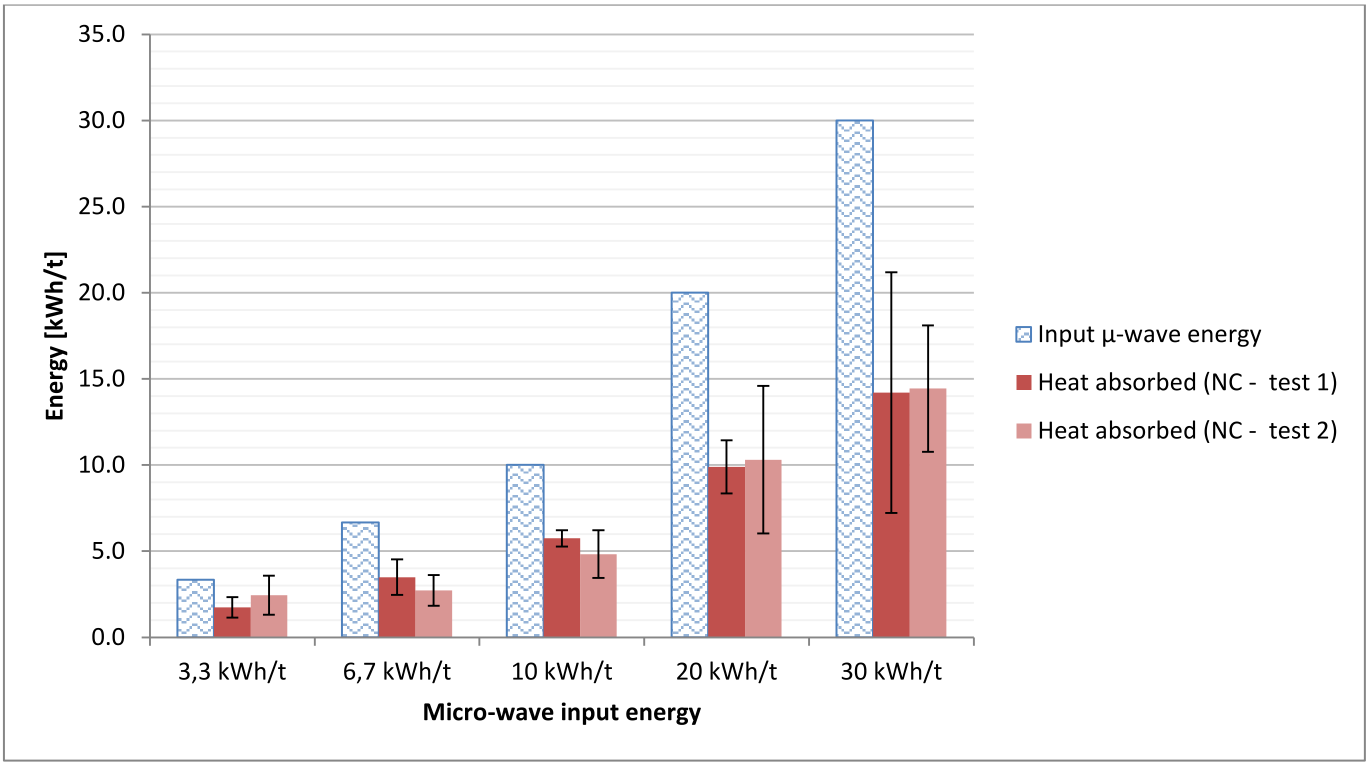


FIGURE 16 - CHART OF INPUT MICROWAVE ENERGY AND HEAT ABSORBED BY NC SAMPLES.

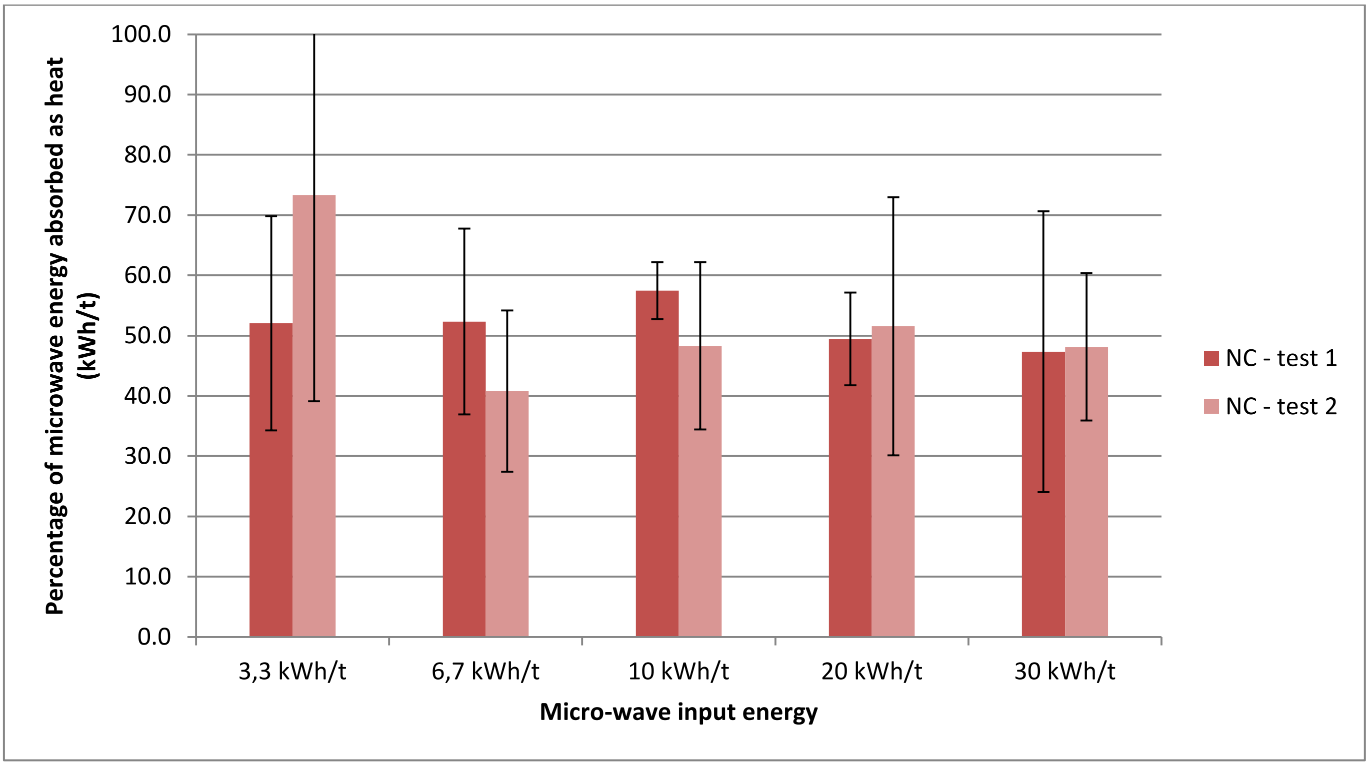


FIGURE 17 - PERCENTAGE OF ENERGY ABSORBED AS HEAT REGARDING THE MICROWAVE TREATMENT OF NC SAMPLES.

BOR

Figure 18 presents the results obtained on a comparative chart between the input micro-wave energy and the heat absorbed by BOR samples. For each test undertaken, the absorbed energy as heat within the samples represents a percentage between 33.8% and 49.7% of the micro-wave input energy (see Figure 19).

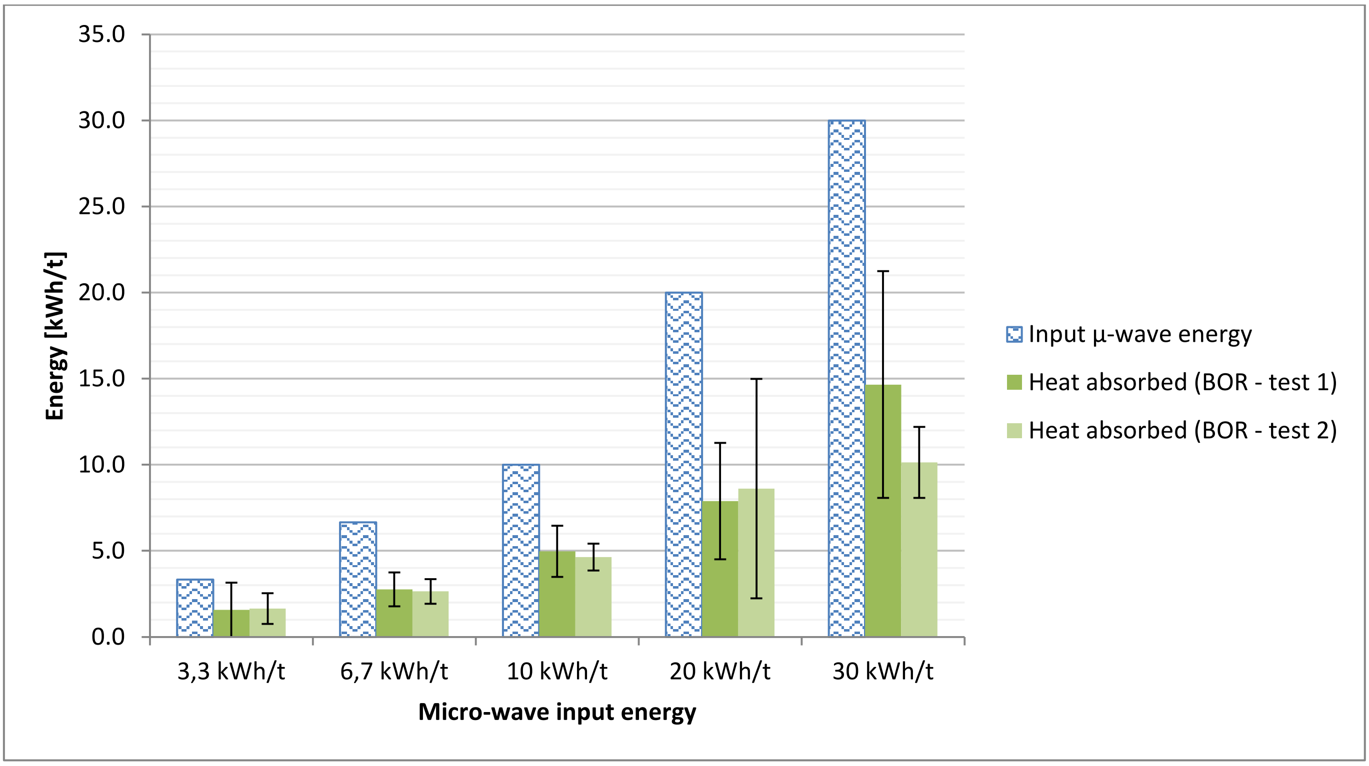


FIGURE 18 - CHART OF INPUT MICROWAVE ENERGY AND HEAT ABSORBED BY BOR SAMPLES.

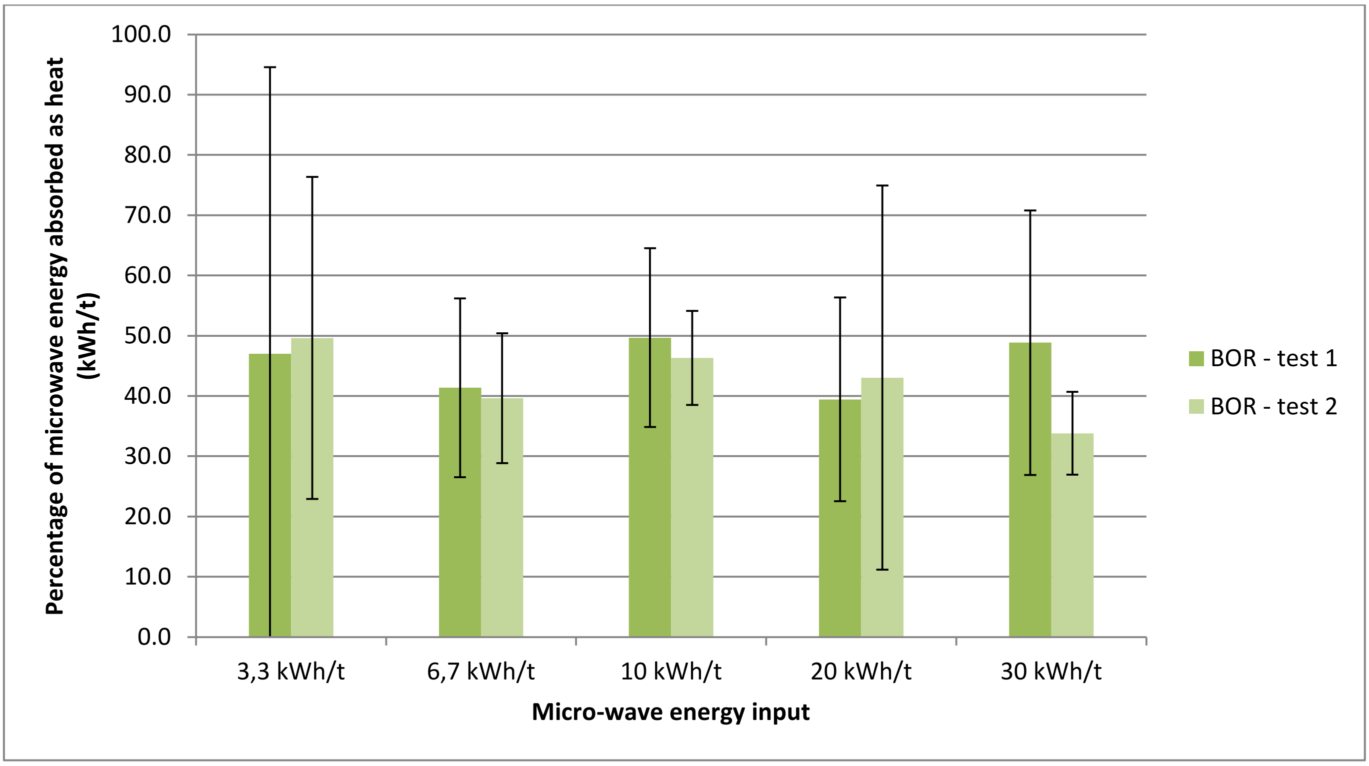


FIGURE 19 - PERCENTAGE OF ENERGY ABSORBED AS HEAT REGARDING THE MICROWAVE TREATMENT OF BOR SAMPLES.

2.3.1.3 MICROWAVE TREATMENT: TEXTURAL AND MINERALOGICAL CHANGES ASSESMENT

Micro-wave treated samples of ores from Cobre Las Cruces (CLC) and Neves Corvo (NC) had been characterized texturally under Scanning Electron Microscope (SEM) to find potential evidences that may lead to energy efficient comminution.

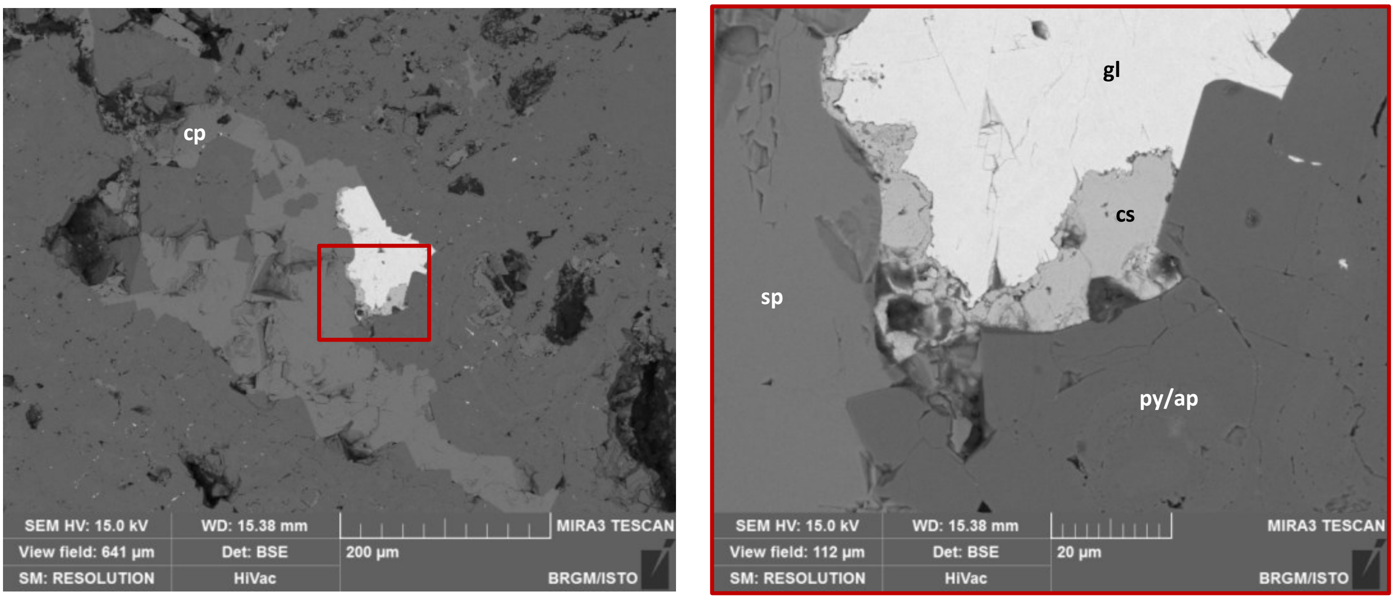


FIGURE 20 - BSE PICTURES OF A CLC ORE SAMPLE TREATED AT 30 KWH/T (GL: GALENA; SP: SPHALERITE; PY: PYRITE; CP: CHALCOPYRITE; AP: ARSENOPYRITE; CS: CERUSSITE).

Energy Dispersive Spectroscopy (EDS) analysis put into evidence the presence of lead carbonate (cerussite, PbCO3), intrusive-like, on the edge of galena's grains regarding a microwave treated CLC sample at 30 kWh/t (Figure 20). This may be the result of both local high temperature desulphurization and carbonation of lead.

However, few weakening figures appear on the boundaries between each Pb-, Zn-, Cu- and iron sulphides.

CLC sample microwave treated at 3.3 kWh/t showed barite mineral phase with desulphurization figure (Figure 21). However, such evidence had not been spotted elsewhere within other treated samples.

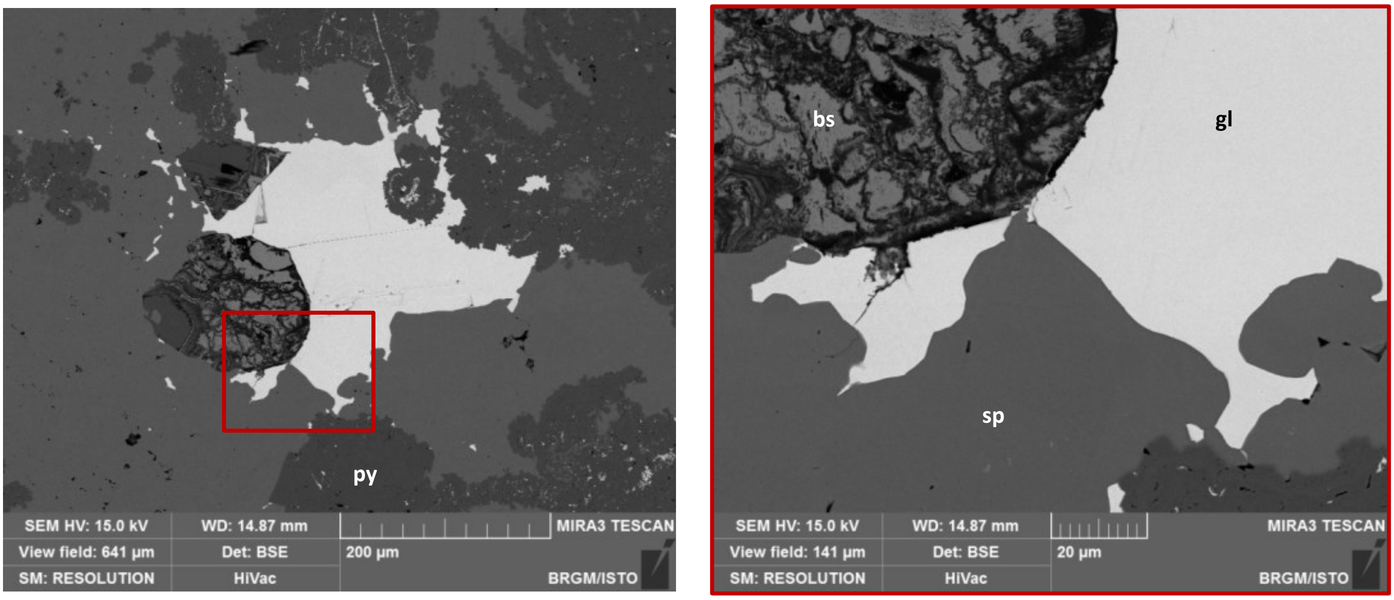


FIGURE 21 - BSE PICTURES OF A CLC ORE SAMPLE TREATED AT 3.3 KWH/T (GL: GALENA; SP: SPHALERITE; PY: PYRITE; BS: BARYUM SULFATE).

SEM investigation of the Neves Corvo ore sample treated at 30 kWh/t showed also little weakening figures (Figure 22).

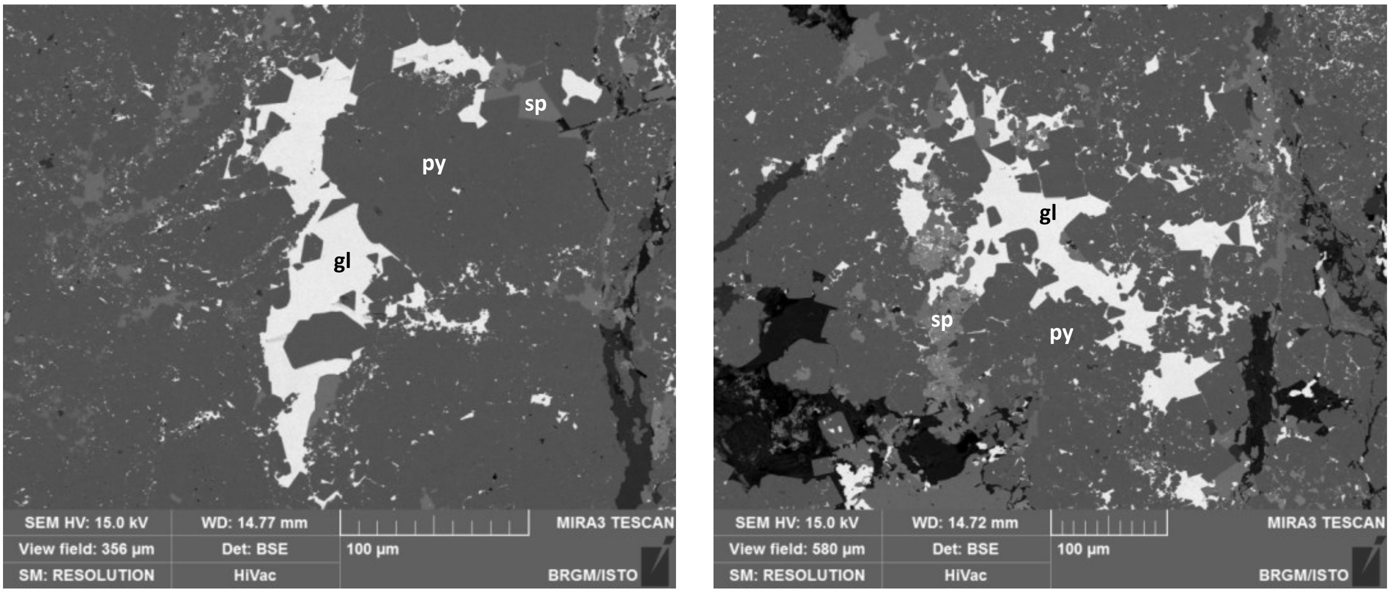


FIGURE 22 - BSE PICTURES OF A NC ORE SAMPLE TREATED AT 30 KWH/T (GL: GALENA; SP: SPHALERITE; PY: PYRITE).

However, intergranular fractures had been spotted through some of the galena phases of the sample (Figure 23). The presence of these fractures also seems to be correlated to the presence of siderite nearby or inside galena phase.

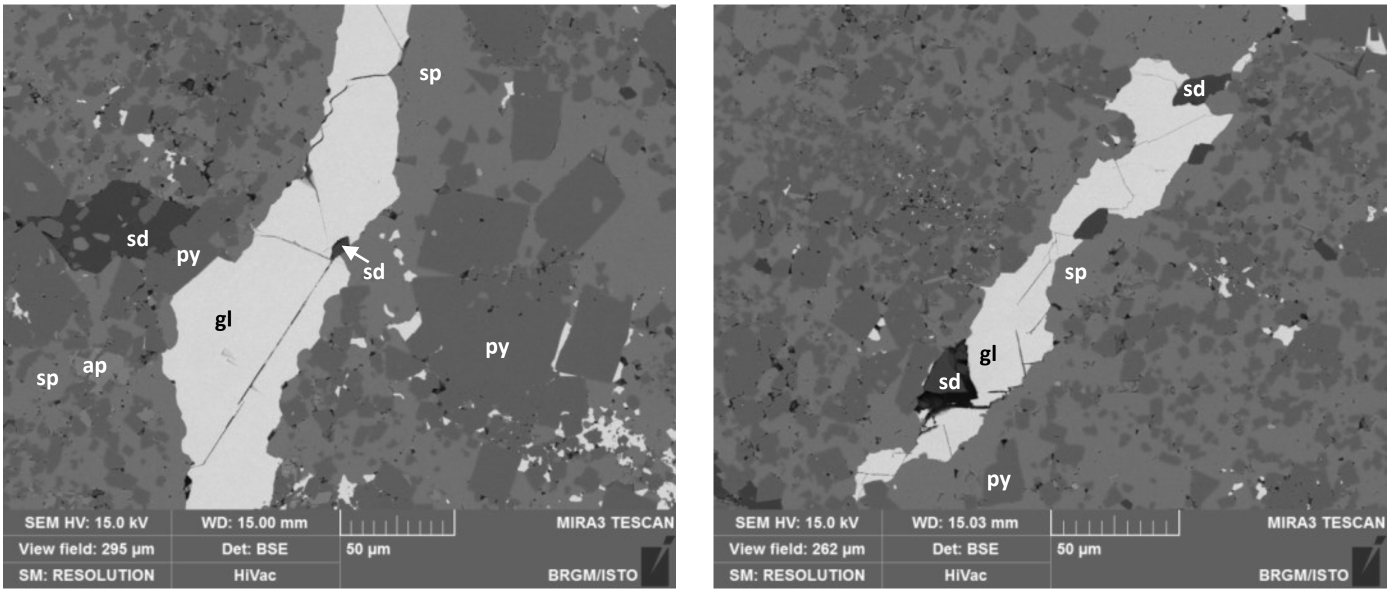


FIGURE 23 - BSE PICTURES OF A NC ORE SAMPLE TREATED AT 30 KWH/T WITH INTRAGRANULAR FRACTURES OF GALENA (GL: GALENA; SP: SPHALERITE; PY: PYRITE; SD: SIDERITE; AP: ARSENOPYTITE).

SEM investigation of the Neves Corvo ore sample treated at 10 kWh/t showed discontinuous boundaries between the silica phase with the chalcopyrite and cassiterite nearby (Figure 24). The presence of siderite here seems not correlated to any intragranular fracture. Once again, no weakening figure appears on the boundaries among sulphides.

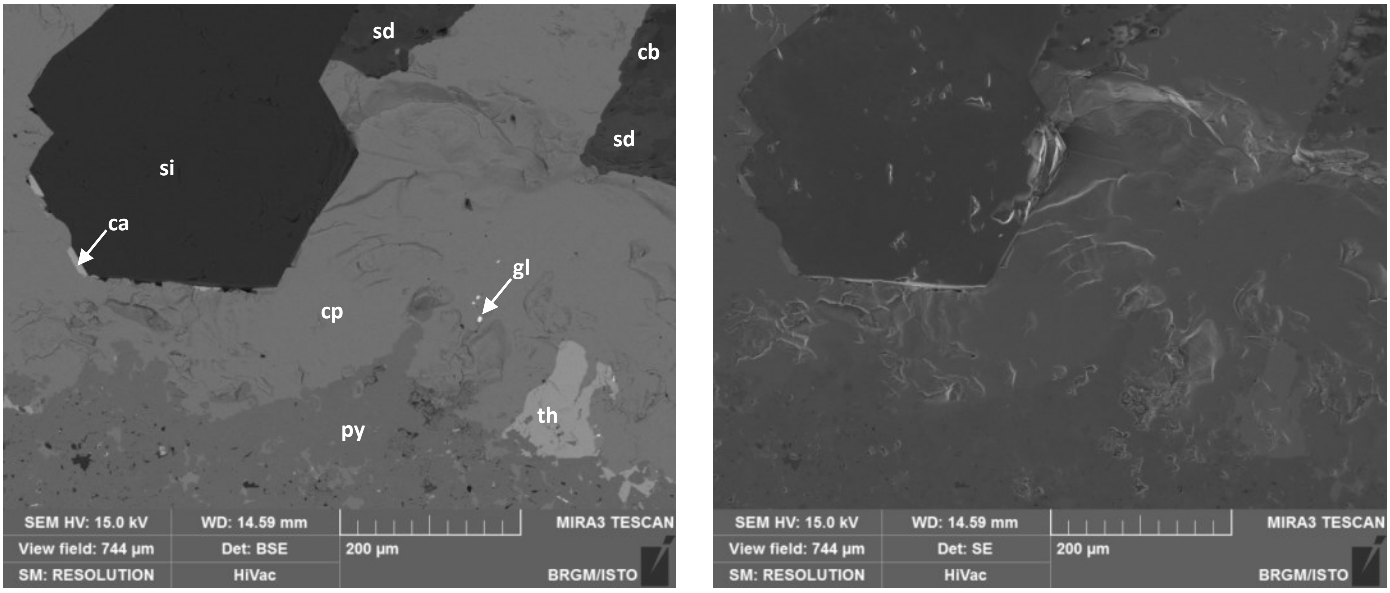


FIGURE 24 – BSE (LEFT) AND SE (RIGHT) PICTURES OF A NC ORE SAMPLE TREATED AT 10 KWH/T (CP: CHALCOPYRITE; TH: TETRAHEDRITE; PY: PYRITE; GL: GALENA; SI: SILICA; SD: SIDERITE; CB: CARBONATE CA/MG; CA: CASSITERITE).

SEM investigation of the BOR ore sample treated at 10 kWh/t show little discontinuous boundaries between silica, barium sulphate and galena phases (Figure 25). However, barite here does not present any desulphurization figure as spotted within CLC sample treated at 3,3 kWh/t.

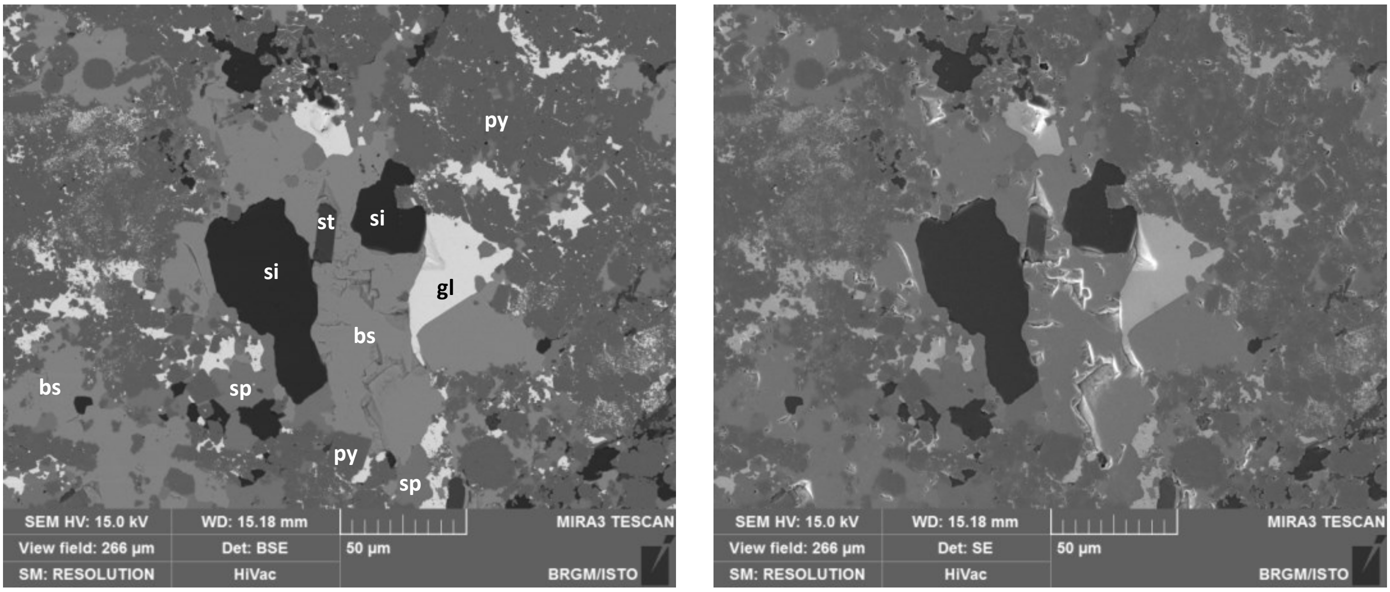


FIGURE 25 - BSE (LEFT) AND SE (RIGHT) PICTURES OF A BOR SAMPLE MICROWAVE TREATED AT 10 KWH/T (BS: BARUYM SULFATE; SP: SPHALERITE; SI: SILICA; ST: SILICATE; GL: GALENA; PY: PYRITE).

2.3.1.4 CONLUSIONS ABOUT THE MICRO-WAVE TREATMENT

The heat capacity of ores from Cobre Las Cruces, Neves Corvo and BOR had been evaluated from their main mineralogical composition and taking into account the minerals heat capacities at 20°C (Waples and Waples 2004). The evaluated heat capacity ranges between 517 and 537 J/K/kg, obviously close from pyrite's which is the main mineral represented within the ore studied.

Microwave treatment had been tested up to an input power of 6 kW during 18 seconds, which corresponds to a maximum energy input of 30 kWh/t.

Temperature monitoring during and after the microwave treatment allowed the evaluation of the maximum temperature reached by the sample, which could locally go up to 120°C. By applying the simplified enthalpy equation, it had been evaluated that microwave energy is absorbed as heat, but mostly with a rate below 50%. However, this evaluation is dependant from local measures of temperature within the sample and generated large standard deviation.

Several textural and mineralogical changes had been spotted through the investigation of microwave treated samples under SEM and EDS:

- Intragranular fractures within galena phases which seem correlated to the presence of siderite within Neves Corvo ore.

- Desulphurization of barite sulphate phase in Cobre Las Cruces ore.
- The presence of lead carbonate (cerussite) intrusive-like on the edges of galena phases in Cobre Las Cruces ore.
- Discontinuous boundaries between galena and gangue mineral such as siderite, silicate, silica, barium sulphate.

However, the presence of these textural and mineralogical changes can hardly constitutes general evidence within the samples and represents isolated figures, and only assignable to a microwave treatment of at least 10 kWh/T.

Textural and mineralogical changes occurred mostly between galena and siderite, mineral with respectively the lower and the higher specific heat capacities within the ores studied (Table 8).

Mineral	Density (g/cm^3)	Specific heat capacity Cp (J/K/kg)	Thermal capacity ($J/cm^3/K$)
Galena	7.55	210	1.59
Siderite	3.944	740	2.92
Quartz	2.648	740	1.96
Pyrite	5.05	510	2.58

TABLE 8 - SPECIFIC HEAT CAPACITIES OF MINERALS (EXTRACTED FROM D.W. WAPLES AND J.S. WAPLES).

2.3.2 RESULTS OF THE ORES GRINDABILITY

2.3.2.1 REFERENCES WORK INDEX: BOND METHODOLOGY

The Bond Ball Mill Work Index had been determined for each run of mine ore. A representative batch of each ore (see Figure 9) had been used to perform the test following the methodology presented.

The main results are presented in Table 9.

Ore / Bond parameter	Feed **XF80** *(µm)*	Screen **XP1** *(µm)*	Product **XP80** *(µm)*	Net production **G** *(g/revolution)*	**BW_i** ***(kWh/t)***
Cobre Las Cruces (untreated)	2016	150	101	1,78	**12,51**
BOR (untreated)	1937	100	68	1,75	**10,96**
Neves Corvo (untreated)	2150	80	55	1,35	**12,35**

TABLE 9 - MAIN RESULTS OF THE DETERMINATION OF THE BOND BALL MILL WORK INDEX FOR EACH RUN OF MINE ORE.

2.3.2.2 WORK INDEX AFTER MICROWAVE TREATMENT: BOND METHODOLOGY

The Bond Ball Mill Work Index had been determined for two CLC batches respectively microwave treated at 3.3 and 6.7 kWh/t. The batches were microwave treated before the secondary crusher step (see Figure 9) and then were used to perform the test following the methodology presented. The main results are presented in Table 10.

Ore / Bond parameter	Feed **XF80** *(µm)*	Screen **XP1** *(µm)*	Product **XP80** *(µm)*	Net production **G** *(g/revolution)*	**BW_i** ***(kWh/t)***
Cobre Las Cruces (untreated)	2016	150	101	1,7804	**12,51**
Cobre Las Cruces (3,3 kWh/t)	2030	150	105	1,8587	**12,33**
Cobre Las Cruces (6,7 kWh/t)	2217	150	97	1,6383	**12,91**

TABLE 10 - MAIN RESULTS OF THE DETERMINATION OF THE BOND BALL MILL WORK INDEX FOR TWO MICROWAVE TREATED CLC BATCHES.

Microwave treated CLC batches have close Ball Mill Work Index from untreated CLC batch. In spite of the microwave energy input, and even considering the rate of energy absorbed as heat only, no decrease of the grindability seems to occur.

Bond methodology stands as a direct approach of the evaluation of the grindability. However, this methodology needs a large amount of material (at least 15 to 20 kg) and is quite time consuming. That’s the reason why the methodology developed by Bruce and Berry (1966) had been implemented in this study in order to evaluate the grindability of microwave treated ores.

2.3.2.3 WORK INDEX AFTER MICROWAVE TREATMENT: COMPARATIVE METHODOLOGY

The Bond Ball Mill Work index regarding each microwave treated sample had been determined using the comparative methodology presented.

Since the Bond Ball mill work index is known for each untreated ore, the microwave treated samples had been ground in the same conditions (see Table 11) than a sample of each untreated ore.

Mass of product (kg)	Mill	Loading charge	Time (min)	Speed (RPM)
2.0	Bond Ball Mill		15	70

TABLE 11 - OPERATIONAL PARAMETERS IMPLEMENTED FOR THE COMPARATIVE METHODOLOGY OF THE BOND BALL MILL WORK INDEX DETERMINATION.

Consequently, in order to apply Equation 3 both F80 (d80 of the feed) and P80 (d80 of the ground product) had been determined (Table 12).

Ore / Sample		*Reference*	A (3,3 kWh/t)	B (6,7 kWh/t)	C (10 kWh/t)	D (20 kWh/t)	E (30 kWh/t)
CLC	F80	*1829*	1836	1856	1804	1777	1775
	P80	*107*	114	118	112	100	100
NC	F80	*1625*	1680	1704	1677	1612	1559
	P80	*88*	94	87	93	89	89
BOR	F80	*1691*	1632	1644	1597	1630	1633
	P80	*83*	80	81	79	77	76

TABLE 12 – D80 DETERMINED FOR EACH FEED AND GROUND PRODUCT OF THE ORE SAMPLES.

Then, the comparative Bond Ball Mill Work Index had been calculated for each microwave treated sample (Figure 26, Figure 27 & Figure 28).

Figure 26 presents also the values of the Bond Ball Mill Work index obtained thought Bond methodology regarding batches microwave treated at 3.3 and 6.7 kWh/t respectively.

At best, based on the values obtained, the microwave treatment only had a slightly decrease of the Bond Ball Mill Work index for Cobre Las Cruces and BOR ores. The maximum decrease reached here is 0.54 kWh/t for these two ores with input microwave energy of 30 kWh/t. That is to say that only 1.8% of the input microwave energy would have been converted in a decrease of the grindability.

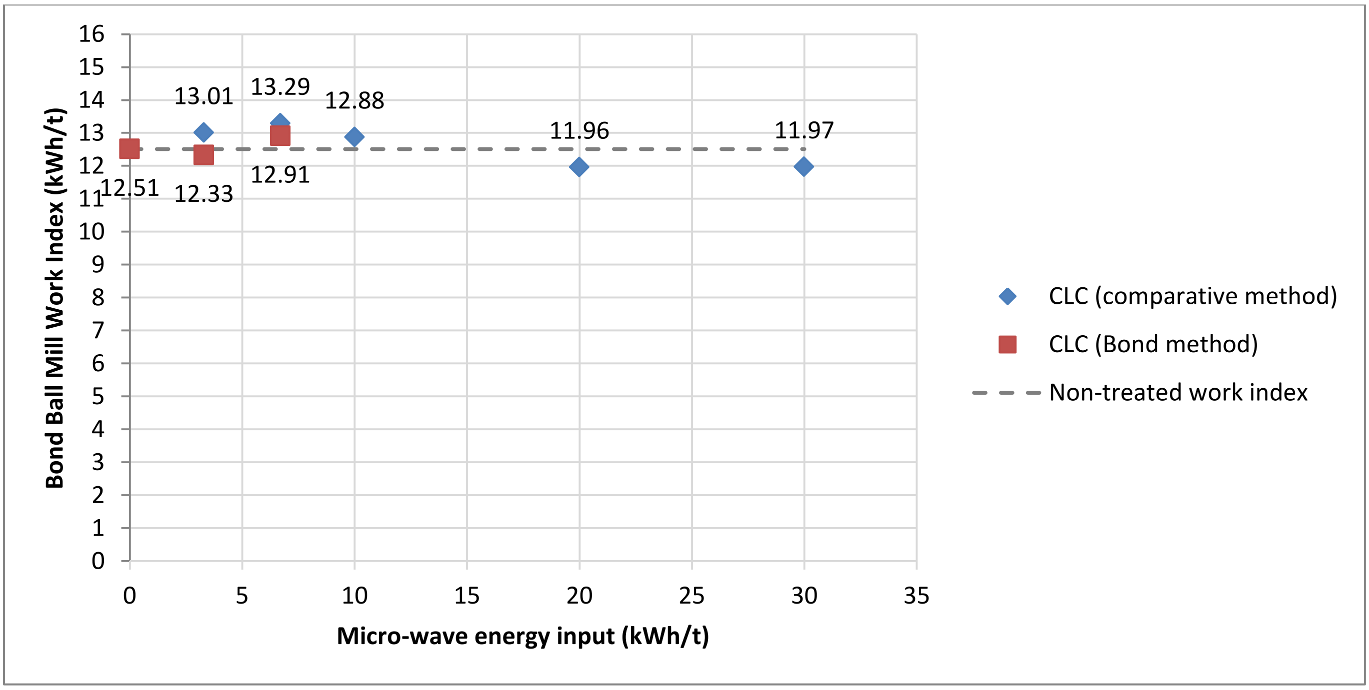


FIGURE 26 – BOND BALL MILL WORK INDEX OF CLC MICROWAVE TREATED AND UNTREATED SAMPLES.

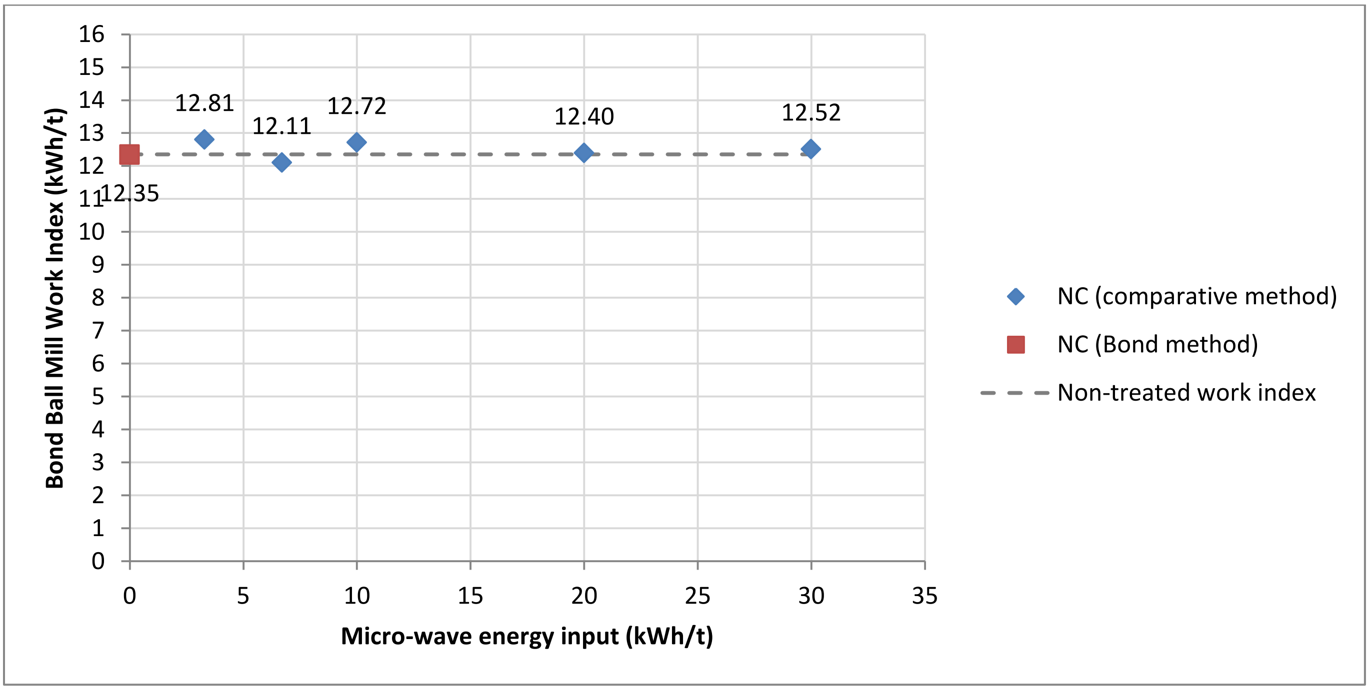


FIGURE 27 - BOND BALL MILL WORK INDEX OF NC MICROWAVE TREATED AND UNTREATED SAMPLES.

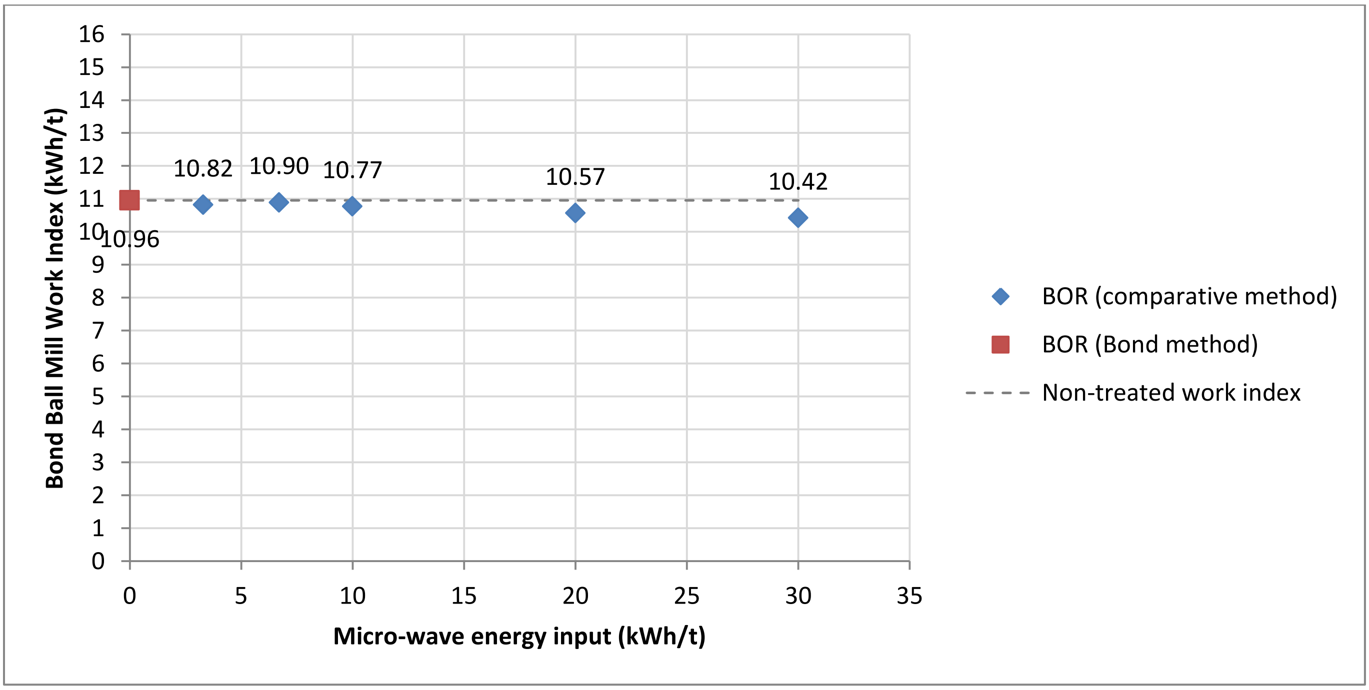


FIGURE 28 - BOND BALL MILL WORK INDEX OF BOR MICROWAVE TREATED AND UNTREATED SAMPLES.

2.3.2.4 COMPARISON TO PREVIOUS WORK ON NEVES CORVO ORE

Microwave assisted-grinding made reference to the work upon Neves Corvo MCZ ore (Kingman, Voster, and Rowson 2000; Vorster, Rowson, and Kingman 2001). They microwave treated ore samples up to 130 kWh/t, and

Figure 29 puts into comparison the Ball Mill Work indexes obtained in each work. Only a microwave energy input above 30 kWh/t resulted in a more significant decrease of the Bond Ball mill work index of the Neves Corvo ore.

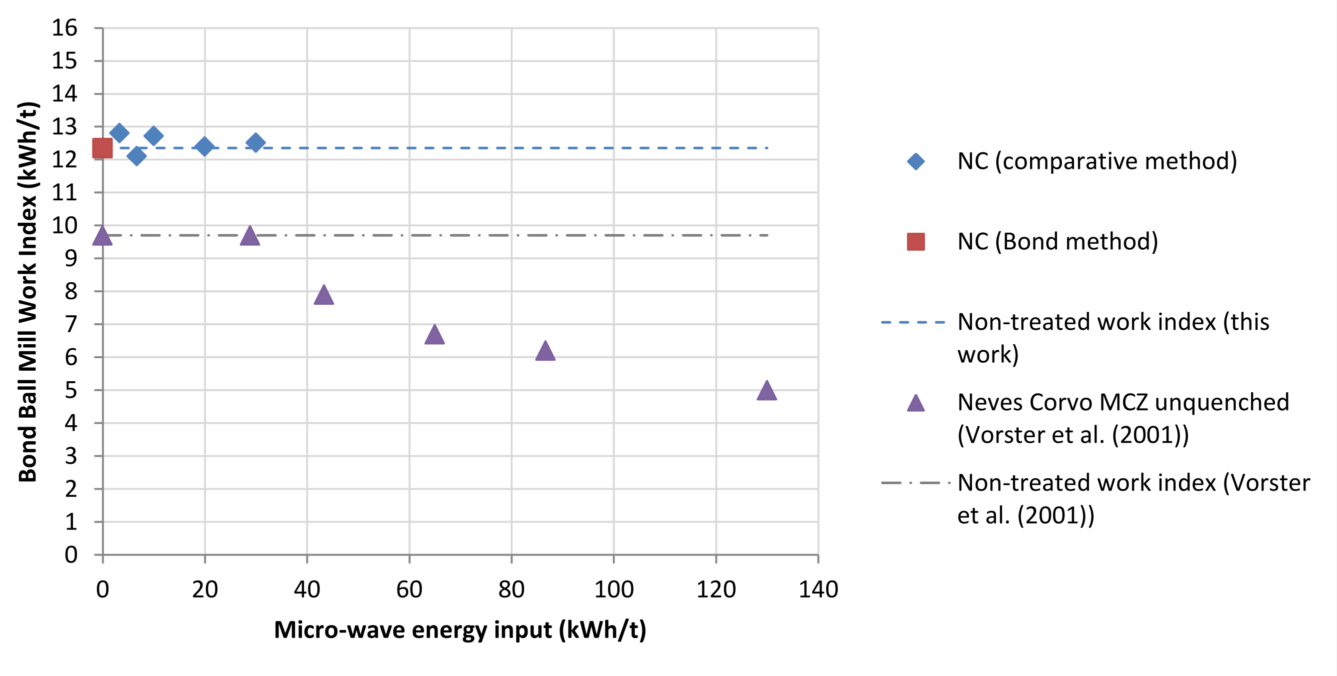


FIGURE 29 – BOND BALL MILL WORK INDEXES OF NEVES CORVO MICROWAVE TREATED AND UNTREATED SAMPLES: COMPARISON WITH THE WORK FROM VORSTER ET AL. (2001).

2.3.2.5 CONCLUSIONS ABOUT THE GRINDABILITY OF ORES

The Bond Ball Mill Work index had been determined through the methodology developed by Bond (Fred C Bond 1961) for the run of mine ores from Cobre Las Cruces, Neves Corvo and BOR. In parallel, the grindability of microwave treated samples was determined using the comparative method developed by Berry and Bruce (Wills and Finch 2016) and applied for the Bond Ball mill work index.

It was found that a microwave treatment up to 30 kWh/t of energy input in a multi-modal oven had little or even no effect on the grindability of the polymetallic ore studied by taking into account the Bond Ball mill work index.

Considering that the Bond ball mill work index of the polymetallic ores studied ranges from 11 to 13 kWh/t, it is irrelevant to test microwave radiation with input energy largely above these value. Indeed, the beneficiation obtained in terms of grindability and afterwards recovery of metals wouldn't reach or overtake the amount of energy input of the microwave treatment.

These polymetallic ores are mainly constituted by microwave absorbers materials such as pyrite, galena or chalcopyrite. Due to the large presence of pyrite, little microwave energy may be focused on and absorbed by galena or chalcopyrite. As a consequence, a high gradient of temperature between these sulphides and the gangue around (which is mostly made of pyrite) can't be reached, and then reducing the chances of fracturing and decreasing the grindability of ores.

Sphalerite constitutes a particular case for it barely heats under microwave radiation. However, no textural changes of sphalerite phases had been observed and interpreted as a result of the microwave treatment within the samples investigated under SEM. Actually, during the microwave treatment, no high gradient of temperature may have taken place around sphalerite (with a “cold” nucleus constituted by the sphalerite). Indeed, its specific heat capacity (450 J/K/kg) is lower than pyrite (510 J/K/kg). As a consequence, the temperature of the sphalerite phase is able to increase due to the heat of the surrounding pyrite and others microwave absorbers materials.

Moreover, the size of the mineral plays an important role on the amount of energy absorbed as heat (Salsman et al. 1996). As a consequence, the textural characteristics of polymetallic ores with fine disseminate sulphides minerals also doesn’t stand as a favourable parameter in order to decrease their grindability.

3. REAGENTS FOR ENHANCED FLOTATION PROCESS

Froth flotation is a highly versatile method for physically separating particles based on differences in the ability of air bubbles to selectively adhere to specific mineral surfaces in a mineral/water slurry.

3.1 INTRODUCTION TO FLOTATION REAGENTS

A number of organic and inorganic reagents are used in flotation processes to achieve the desired separation. These can be classified into collectors, frothers, extenders, activators, depressants, deactivators, flocculants and dispersants.

Collectors

The primary role of collectors is to adsorb selectively in order to impart hydrophobicity to particles of the mineral to be floated. Having this dual ability to adsorb and to impart hydrophobicity requires the collector molecule to contain two functional parts:

- A nonpolar group of sufficient hydrophobicity. For sulphides flotation the nonpolar group is usually a short-chained hydrocarbon (2-15 CH_2 or CH_3 groups).
- A polar or ionic group that will be electrostatically or chemically reactive toward species on the mineral surface. This polar part is usually anionic sulphate, sulfonate, phosphate, carboxylate, oxime or thiocarbonate, cationic amine or non-ionic oximes.

Following tables give examples of collectors used in froth flotation:

Amine	Formula
n-amyl amine	$C_5H_{11}NH_2$
n-dodecylamine	$C_{12}H_{25}NH_2$
Di-n-amylamine	$(C_5H_{11})_2NH$
Tri-n-amylamine	$(C_5H_{11})_3N$
Tetramethylammonium chloride	$[(CH_3)_4N]^+Cl^-$
Tallow amine acetate	RNH_3Ac (96% C_{18})

TABLE 13 - CATIONIC COLLECTORS.

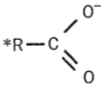
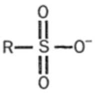
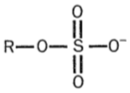
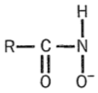
Collector	Structural Formula
Carboxylate	 ......Na^+
Sulfonate	 $R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-$ ......Na^+
Alkyl sulfate	 $R-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-$ ......Na^+
Hydroxamate	 $R-\underset{\underset{O}{\|}}{C}-\overset{\overset{H}{\vert}}{\underset{\underset{O^-}{\vert}}{N}}$ ......Na^+

TABLE 14 - STRUCTURAL FORMULAS OF SODIUM SALTS OF ANIONICS COLLECTORS.

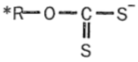
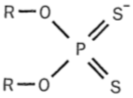
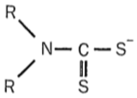
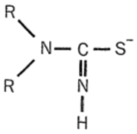
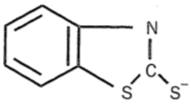
Collector	Structural Formula
Xanthate	 $^*R-O-\underset{\underset{S}{\|}}{C}-S^-$ ......Na^+
Thiophosphate	 ......Na^+
Thiocarbamate	 ......Na^+
Mercaptan	$R-S^-$ ......Na^+
Thiourea	 ......Na^+
Mercaptobenzothiazole	 ......Na^+

TABLE 15- ANIONIC SULPHYDRYL COLLECTORS.

Collection by these reagents depends on properties as ionization, solubility, critical micelle concentration or emulsifying power:

- A highly soluble surfactant has a low tendency to depart from the solution and adsorb on interfaces.
- The tendency to form micelles also influences the utility of the collector for flotation. The surfactant forms micelles when its bulk concentration reaches the “critical micelle concentration” (CMC). Above the CMC, properties of the surfactant solutions change, as surface tension of water, which decreases up to the CMC and remains approximately constant above CMC, which indicates that the activity of the surface-active monomer species is constant above the CMC and the micelles themselves are not-surface active.

Additionally, the solubility of salts formed by surfactants with mineral dissolved species and other additives can have an important influence on the extent of flotation. Nevertheless, precipitation can also occur on the mineral surface and lead to good flotation.

Frothers

To achieve an adequate flotation, bubbles that rise to the top of the flotation cell must not break until they are skimmed off to collect the floated particles. This is the reason why non-ionic surfactants are usually added to produce the desired stability of the froth. This may happen that a collector can act as a frother; such is the case of long-chained collectors which will adsorb also at bubble surface in sufficient amounts to achieve an elastic surface and stable bubbles. On the other hand, when short-chained chemicals are used as collectors, additional reagents must be added for froth stability.

Common frothers are cresylic acid, MIBC, polyglycols or pine oil, whose constituent are xylenol, methyl isobutyl carbinol, polypropylene and terpineol respectively.

Extenders

In addition to frothers and collectors, non-ionic and nonpolar surface-active agents are used in to enhance the hydrophobicity of the particles and the resultant flotation recovery. These reagents act by forming a multilayer coating on the already partly hydrophobic surfaces. They can also act like frothers by co-adsorbing with collectors.

Activators

Many minerals do not adsorb collectors, so special reagents are necessary to activate their adsorption. An activator normally acts by adsorbing on the mineral, providing sites for adsorption of the collector species. As example, copper sulphate acts as an activator for the flotation of sphalerite using xanthate as a collector at relatively low concentration. Copper ion exchanges for zinc ion of the mineral surface, and the sphalerite particle then behaves in flotation like a copper sulphide particle.

Depressants

Depressants retard or inhibit flotation of a desired solid. The depressing agent is adsorpted on the particle surface, which pre-empts the collector from adsorbing and masks the adsorbed collector from the bulk solution and achieves the particle does not exhibit a hydrophobic exterior. Chemicals used as depressants include multivalent ions as phosphate, silicates, chromates, aluminium salts or organics. Common examples include starch, tannin, quebracho and dextrin.

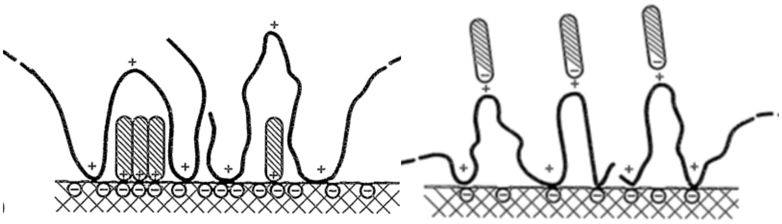


FIGURE 30 - CO- ADSORPTION ON MINERAL PARTICLES RESULTING IN FLOTATION DEPRESSION AND FLOTATION ACTIVATION.

Figure above illustrates depression of flotation through action of a cationic polymer; the same polymer can activate flotation using an anionic collector.

Deactivators

Deactivators react with activators to form inert species and prevent flotation.

Dispersants and flocculants

Flotation is often hampered by the presence of fine particles or slimes, which can coat the coarser mineral particles and consume excessive amounts of reagent because of their large specific surface areas. To solve this problem dispersants are used in order to disperse these slimes.

Flocculants are used to deal with fines. Polymers are used to flocculate particles into larger aggregates or flocs by forming bridges between them. On mineral particles, adsorption of polymers is attributed to hydrogen bonding between functional groups, or chemical or electrostatic bonding between polymer functional groups and surface sites. Then, it is followed by separation of the flocs.

pH as Modifier

The pH in the pulp is a key variable to maximize recovery and selectivity, so it must be carefully controlled. Lime, sodium hydroxide, sodium carbonate, ammonia, hydrochloric acid or sulphuric acid are used to control pH.

Main stages included in all the processing routes are: conditioning, rougher, scavenger, cleaning, thickening and filtration. Grinding and Regrinding (including the necessary classification operation unit) stages are needed to ensure mineral liberation from gangue.

3.2 COBRE LAS CRUCES LAB FLOTATION TESTWORK

Cobre Las Cruces test work has the purpose of develop the metal recovery process from the primary polymetallyc ore coming from its new deposit of the mine aiming to extend the life of the mine. Due to the complexity and low grade of the ore a bulk flotation process followed by an hydrometallurgical plant to recover the base metals is proposed.

To that end, several flotation tests have been performed using different flotation conditions. Following parameters have been checked:

- Pre-aeration and flotation time.
- Particle size.
- Different type of reagents and dose of depressants, collectors, promoters and modifiers (as xanthates and derivatives, dithiophosphates, thionocarbamates hydrocarbon sulphides and mercaptobenzothiazols; Nasaco series: BETAMIN flotation reagents; Cytec series: AEROPHINE, AERO and AEROFLOAT; Pionera reagents, $CuSO_4$, etc.).
- BASF and NALCO new developed reagents have been also studied.

3.2.1 ORE CHARACTERIZATION

Before any research activity in flotation is very important to know the composition and mineralogy of the ore. For the lab research activities two samples of the new deposit were selected:

- DPP ore: primary polymetallic sulphides product of previous prospections used to design the pilot plant.
- HPP ore: primary polymetallic sulphides prepared in mine to be processed later in the pilot plant in order to produce bulk concentrate.

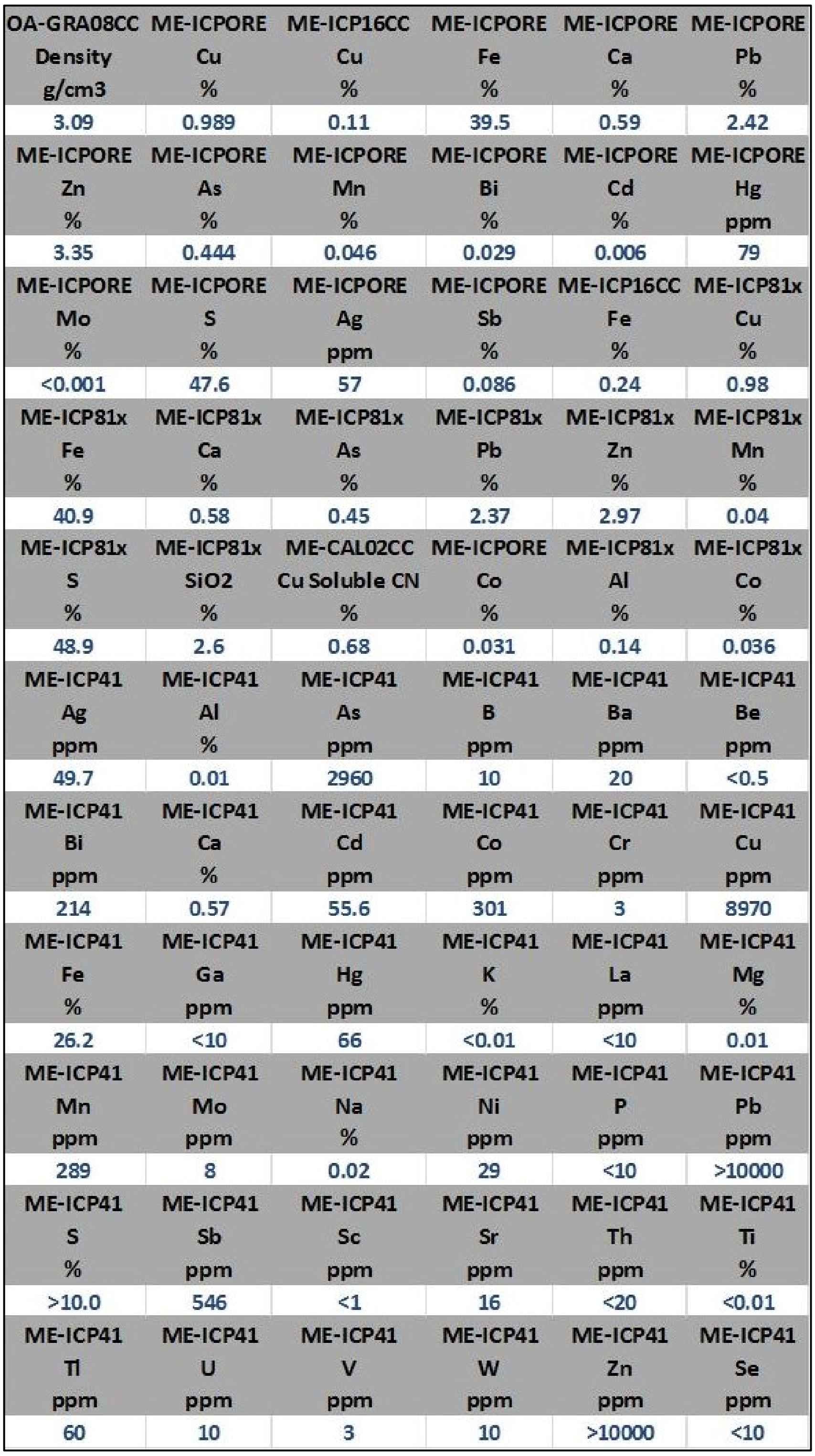
FIGURE 31 - DPP SAMPLE VIEW.

FIGURE 32 - HPP SAMPLE.

Chemical characterization of both ores investigated (DPP & HPP ore) showed the following values:

ME-ICPORE	**ME-ICPORE**	**ME-ICPORE**	**ME-ICPORE**
CuT	**Pb**	**Zn**	**Ag**
%	**%**	**%**	**ppm**
1,05	**1,32**	**2,95**	**30**
ME-ICPORE	**ME-ICPORE**	**ME-ICP81x**	**ME-ICPORE**
Fe	**S**	**SiO2**	**Ca**
%	**%**	**%**	**%**
36,93	**46,67**	**3,60**	**0,31**
ME-ICPORE	**ME-ICPORE**	**ME-ICPORE**	**ME-ICPORE**
As	**Mn**	**Bi**	**Cd**
%	**%**	**%**	**%**
0,38	**0,04**	**0,02**	**0,01**
ME-ICPORE	**ME-ICPORE**	**ME-ICPORE**	**ME-ICPORE**
Hg	**Mo**	**Sb**	**Co**
ppm	**%**	**%**	**%**
27,33	**0,00**	**0,06**	**0,04**

TABLE 16 - DPP ORE CHEMICAL CHARACTERIZATION.



OA-GRA08CC	ME-ICPORE	ME-ICP16CC	ME-ICPORE	ME-ICPORE	ME-ICPORE
Density	Cu	Cu	Fe	Ca	Pb
g/cm3	%	%	%	%	%
3.09	0.989	0.11	39.5	0.59	2.42
ME-ICPORE	ME-ICPORE	ME-ICPORE	ME-ICPORE	ME-ICPORE	ME-ICPORE
Zn	As	Mn	Bi	Cd	Hg
%	%	%	%	%	ppm
3.35	0.444	0.046	0.029	0.006	79
ME-ICPORE	ME-ICPORE	ME-ICPORE	ME-ICPORE	ME-ICP16CC	ME-ICP81x
Mo	S	Ag	Sb	Fe	Cu
%	%	ppm	%	%	%
<0.001	47.6	57	0.086	0.24	0.98
ME-ICP81x	ME-ICP81x	ME-ICP81x	ME-ICP81x	ME-ICP81x	ME-ICP81x
Fe	Ca	As	Pb	Zn	Mn
%	%	%	%	%	%
40.9	0.58	0.45	2.37	2.97	0.04
ME-ICP81x	ME-ICP81x	ME-CAL02CC	ME-ICPORE	ME-ICP81x	ME-ICP81x
S	SiO2	Cu Soluble CN	Co	Al	Co
%	%	%	%	%	%
48.9	2.6	0.68	0.031	0.14	0.036
ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41
Ag	Al	As	B	Ba	Be
ppm	%	ppm	ppm	ppm	ppm
49.7	0.01	2960	10	20	<0.5
ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41
Bi	Ca	Cd	Co	Cr	Cu
ppm	%	ppm	ppm	ppm	ppm
214	0.57	55.6	301	3	8970
ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41
Fe	Ga	Hg	K	La	Mg
%	ppm	ppm	%	ppm	%
26.2	<10	66	<0.01	<10	0.01
ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41
Mn	Mo	Na	Ni	P	Pb
ppm	ppm	%	ppm	ppm	ppm
289	8	0.02	29	<10	>10000
ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41
S	Sb	Sc	Sr	Th	Ti
%	ppm	ppm	ppm	ppm	%
>10.0	546	<1	16	<20	<0.01
ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41	ME-ICP41
Tl	U	V	W	Zn	Se
ppm	ppm	ppm	ppm	ppm	ppm
60	10	3	10	>10000	<10

TABLE 17 - HPP ORE CHEMICAL CHARACTERIZATION.

The analytical methods used were:

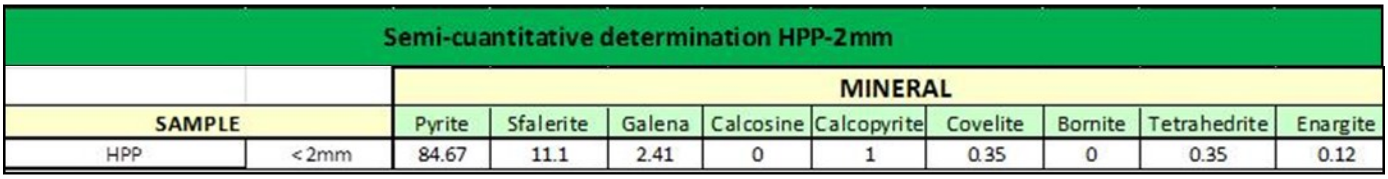
- ME-ICPORE: multi-element analysis of base metal ores and mill products by optical emission spectrometry using the Varian Vista inductively coupled plasma spectrometer.

- ME-ICP81x: evaluation of ores and high grade materials by fusion Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES).
- ME-ICP41m: trace level methods using conventional ICP-AES analysis.

Semicuantitative analysis have been done to obtain more information about the ores under study and to determine the main mineral species that can be found on them. Results are showed in the following tables:

Semi-cuantitative determination DPP										
	MINERAL									
SAMPLE	Pyrite	Sfalerite	Galena	Chalco Py	Chalcosite	Covelite	Arseno Py	Calcium C	Silica	Others
DPP	76,4	4,4	1,5	1,2	0,4	0,3	0,8	0,8	3,6	10,7

TABLE 18 - DPP ORE SEMI-CUANTITATIVE ANALYSIS.



Semi-cuantitative determination HPP-2mm										
		MINERAL								
SAMPLE		Pyrite	Sfalerite	Galena	Calcosine	Calcopyrite	Covelite	Bornite	Tetrahedrite	Enargite
HPP	<2mm	84.67	11.1	2.41	0	1	0.35	0	0.35	0.12

TABLE 19- HPP ORE SEMI-CUANTITATIVE ANALYSIS.

In addition, mineralogical study of HPP and DPP polymetallic ore samples from the mine to be used for concentrate production in the flotation pilot plant was done. Next figure shows the metallographic microscope used for this purpose.

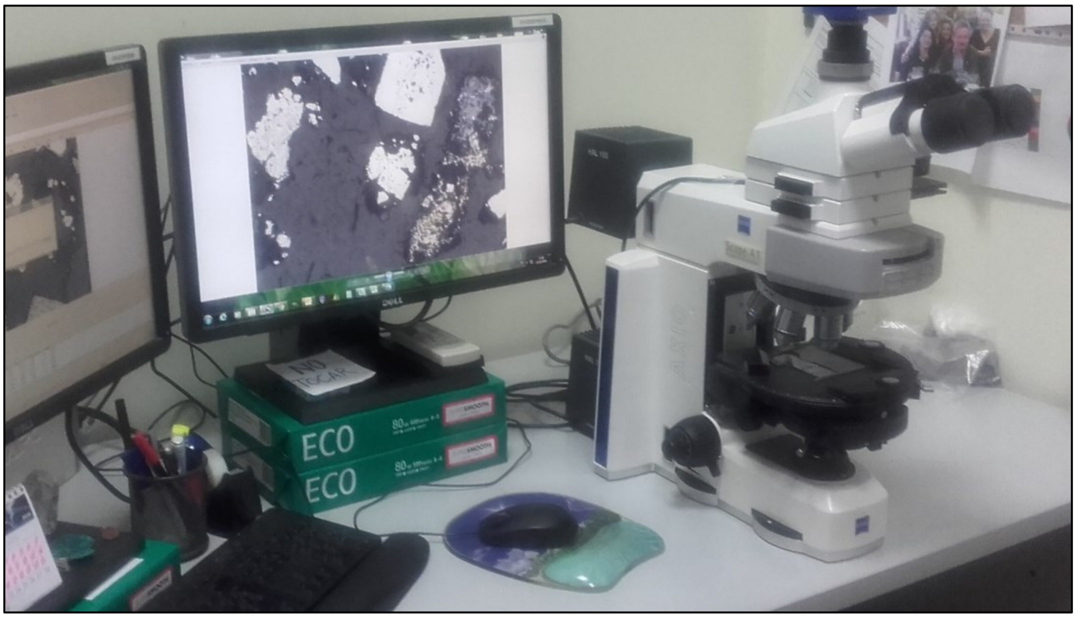


FIGURE 33 - METALLOGRAPHIC MICROSCOPE.

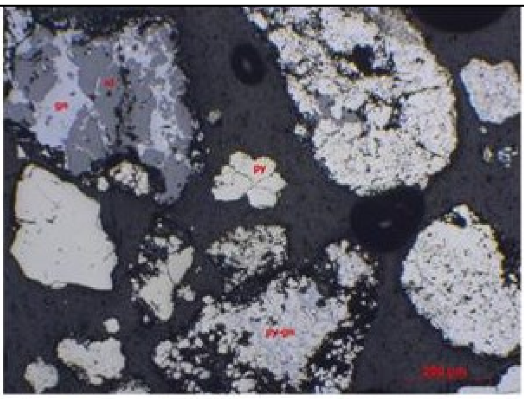


Figure 1.1. Big particle size with pyrite (py) subhedral-anhedral & primary + secondary sulphides

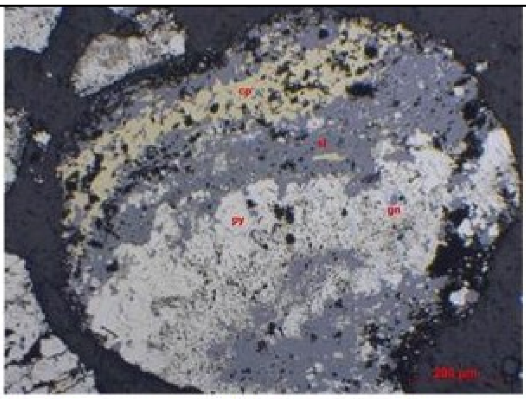


Figure 1.2. Primary sulphide with pyrite (py), sfalerite (sl) & calchopyrite (cp) in. Minor presence of, galena (gn)

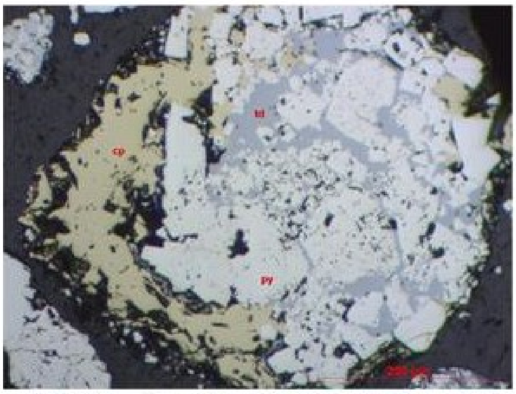


Figure 1.3. Polymetallic particle with pyrite (py) with tetrahedrite (td) & chalcopyrite (cp)

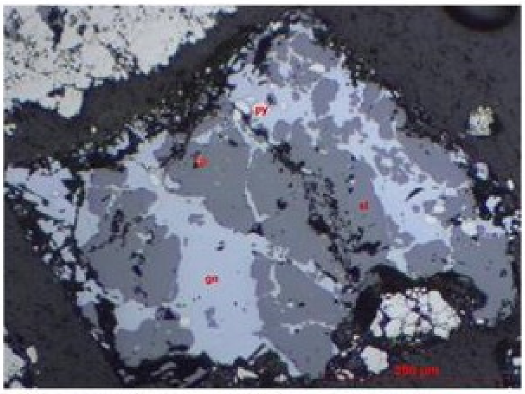


Figure 1.4. Polyimineralic fragment of primary mineralization composed of galena (gn) and sphalerite (sl) intercrecid. In the sphalerite (sl) there are relics of chalcopyrite (cp)

Foto obtenida con nícoles paralelos y objetivo 10x

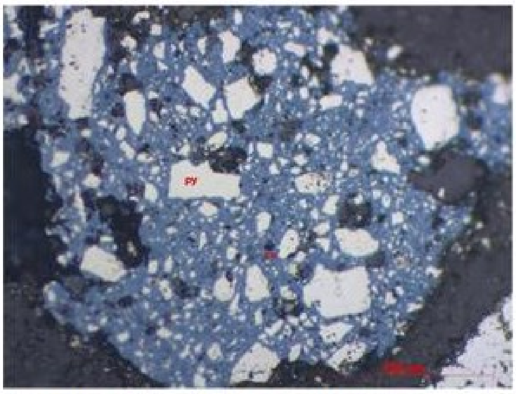


Figure 1.5. Detail of a polyimineral fragment composed of pyrite (py) and covellina (cv)

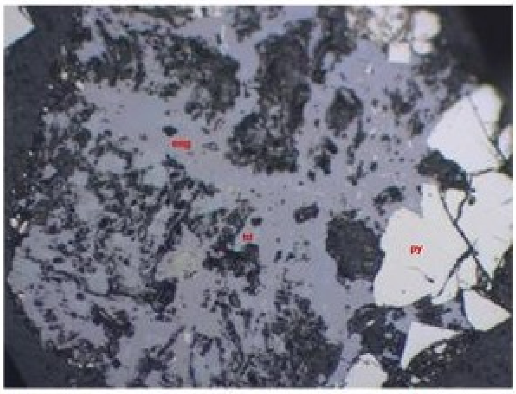


Figure 1.6. Detail of a fragment composed of tetrahedrite (td) that has been massively replaced by enargite (eng)

FIGURE 34 - HPP ORE METALLOGRAPHIC MICROSCOPE PICTURES.

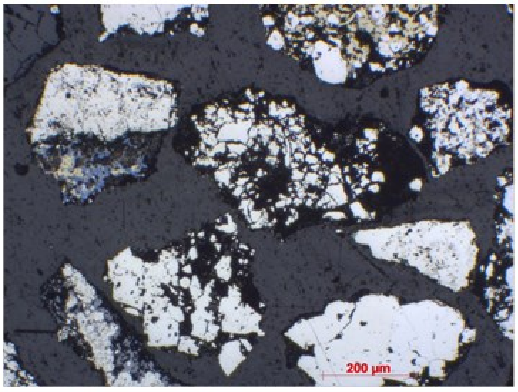


Foto 1.1. Aspecto general de la muestra constituida por pirita (py) euhedral-anhedral y sulfuros tanto primarios como secundarios. Estos últimos en menos proporción

Foto obtenida con nicoles paralelos y objetivo 5x

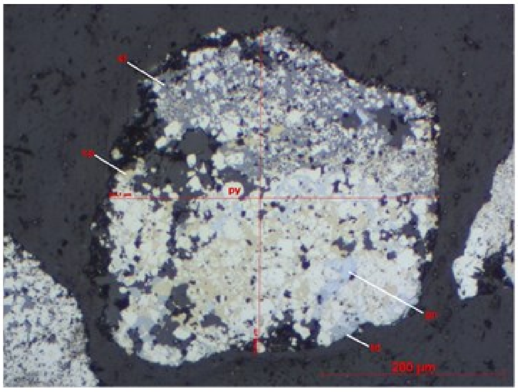


Foto 1.2. Fragmento de mineralización primaria compuesto por pirita (py) y galena (gn), calcopirita (cp) y esfalerita (sl) intersticial

Foto obtenida con nícoles paralelos y objetivo 10x

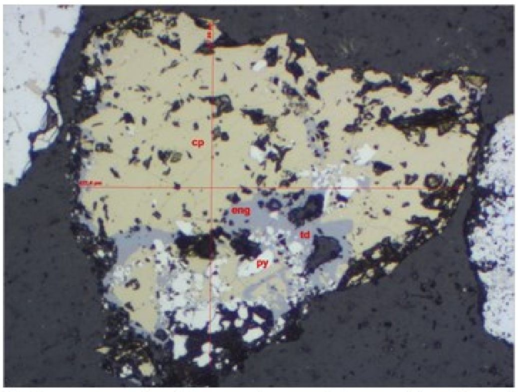


Foto 1.3. Fragmento polimetálico en el que se observan pirita (py), calcopirita (cp), tetraedrita (td) y enargita (eng)

Foto obtenida con nicoles paralelos y objetivo10 x

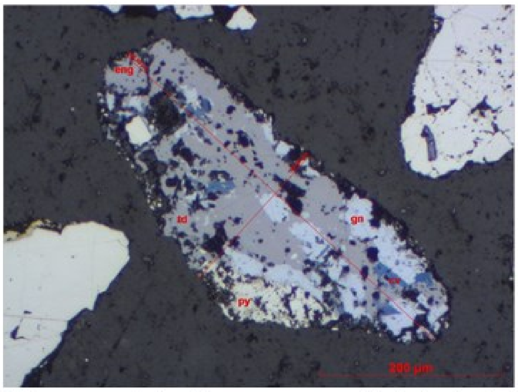


Foto 1.4. Fragmento polimineralico compuesto por pirita (py), galena (gn), tetraedrita (td), enargita (eng) y covellina (cv)

Foto obtenida con nícoles paralelos y objetivo 10x

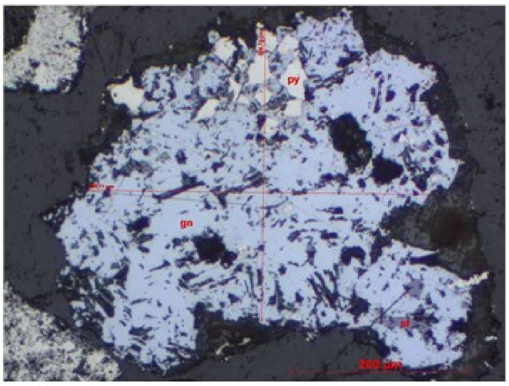


Foto 1.5. Detalle de un fragmento monomineralico de galena (gn)

Foto obtenida con nicoles paralelos y objetivo 10x

Foto 1.6. Detalle de un fragmento monominerálico de covellina (cv)

Foto obtenida con nícoles paralelos y objetivo 10x

FIGURE 35 - DPP ORE METALOGRAPHIC MICROSCOPE PICTURES.

3.2.2 REAGENTS

Different reagents and concentrations have been tested to determine which collectors, promoters, frothers and depressants gives better results. Also different regimes and dosages have been studied in order to optimizing flotation results and maximizing valuable metals recoveries.

These are the reagents which have been used in flotation tests:

- Lime to adjust pH.
- Copper sulfate ($CuSO_4$) to activate sphalerite.
- Depressants:
  - Pionera 250 as a pyrite deppresant.
  - Betamin 312, Betamin 469 and Betamin 584 also as deppresants from Betachem.
- Promoters:
  - Aero 9863, Aero 404, Aero 726, Aero XD, Aeropromoter 845 Aerofloat 242 and Aerophine 3418A as promoters from Cytec.
  - Nascol 451 and Nascol CSC 12 also as promoters from Nasaco.
- Frothers:
  - Methyl Isobutyl Carbinol (MIBC).
  - Nasfroth from Nasaco.
- Sodium hydrosulphide.
- Oxygen, replacing air added in flotation stages.
- Hydrogen peroxide.

Other additional reagents tested were BASF and Nalco reagents.

FIGURE 36 - REAGENTS ADDITION IN LAB FLOTATION TESTS.

3.2.3 GRINDING

Grinding is closely linked to flotation. Getting an adequate flotation requires an appropriate particle size of the ore to be treated to accomplish the liberation of valuable metals contained in it.

A laboratory ball mill has been used to process mineral investigated and get the required particle size before flotation testwork.

FIGURE 37. LABORATORY BALL MILL.

One grinding batch comprises 9,3 kg of steel balls, 1 kg of <2 mm ore sample and 500 ml water.

The following graphics demonstrate the influence of particle size on flotation mass recovery, flotation kinetics, metals grade of concentrate and metal recoveries.

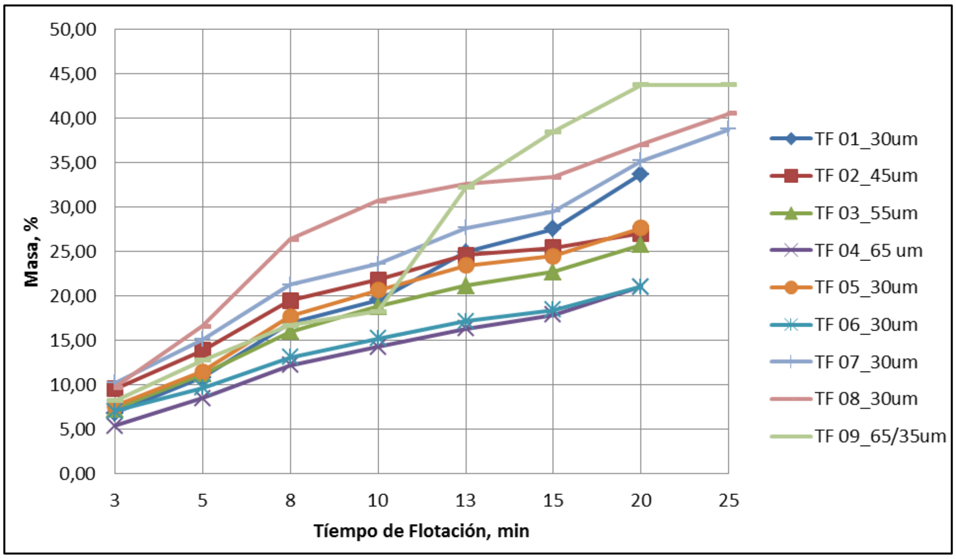


TABLE 20 - P80 AND MASS RECOVERY RELATION.

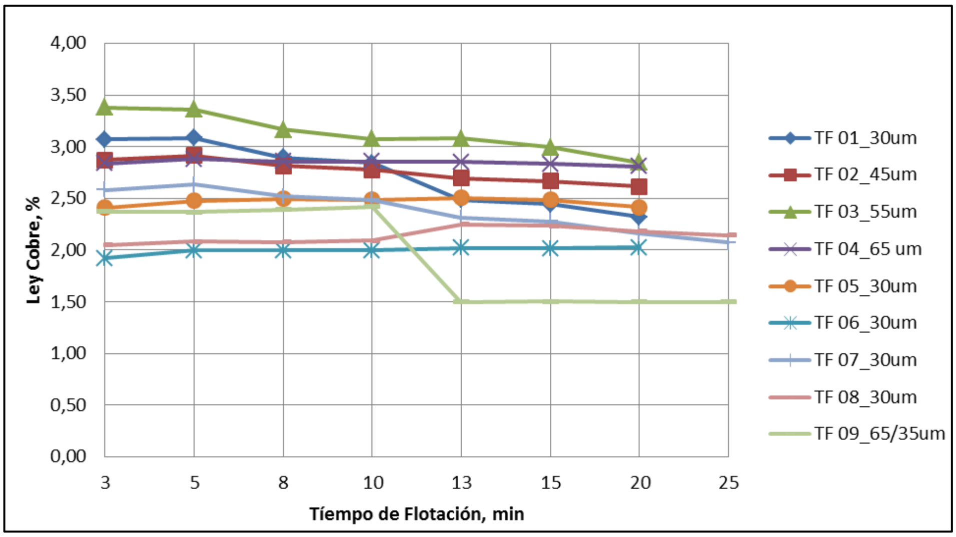


TABLE 21 - P80 AND COPPER GARDE RELATION.

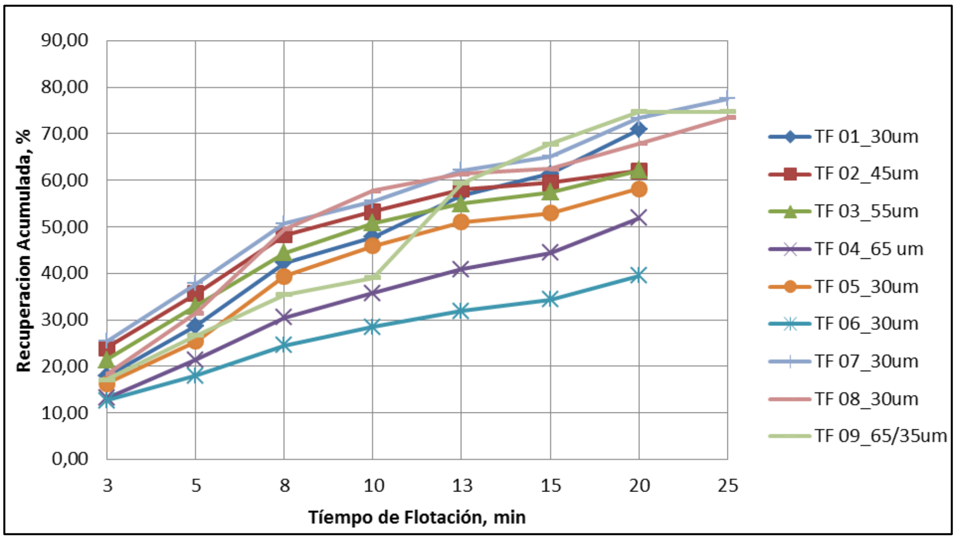


TABLE 22. P80 AND KINETIKS RELATION.

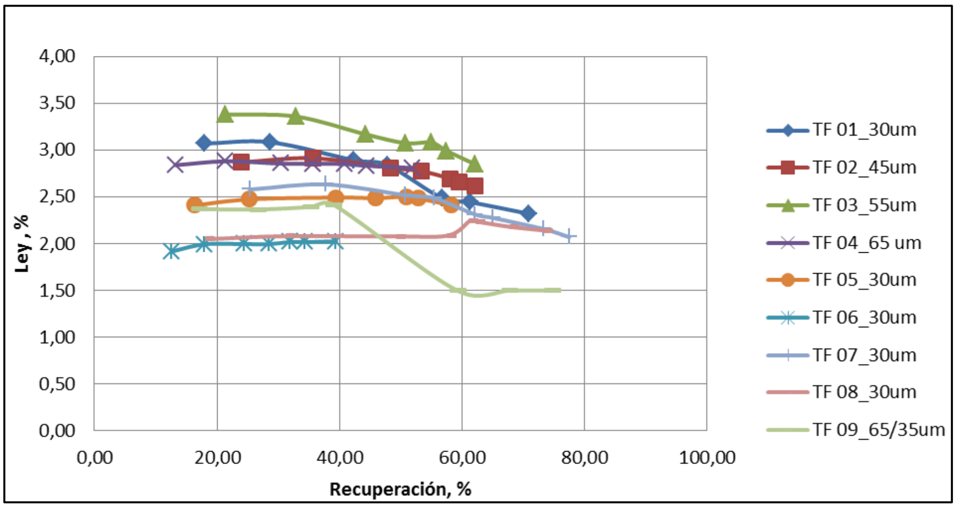


TABLE 23. P80 AND METAL RECOVERY FLOTATION.

3.2.4 LABORATORY FLOTATION

For laboratory flotation testwork it has been used a manual flotation lab cell. It is a Denver D-12 lab cell with 2.5 litres capacity.

FIGURE 38 - LAB FLOTATION CELL.

Froth had to be removed manually and pH was controlled using a pHmeter.

Flotation gas used in tests was air or oxygen with a delivery rate of 1.5 litre/min approximately.

The rotor/stator speed was 1300 rpm.

Flotation tests have been conducted in batch. As mentioned above, tests purposes were:

- Valuable metals concentrate recoveries prediction.
- Select and optimize the reagents dosage.
- Optimal particle size selection.
- Determine the flotation rate in each flotation stage.

After filtration, product obtained were dried and weighed to determine its dry mass. Samples were prepared to be chemically analysed and obtain different metals contents. The methods used for analysis were ME-ICPORE, ME-ICP81x and ME-ICP41m.

3.2.5 FLOTATION TEST WORK

Flotation test work was conducted to study and determine:

- The effect of pre-aeration time in flotation, using air to pre-aireate.
- The effect of Particle Size, P80.
- The effect of pyrite depressants.
- The best combination of different collectors and their optimal dosage.

Pre-aeration time

Pre-aeration stage is essential in the flotation process to condition the ore processed before flotation stages. Flotation test work carried out has proven that pre-aeration time has a strong influence on mass recovery and metals recoveries obtained in the global flotation process. Test results showed how pre-aeration time affects flotation, as it is indicated next:

- More pre-aeration time, less recovery of mass and iron.

The effect can be observed in the following figures obtained during the lab test work.

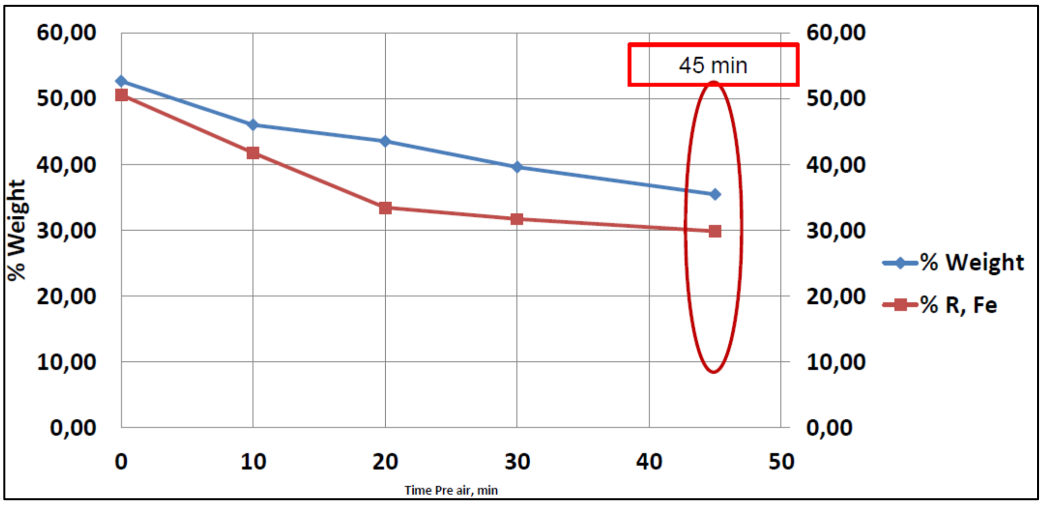


FIGURE 39 - WEIGHT RATIO VS PRE-AERATION TIME.

- More pre-aeration time, best recovery and grade of target metals: copper, zinc, silver and lead.

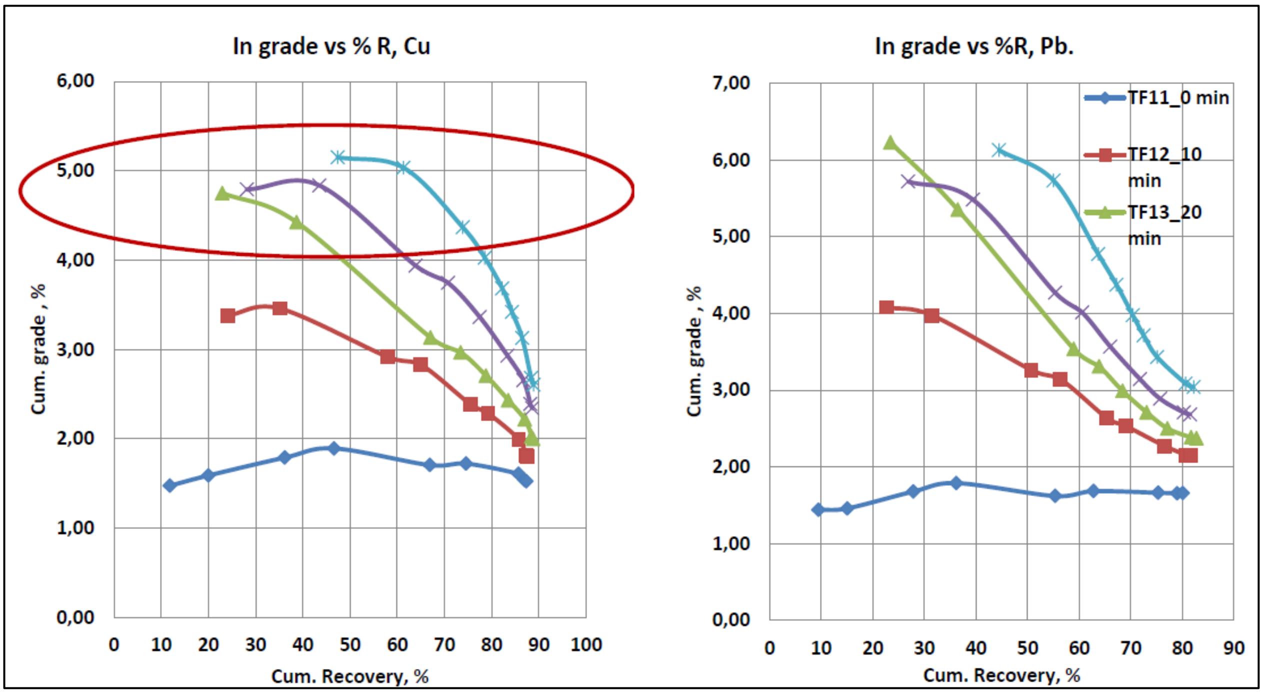


FIGURE 40 - COPPER AND LEAD RECOVERY VS PRE-AERATION TIME.

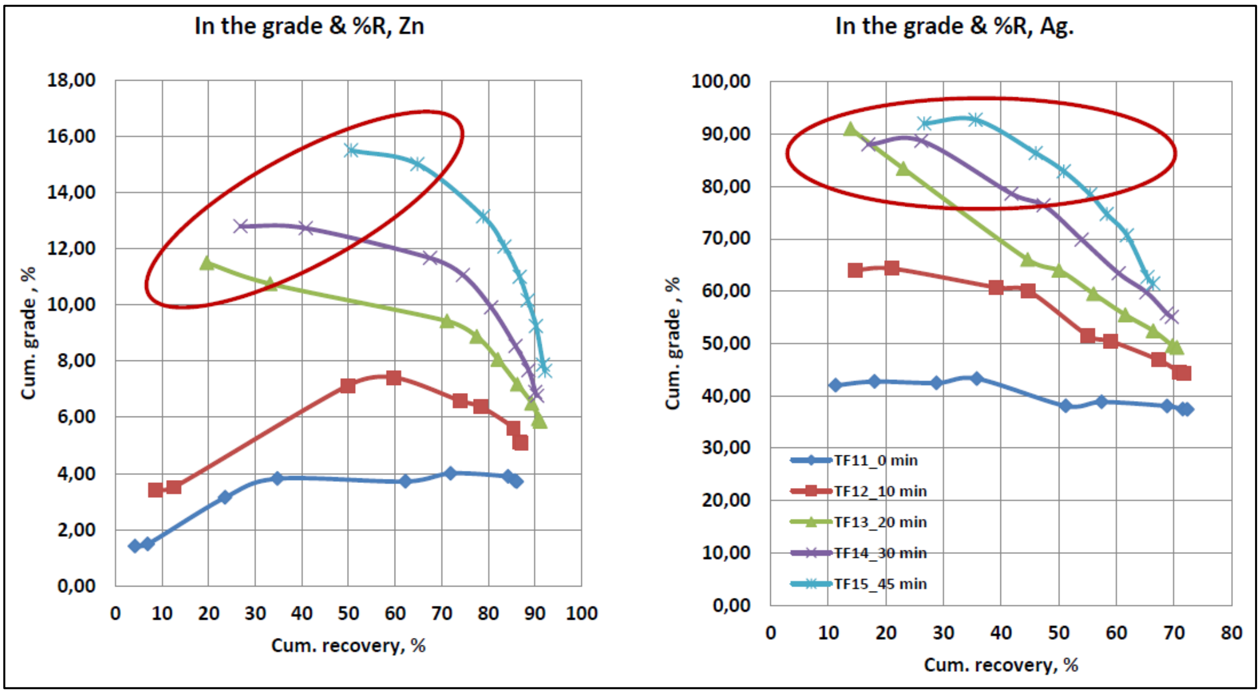


FIGURE 41 - ZINC AND SILVER RECOVERY VS PRE-AERATION TIME.

Figures above demonstrate that the tendency changes with pre-aeration time, since mass recovery decreases and metals recoveries and grades increase when there is increase in the pre-aeration time.

Particle size

The particle size P80 in the processed mineral is linked to metals kinetics, grades and recoveries. Below are the figures with flotation test results which demonstrate the relation between these parameters.

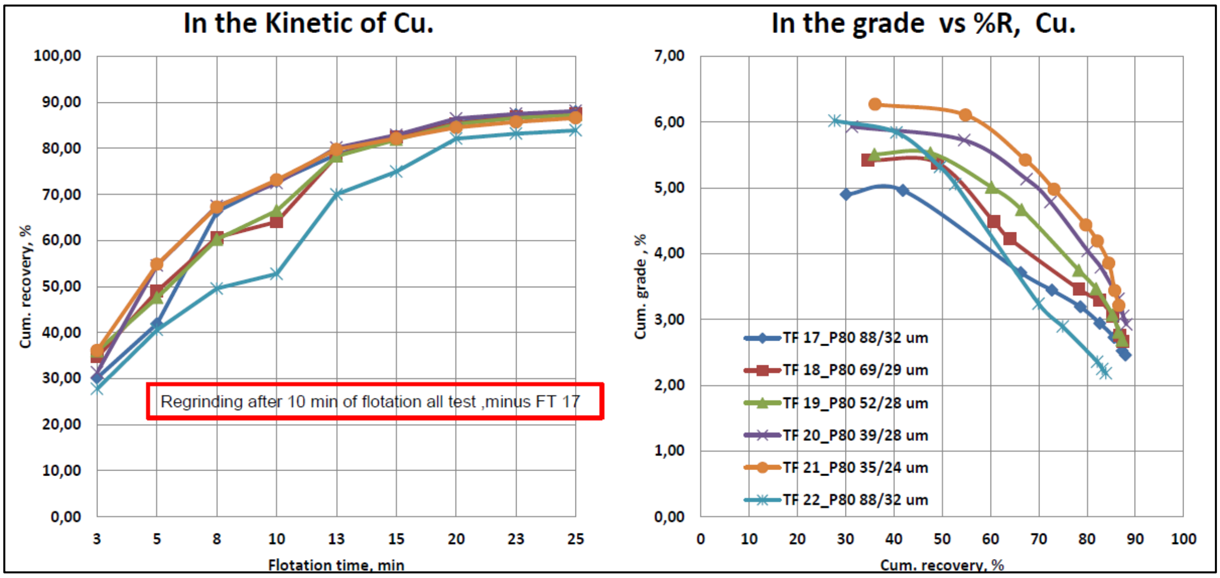


FIGURE 42 - COPPER KINETIC, GRADE AND RECOVERY VS PARTICLE SIZE.

These figures reflect that the kinetics is more uniform when P80 is under 35 µm, but good recovery was achieved too with an initial grinding to 69 µm followed by regrinding to 29 µm.

That means that particle size is a relevant parameter in the flotation process, since it determine the metals recoveries from the ore treated.

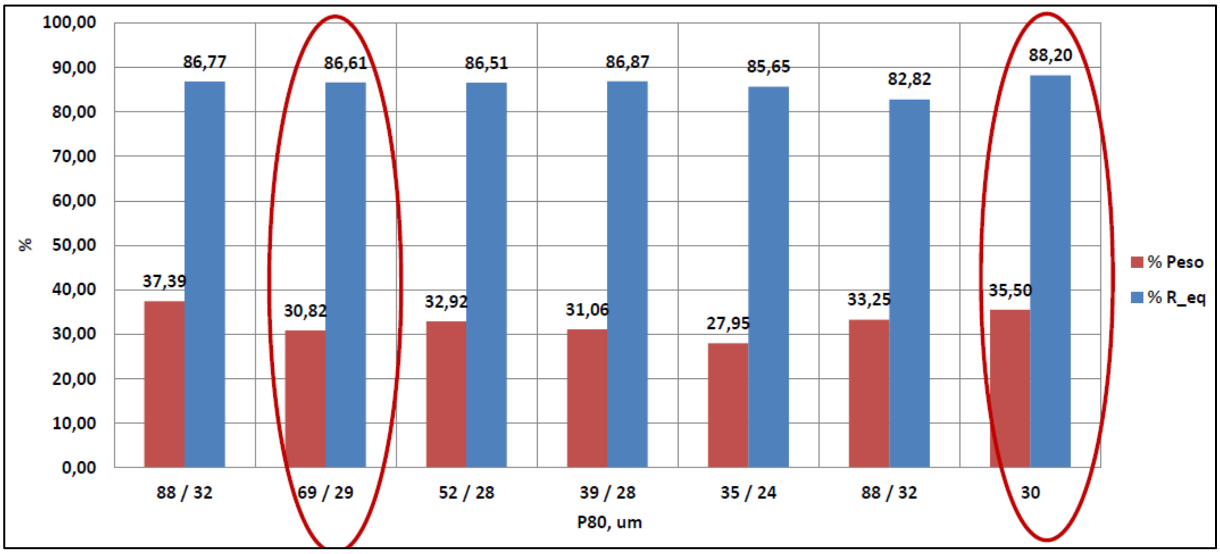


FIGURE 43 - P80 EFFECT IN MASSPULL AND EQUIVALENT RECOVERY.

In addition, tests showed that there are several particle size alternatives for the flotation, but in this case, only two have been selected as the best ones: grinding to 70 µm, 52 µm and regrinding to 30 µm or only grinding to P80 30 microns.

Pyrite depressants

Several pyrite depressants have been studied and tested to compare the effect they produced in mass recovery and metals recoveries from ore under investigation.

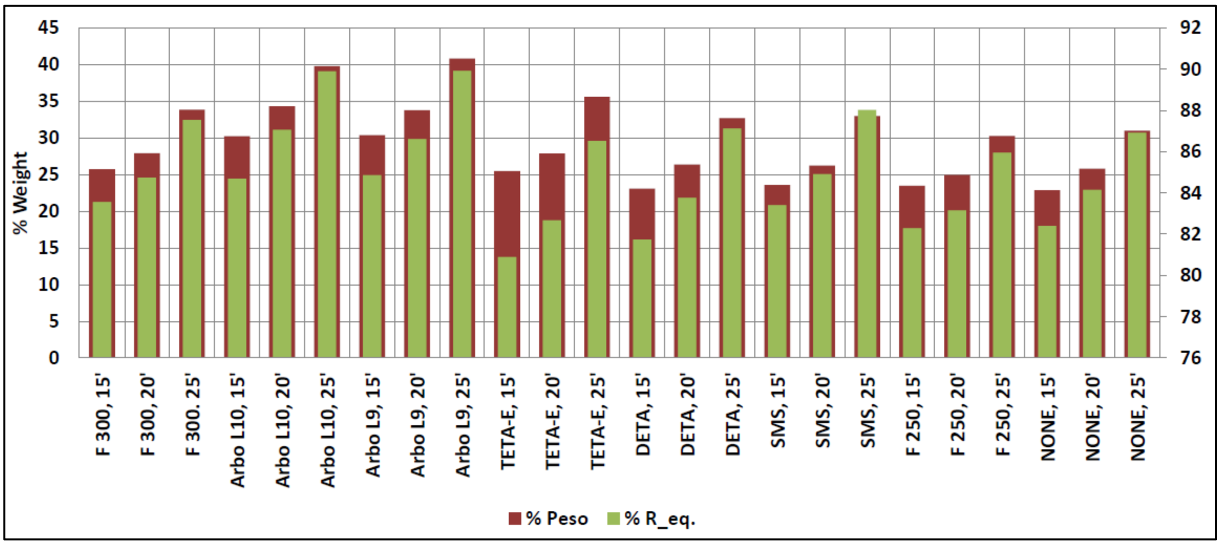


FIGURE 44 - MASS RECOVERY VS PYRITE DEPRESSANTS.

Lab flotation tests demonstrate that adding the depressant was better in regrinding stage or after 10 minutes of flotation. Without depressant in the first 10 minutes, concentrates obtained high grades in copper, lead, zinc and silver, as it is showed in next figures:

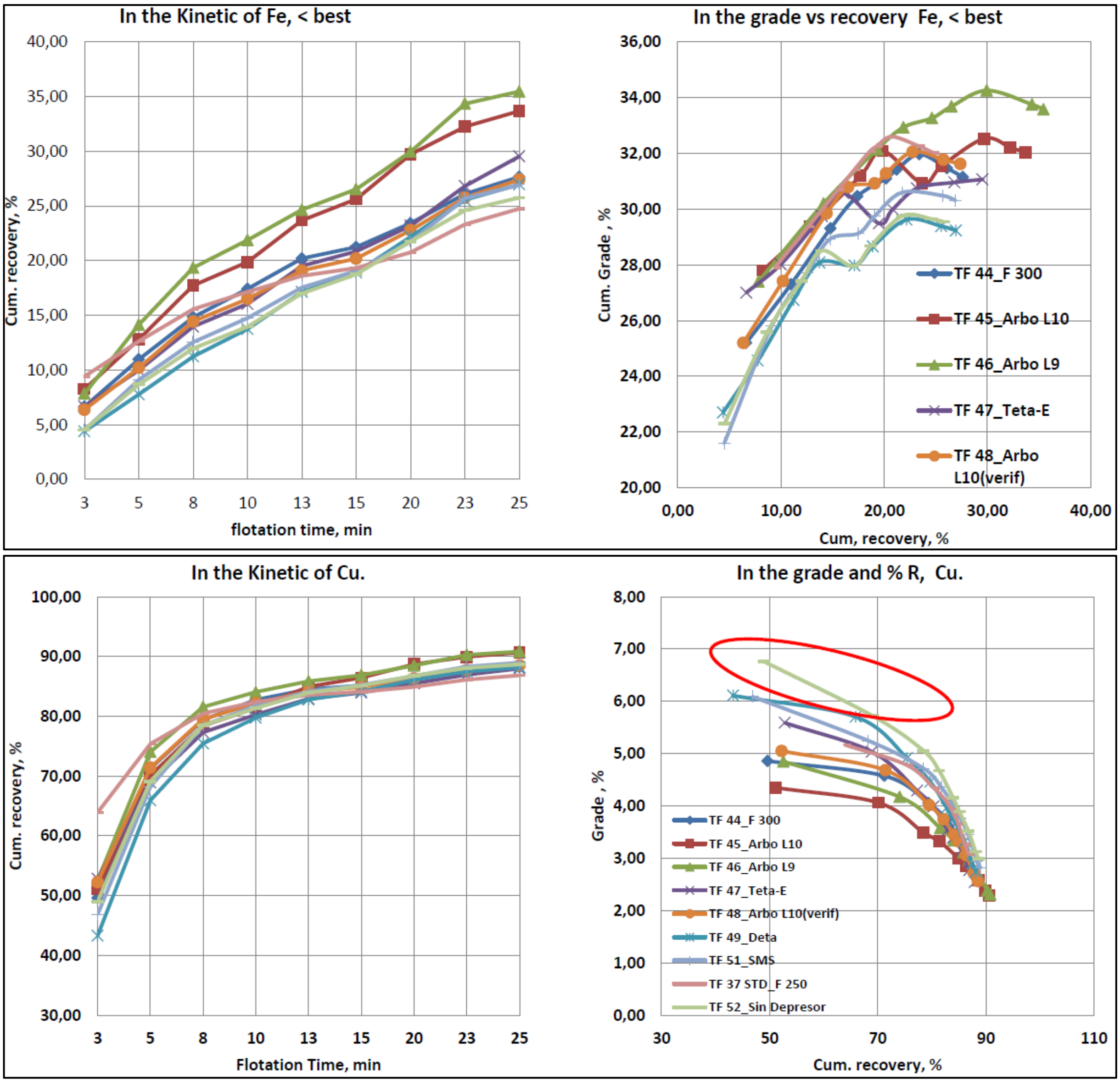
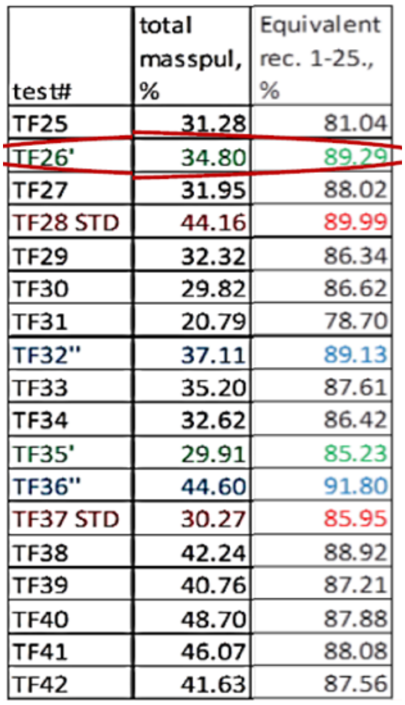


FIGURE 45. EFFECT OF PYRITE DEPRESSANTS.

Collector choice and dosage optimization

To complete laboratory test work, tests were performed to determine different flotation stages were needed, choice more suitable collector for this ore optimize their dosage to reach best flotation results.



test#	total masspul, %	Equivalent rec. 1-25., %
TF25	31.28	81.04
TF26'	34.80	89.29
TF27	31.95	88.02
TF28 STD	44.16	89.99
TF29	32.32	86.34
TF30	29.82	86.62
TF31	20.79	78.70
TF32"	37.11	89.13
TF33	35.20	87.61
TF34	32.62	86.42
TF35'	29.91	85.23
TF36"	44.60	91.80
TF37 STD	30.27	85.95
TF38	42.24	88.92
TF39	40.76	87.21
TF40	48.70	87.88
TF41	46.07	88.08
TF42	41.63	87.56

FIGURE 46. COLLECTOR CHOICE TESTS.

To sum up, the principal aim of all this laboratory test work detailed above was to know the optimal parameters and process conditions to get the best flotation circuit configuration to run the pilot plant and get good recoveries of objective metals contained in this primary sulphide mineral. Finally the defined pilot plant flowsheet is included in next figure.

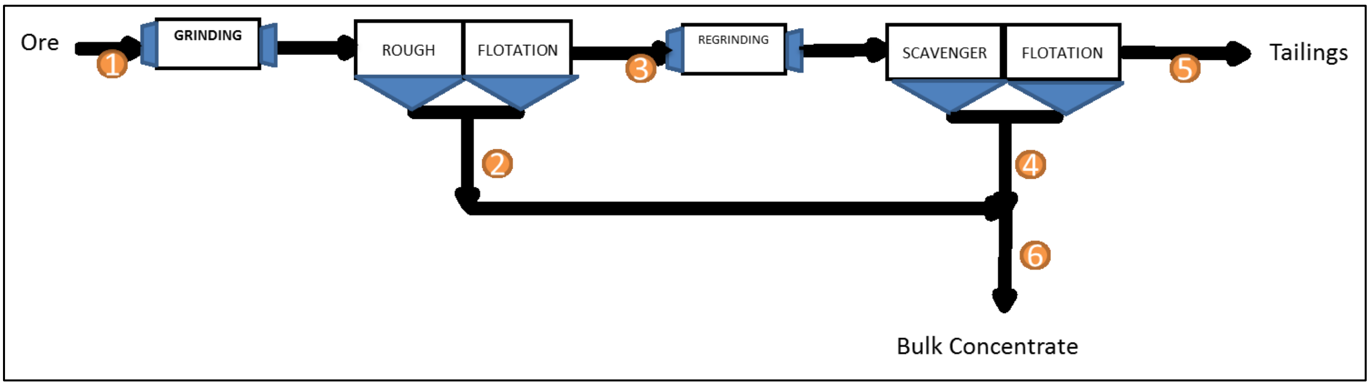


FIGURE 47. FLOTATION SCHEME.

3.2.6 RESULTS

First summary results showed average metal recoveries from 80 % to 90 % (calculated based on 3 Cu + 1 Zn + 1 Pb to highlight the economic value) with mass recoveries from 30 % to 40 % for the ore sample that represents 80% of the deposit (DPP ore).

Nevertheless, in the case of the sample used in the Pilot Plant (HPP sample), mass recovery obtained in lab tests were higher than previous results obtained in tests with DPP ore, for same metals recoveries. The reason to explain this fact was that the HPP ore presents a higher content of oxidized minerals. And this was the reason why more lab test work was required for HPP samples.

HPP ore lab scale flotation tests were submitted to adjust process parameters in the flotation pilot plant. Results from these tests showed that the ore had a different behavior than the previous sample due to a high secondary copper content. For this mineral, best results showed average metal recoveries of 75% (calculated based on 3 Cu + 1 Zn + 1 Pb) with 33% mass recovery.

This situation led to perform additional lab tests with HPP ore to improve process adapted to pilot plant operation and its process conditions to deal with high level of oxidize sulphides contained in the treated sample. Best results showed average metal recoveries of 81% and mass recovery of 39%.

Finally, lab scale flotation tests have been performed with reagents from BASF in order to improve results obtained so far. It was got average metal recoveries between 80% - 90% (calculated based on 3 Cu + 1 Zn + 1 Pb) with 40% - 55% of mass recoveries.

Listed below are the most important parameters provided by prior flotation studies, which include:

- The optimum particle size at which the most efficient recovery can be obtained in flotation and further leaching process. It was proposed to check two sizes for feed material to flotation: F80=70µm and 30 µm.
- Reagents quantity required and addition points for collectors and frothers. Best results obtained in laboratory test work indicate the best reagent combination was: 3418A + 9863 + 404 + MIBC.
- Reagents required and point of adding pH modifiers and pyrite depressors: pH=11.5 (lime as pH modifier) + aireation + F250 as pyrite depressor. Copper sulphate was recommended to activate sphalerite flotation.
- Although lab flotation tests were carried out at 32% solids density (w/w), best conditions should be determined directly in the pilot plant.
- Experimental data test work gave 25 min flotation time. However, it depends on the particle size and reagents used.
- Pulp temperature affects flotation kinetics. Water at room temperature (20-25ºC) was used in lab test work.
- The extent of uniformity (mainly mineralogy) of the ore to feed the pilot plant; variations in hardness, grindability, mineralogy, and floatability has been investigated in the large sample to feed the pilot plant. The main intention was check flotation behaviour of that material.

- Corrosion and erosion qualities of the pulp were factors which were taken into consideration to select specific materials used to construct the pilot plant.

3.3 OUTOTEC LAB FLOTATION TESTWORK

The aim of Outotec testwork was to conduct bulk Cu-Zn-Pb rougher flotation tests for two different ores types with different reagents regimes in order to obtain:

- Recovery over 90% of copper, zinc and lead.
- Mass pull less than 40%.
- Optimizing reagent dosages or replacing with more suitable.
- Optimizing pre-aeration time.

3.3.1 ORE TYPES

Two different ore types were under investigation, ores from Cobre Las Cruces (CLC) and Neves Corvo.

The mineralogy research was not part of the WP2 and the mineralogy was investigated during this work to a sufficient extend to evaluate possible reagent regimes, grinding particle fineness and conduct the flotation test work.

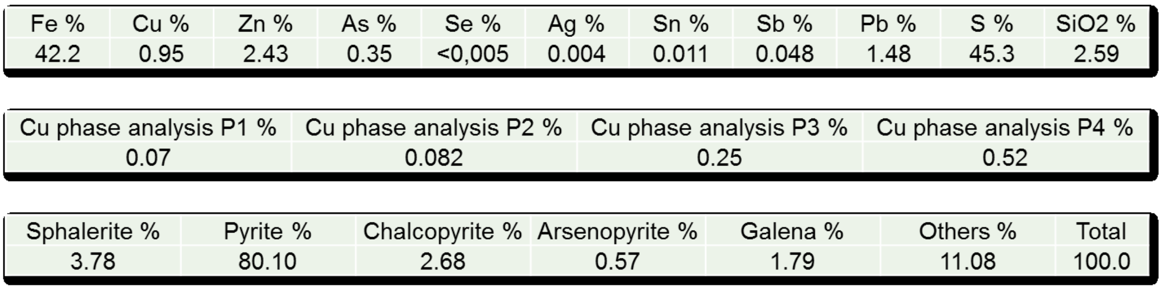
Mineral quantification was performed using HSC Chemistry software v.7.1 using mineral information gathered from external mineralogy studies and elemental assays.

Cobre Las Cruces ore

The CLC ore sample is a massive sulphides ore with a quite high Zn content and with a pycnometer measured density of 4.78 g/cm^3.

The chemical composition, including the copper phase analysis, and basic mineralogy are presented below.

The Cu distribution in phase analysis: P1=water soluble, P2=acid soluble, P3=KCN and P4=HNO_3-soluble copper.



Fe %	Cu %	Zn %	As %	Se %	Ag %	Sn %	Sb %	Pb %	S %	SiO2 %
42.2	0.95	2.43	0.35	<0,005	0.004	0.011	0.048	1.48	45.3	2.59

Cu phase analysis P1 %	Cu phase analysis P2 %	Cu phase analysis P3 %	Cu phase analysis P4 %
0.07	0.082	0.25	0.52

Sphalerite %	Pyrite %	Chalcopyrite %	Arsenopyrite %	Galena %	Others %	Total
3.78	80.10	2.68	0.57	1.79	11.08	100.0

TABLE 24 - CHEMICAL COMPOSITION AND MINERALOGY FOR CLC ORE.

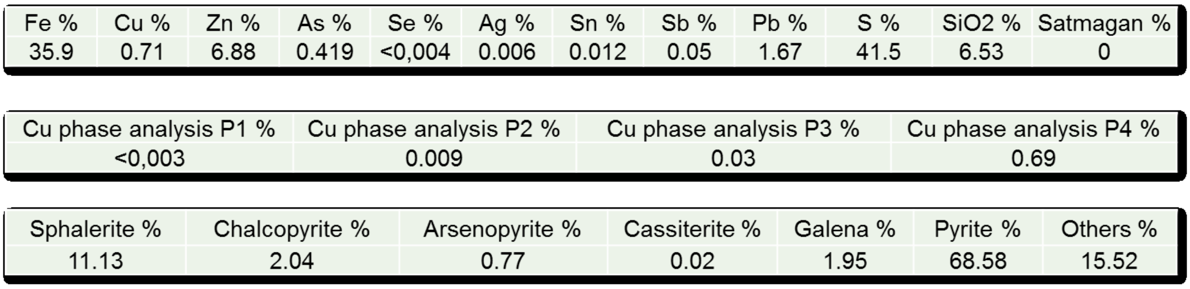
The amount of Cu P3 phase indicates that a part of the Cu is not only in chalcopyrite but also in secondary copper sulfides, like chalcocite, bornite and covellite. Chalcopyrite was used as the copper sulfide mineral in the mass balance calculations.

Neves Corvo ore

The Neves Corvo ore sample is a massive sulfides ore with a considerably high Zn content and with a pycnometer measured density of 4.61 g/cm^3.

The chemical composition, including the copper phase analysis, and basic mineralogy are presented below

The Cu distribution in phase analysis: P1=water soluble, P2=acid soluble, P3=KCN and P4=HNO_3-soluble copper.



Fe %	Cu %	Zn %	As %	Se %	Ag %	Sn %	Sb %	Pb %	S %	SiO2 %	Satmagan %
35.9	0.71	6.88	0.419	<0,004	0.006	0.012	0.05	1.67	41.5	6.53	0

Cu phase analysis P1 %	Cu phase analysis P2 %	Cu phase analysis P3 %	Cu phase analysis P4 %
<0,003	0.009	0.03	0.69

Sphalerite %	Chalcopyrite %	Arsenopyrite %	Cassiterite %	Galena %	Pyrite %	Others %
11.13	2.04	0.77	0.02	1.95	68.58	15.52

TABLE 25 - CHEMICAL COMPOSITION AND MINERALOGY FOR NEVES CORVO ORE.

3.3.2 REAGENTS

The starting reagent regime and dosages for the baseline flotation tests were set:

- pH adjustment: pH 11.0 with Lime
- Collectors/promoters:

  100 g/t Amyl dithiophosphate (Aerofloat 242)

  25 g/t mercaptobenzothiozole (Aero 404)

  150 g/t dithiophosphinate (Aerophine 3418A)
- Frother: 50 g/t Methyl isobutyl carbinol (MIBC)

Additional activation of the sphalerite mineral was ensured with copper sulfate ($CuSO_4$).

The other suitable reagents tested were sodium isobutyl xanthate (SIBX), potassium ethyl xanthate (KEX), sodium metabisulfite, zinc sulfate, sodium cyanide and polypropylene glycol methyl ether (Dowfroth 250) as frother.

3.3.3 GRINDING

Laboratory ball mill

Laboratory ball mill used was a 7.0 l laboratory ball mill, 205 mm in diameter and 212 mm in height. Both ores were comminuted to fineness 100% - 1 mm before grinding. One grinding batch consisted of 11.5 kg of mild steel balls (8.2 kg of 19 mm balls and 3.3 kg of 27 mm balls), 1.0 kg of -1 mm ore sample and 540 ml tap water. The solids content was 65 %. The laboratory ball mill is shown below:

FIGURE 48. LABORATORY BALL MIL.

High Intensity Grinding mill (HIGmill)

High intensity grinding (HIG) was used to test the effect of a higher mineral liberation and smaller particle fineness on the final mineral recoveries and concentrate grade from the flotation process.

Before fine grinding, using HIGmill, the test materials were ground using a ball mill. The mill used, was 268x268 mm, the ball charge was 22 kg, from 38 to 13 mm, ball sizes. Slurry density was 55 %.

Sufficient grinding time for producing material for fine grinding was determined by grinding both materials three grinding periods, 500, 1000 and 1500 mill revolutions.

Particle size analyses from the ball mill were measured using wet sieving.

The sample solids for the HIGmill were mixed in a mixing tank for appropriate milling density. The pump speed was adjusted based on pump calibration curves according to the target flow. The test was performed as a semi continuous test, where the product of the previous grinding round was feed for the next round. The mill speed was kept constant during the whole test. Ceramic grinding beads (2-4 mm) were used as grinding media. Both torque and motor based data are recorded.

HIGmill Grinding media size, quality and grinding parameters were chosen according the feed size.

- Grinding media (beads) filling rate: 60% of mill volume.

- Ceramic grinding media: SG 3.9 kg/dm^3.
- Media charge: 70% 2-3 mm beads, 30% 3-4 mm beads.
- Milling density: 55 % w/w corresponding 1.7 kg/l.
- Feed flow rate 200 l/h => 1.2 min retention time.

The HIGmill product particle size analyzes were done with a Malvern laser particle size analyzer.

3.3.4 LABORATORY FLOTATION WITH A LABCELL™

The flotation test work was executed with an automated GTK-Outotec LabCell™ and the electrochemical potential of the slurry was measured on-line with pH, platinum (Pt), galena (PbS) and pyrite (FeS_2) electrodes with a silver chloride reference electrode ($Ag/AgCl_2$).

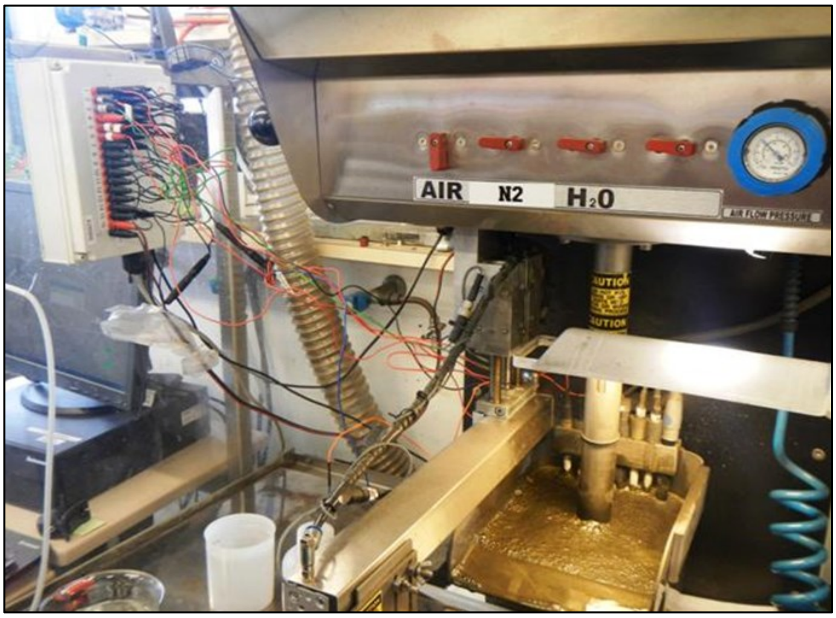


FIGURE 49 - GKT-OUTOTEC LABCELL^{TM}.

- The LabCell has 4 different cell sizes that can be used: 2, 4, 8 and 12 liters.
- Outotec rotor/stator mechanism.
- Equipped with automatic froth scrapers.
- The flotation gas can be air, nitrogen or mixture and measured with a flow meter.
- Monitoring & control of pH, redox (Pt) and mineral electrode potentials.
- Automated collection of electrode potentials and pH for each flotation test.
- Metal electrodes give qualitative information about the chemical composition of the slurry, Eh-pH window for optimal flotation results.

Basic and kinetic batch flotation tests are conducted to predict concentrate recoveries, optimization of the pulp potential, reagent selection and optimization, optimal selection of the grind size and solids content, and flotation rate of minerals in different flotation stages.

The flotation cell size used in the flotation test was 2 liters, air flow 2 liter/min, rotor/stator rotation speed 1200 rpm and froth scraper sequence every 4 seconds.

The flotation test products were filtered, dried and weighed for dry mass. Cu, Zn, Pb, Fe and SiO_2 contents in flotation test products were analysed by ICP-method after total dissolution. Total sulphur content was analysed with an Eltra analyzer. Mass balance was then calculated from product masses and chemical assays using Rex-software.

3.3.5 FLOTATION TEST WORK

Same flotation test work was conducted for both ores. The flotation test work included:

1. Baseline bulk flotation with aeration and provided reagent regime and an additional scavenger stage.
2. Bulk flotation without aeration, provided reagent regime used and additional scavenger stage.
3. Bulk flotation, shorter aeration time, simple reagent regime, grinding stage lime addition and regrinding of scavenger flotation feed.
4. Bulk flotation, short aeration, finer rougher flotation feed, higher pH and decreasing reagent dosages.
5. Sequential Cu-Zn-Pb flotation with the metabisulfite method, short aeration time.
6. Bulk flotation High Intensity Grinding (HIG) series, moderate aeration, HIG finer rougher flotation feed, higher pH and decreasing reagent dosages.

Baseline bulk flotation with aeration

The parameters for the baseline bulk flotation were:

- Grinding at natural ore pH to P80=40 µm, natural ore pH was pH=6.9 for Neves Corvo ore and pH=6.5 for Cobre Las Cruces ore.
- Aeration in conditioner was set to 45 min with 1 liter/min air feed.
- pH adjustment with lime in conditionerRougher flotation pH=11, Scavenger flotation pH=11.5
- Reagents :

  RF: Aerofloat 242 (100 g/t), Aero 404 (25 g/t), Aerophine 3418A (150 g/t), MIBC (50 g/t).

  SF: SIBX (10 g/t), $CuSO_4$ (250 g/t), MIBC (10 g/t).
- Flotation times: RF 1+2+4+6=13 min, SF=4 min.

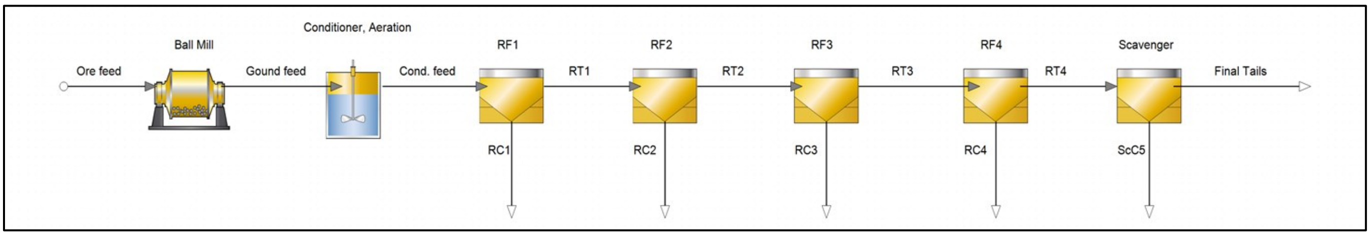


FIGURE 50 - PROCESS FLOWSHEET FOR BASELINE BULK FLOTATION WITH AERATION.

FIGURE 51 - INTMET WP2 BULK FLOTATION WITH GTK-OUTOTEC LABCELL^{TM}.

The final recoveries and grades are presented in next table.

	Cu		Zn		Pb		Mass pull
	Grade %	Rec %	Grade %	Rec %	Grade %	Rec %	%
Neves Corvo	1.4	84.2	13.9	87.3	3.0	75.8	42.4
Cobre Las Cruces	1.9	74.6	6.1	88.6	2.3	59.9	36.5

TABLE 26 - BASELINE BULK FLOTATION CUMULATIVE RECOVERIES.

Bulk flotation without aeration

The parameters were the same as for the baseline bulk flotation but without aeration time.

The final recoveries and grades are presented in next table.

	Cu		Zn		Pb		Mass pull
	Grade %	Rec %	Grade %	Rec %	Grade %	Rec %	%
Neves Corvo	1.0	91.3	9.1	85.9	2.1	79.5	64.5
Cobre Las Cruces	1.8	53.1	5.5	60.6	2.2	41.3	27.1

TABLE 27 - CUMULATIVE RECOVERIES FROM BULK FLOTATION WITHOUT AERATION.

Bulk flotation with shorter aeration time, simplified reagent regime and regrinding

The parameters for the bulk flotation with a simplified reagent regime and regrinding of the scavenger feed were:

- Grinding with lime addition to the grinding stage, P80=40 µm, pH=11.
- Aeration in conditioner 30 min.
- Regrinding of the scavenger flotation feed, P80=35 µm.
- Reagents:

  RF: SIBX (100 g/t), 3418A (100 g/t), MIBC (50 g/t).

  SF: SIBX (20 g/t), $CuSO_4$ (50 g/t), MIBC (10 g/t).

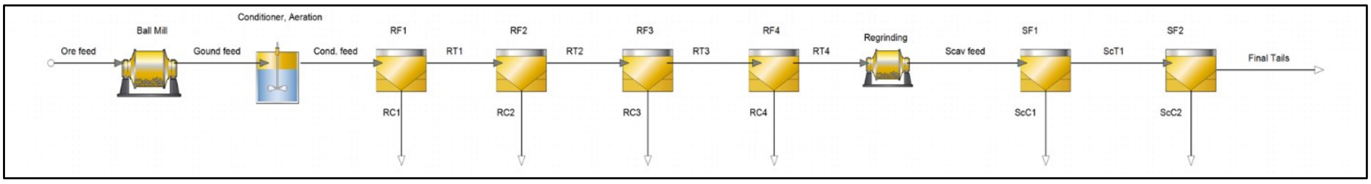


FIGURE 52. PROCESS FLOWSHEET FOR BULK FLOTATION WITH REGRINDING STEP.

The final recoveries and grades are presented in next table:

	Cu		Zn		Pb		Mass pull
	Grade %	Rec %	Grade %	Rec %	Grade %	Rec %	%
Neves Corvo	1.5	84.5	14.6	88.8	3.2	76.3	40.7
Cobre Las Cruces	1.7	73.1	5.9	91.1	2.5	67.8	39.8

TABLE 28 - CUMULATIVE RECOVERIES FROM BULK FLOTATION WITH SHORTER AERATION TIME.

Bulk flotation with short aeration, finer rougher flotation feed, higher pH and decreasing reagent dosages

The parameters for the bulk flotation with short aeration time, finer rougher flotation feed, higher pH and decreasing reagent dosages were:

- Grinding with lime addition to the grinding stage, P80=34 µm, pH=11.
- Aeration time in conditioner 15 min.
- Lower reagent dosages of original baseline:

  RF: Aerofloat 242 (80 g/t), Aero 404 (20 g/t), Aerophine 3418A (125 g/t), MIBC (40 g/t).

  SF: SIBX (10 g/t), $CuSO_4$ (200 g/t), MIBC (10 g/t).

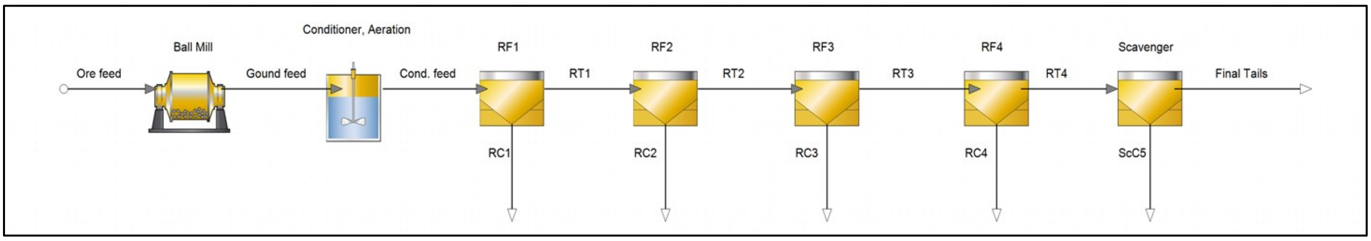


FIGURE 53 - PROCESS FLOW SHEET FOR BULK FLOTATION.

These are the final recoveries and grades:

	Cu		Zn		Pb		Mass pull
	Grade %	Rec %	Grade %	Rec %	Grade %	Rec %	%
Neves Corvo	1.4	81.4	14.0	90.6	3.1	80.1	46.0
Cobre Las Cruces	2.0	33.4	8.5	51.7	3.9	41.3	15.1

TABLE 29 - CUMULATIVE RECOVERIES FROM BULK FLOTATION WITH A SHORT AERATION TIME.

Sequential metabisulfite method Cu-Zn-Pb flotation with a short aeration time

A sequential flotation was tested. The parameters for the sequential flotation with a short aeration time were:

- Grinding P80=40 µm, pH<7.
- Aeration time in conditioner 15 min.
- Sequential pH adjustment with lime in conditioner before each flotation stage: Cu circuit pH=6.6, Zn circuit pH=9, Pb circuit pH=11.5.
- Reagents:

  Cu cirquit: Na2S2O5 (5500 g/t), KEX (50 g/t), ZnSO4 (350 g/t), MIBC (30 g/t).

  Zn cirquit: KEX (60 g/t), Aero 3477 (10 g/t), MIBC (30 g/t), NaCN (50 g/t).

  Pb cirquit: SIBX (30 g/t), $CuSO_4$ (700 g/t), Dow 250 (10 g/t).

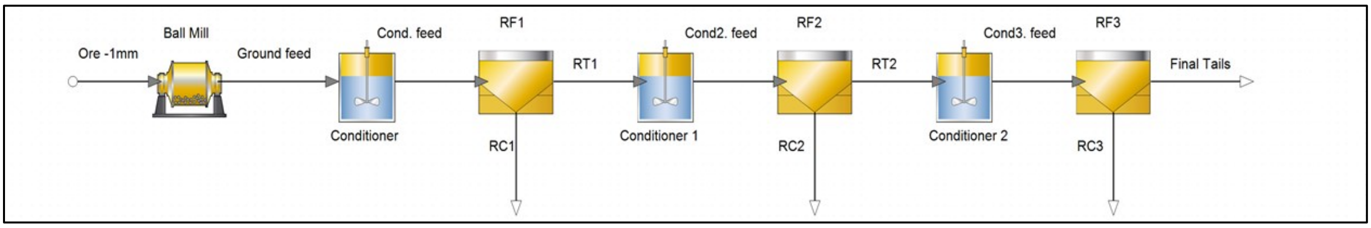


FIGURE 54 - PROCESS FLOW SHEET FOR SEQUENTIAL FLOTATION.

The final recoveries and grades are presented in this table.

	Cu		Zn		Pb		Mass pull
	Grade %	Rec %	Grade %	Rec %	Grade %	Rec %	%
Neves Corvo	4.5	68.3	16.5	26.1	4.8	31.3	10.6
Cobre Las Cruces	3.7	46.7	16.1	73.9	4.4	35.5	11.1

TABLE 30 - CUMULATIVE RECOVERIES FROM SEQUENTIAL METABISULFITE FLOTATION METHOD.

Bulk flotation with High Intensity Grinding (HIG) series, moderate aeration, HIG finer rougher flotation feed, higher pH and decreasing reagent dosages

The parameters for the bulk flotation with feed from High Intensity Grinding were:

- Grinding with High Intensity Grinding, partial lime addition in grinding step, feed particle fineness series to flotation:

  Neves Corvo P80=28.5 µm, 14.8 µm and 10.8 µm.

  Cobre Las Cruces P80=25.6 µm, 18.3 µm and 11.5 µm.

- pH adjustment with lime in conditioner before each flotation step: RF pH=11; SF pH=11.5.
- Aeration time in first conditioner 25 min.
- Reagents regime more simple and lower dosages of original baseline:

  RF: Aerophine 3418A (100 g/t), SIBX (100 g/t), MIBC (50 g/t).

  SF: SIBX (20 g/t), $CuSO_4$ (150 g/t), MIBC (10 g/t).

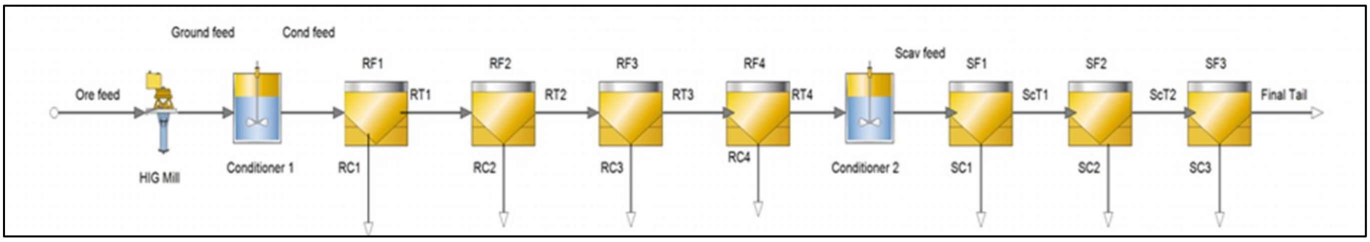


FIGURE 55 - PROCESS FLOW SHEET FOR HIGMILL TEST SERIES.

The final recoveries and grades from the HIG series are presented next:

	Cu		Zn		Pb		Mass pull
HIG 1	Grade %	Rec %	Grade %	Rec %	Grade %	Rec %	%
Neves Corvo 28.5 µm	1.7	77.9	15.8	74.7	3.5	66.4	31.9
Cobre Las Cruces 25.6 µm	3.2	51.1	11.2	68.8	3.9	40.3	14.6
	Cu		Zn		Pb		Mass pull
HIG 2	Grade %	Rec %	Grade %	Rec %	Grade %	Rec %	%
Neves Corvo 14.8 µm	1.9	79.9	14.3	64.0	3.9	70.2	29.2
Cobre Las Cruces 18.3 µm	2.8	59.0	10.9	86.9	3.2	42.6	19.2
	Cu		Zn		Pb		Mass pull
HIG 3	Grade %	Rec %	Grade %	Rec %	Grade %	Rec %	%
Neves Corvo 10.8 µm	1.9	75.8	11.4	49.3	3.6	63.1	28.3
Cobre Las Cruces 11.5 µm	2.5	58.7	10.0	89.6	2.7	40.5	21.7

TABLE 31 - CUMULATIVE RECOVERIES FROM THE BULK FLOTATION TESTS WITH HIGH INTENSITY GRINDED (HIG) FEED.

3.3.6 RESULTS

The aim of the bulk Cu-Zn-Pb rougher flotation test work was to get information about the floatability of the minerals with different reagent regimes, grinding fineness and aeration times.

Electrochemical measurements

Electrochemistry plays an important role in the flotation of sulphide minerals. The effect of aeration time on the pH, redox and pulp electrochemical potentials was followed by on-line pH and mineral electrode measurements. The electrodes that were used were platina (Pt), pyrite (FeS_2), galena (PbS). A silver chloride reference electrode ($Ag/AgCl_2$) was used.

The aeration before flotation keeps the electro potential for galena below zero mV, throughout the rougher flotation, for both ores. The electro potential for pyrite and redox rises over 0 Eh after a short time in the rougher flotation.

The electro potential for galena follow the electro potential of pyrite, when no aeration is used, and rises over zero Eh.

The lime addition and higher pH moves the electro potential of both galena and pyrite towards the negative potential. The copper sulfate and higher pH in the scavenger flotation keeps the redox and mineral electro potentials negative. With a shorter aeration time of 30 minutes the electro potential of pyrite changes form negative to positive during the scavenger flotation. With an even shorter aeration time of 15 minutes, the electro potential of pyrite stays on the positive side during scavenger flotation while the electro potential of galena stays on the negative side.

Cumulative recoveries and mass pull

Neves Corvo ore

Recoveries of 68.3-91.3 % for copper, 26.1-90.6% for Zinc and 31.3-80.1% for lead could be achieved.

Mass pull varied from 10.6–64.5 %.

Reagent dosages and aeration time could be decreased from the baseline.

The best bulk flotation result was achieved with a feed fineness of P80=34 µm resulting in Cu=81.4 Rec %, Zn=90.6 Rec % and Pb=80.1 Rec % with a mass pull of 46.0 %.

The mass pull increases with decreased aeration time and without aeration the selectivity is reduced and the pyrite content in the concentrate is increased dramatically.

With High Intensity Grinding (HIG) trials, the finer and narrower particle size distributed flotation feed resulted in lower Mass Pull % and recoveries of valuable minerals did not increase with better liberation of the valuable minerals. The reason could be the combination of the small particles being difficult to flotate and increased particle surface areas in the slurry that would have demanded higher reagent dosages.

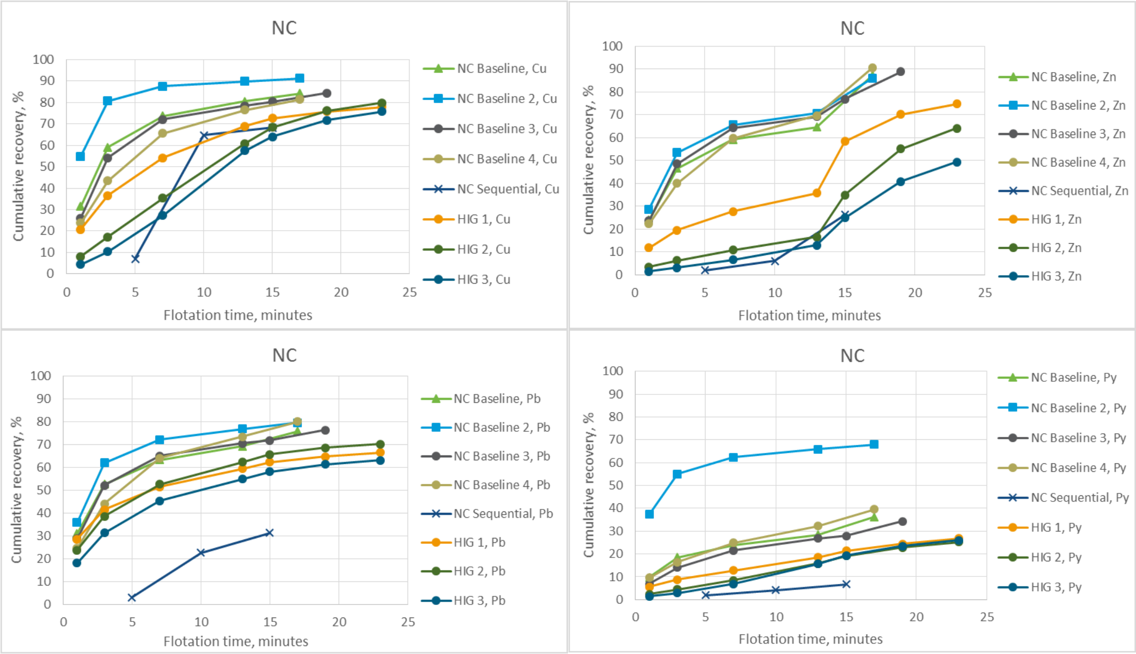


FIGURE 56 - CUMULATIVE RECOVERIES FOR COPPER, ZINC, LEAD AND PYRITE FOR THE FLOTATION TESTS WITH NEVES CORVO ORE.

Cobre Las Cruces ore

Recoveries of 33.4–74.6 % for copper, 51.7–91.1% for Zinc and 34.5–67.8% for lead could be achieved.

Mass pull varied from 11.1–39.8 %.

A simpler reagent regime could be used and the aeration time could be decreased from the baseline.

The best bulk flotation result was achieved with a feed fineness of P80 = 40 µm and regrinding of the scavenger feed to P80=39 µm (measured from tailings) resulting in Cu=73.1 Rec %, Zn=91.1 Rec % and Pb=67.8 Rec % with a mass pull of 39.8 %.

For the CLC ore the mass pull decreased, contrary to the Neves Corvo ore, when short 15 minutes aeration or no aeration was used. At the same time the recoveries of the valuable minerals also decreased.

With High Intensity Grinding (HIG) trials, the finer and narrower particle size distributed flotation feed resulted in lower Mass Pull % and recoveries of valuable minerals did not increase with better liberation of the valuable minerals. The reason could be the combination of the small particles being difficult to flotate and increased particle surface areas in the slurry that would have demanded higher reagent dosages.

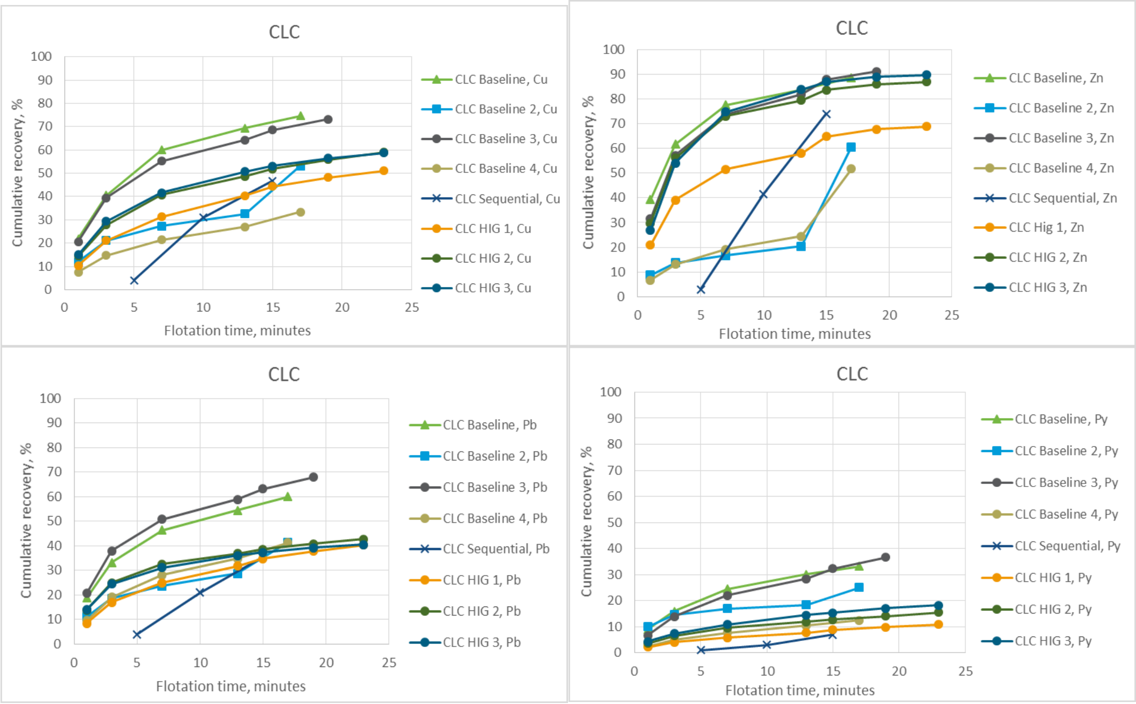


FIGURE 57 - CUMULATIVE RECOVERIES FOR COPPER, ZINC, LEAD AND PYRITE FOR THE FLOTATION TESTS WITH CLC ORE.

In conclusion, Outotec laboratory flotation results show that an acceptable copper-zinc-lead concentrate grade with high recoveries and a mass pull under 40 % can be achieved with moderate aeration times and a more simplified reagent regime.

Both ores, Neves Corvo and Cobre Las Cruces, are very complicated massive sulphides ores and most valuable minerals are fragmented and locked with pyrite. The liberation of minerals for good selective flotation is difficult without very high grain fineness in grinding. Very fine grains in flotation are somewhat problematic and the increased surface is demands increased reagent dosages.

3.4 SOMINCOR LAB FLOTATION TESTWORK

The main objective of Somincor's intervention in the INTMET project is to increase economic value of the orebody through the economic production of a low-grade bulk Cu-Pb concentrate from the complex polymetallic ores at Neves Corvo.

A hydrometallurgical process developed in the INTMET project would maximise the recovered value from the lead and copper present in polymetallic zinc ores. Eventually, a viable hydrometallurgical process on low-grade and bulk Cu-Pb concentrate would simplify the whole process and turn non-economic polymetallic mineralisation into valuable ore, thus increasing ore reserves, production and mine life.

3.4.1 ORE MINERALOGY

Although 5 masses are being exploited in Neves-Corvo mine at the moment, 65% of the material that feeds the zinc plant comes from the Lombador South deposit. A mineralogical study was performed with samples from Lombador, classified into 2 categories: MZ–massive zinc mineralisation with low-lead and MZP–high-lead massive zinc mineralisation.

MZ ore

The representative sample of MZ assayed (in terms of elements of interest): 0,35% Cu, 0,46% Pb and 7,67% Zn. The grains consisted of predominately pyrite with occasional silicate gangue and disseminated sphalerite, chalcopyrite and galena. These are the only metallic mineralisation find in the sample. A descriptive analysis of the minerals is made in the next table.

	Description	Grain Size Range (µm)	Percentage within specimen (%)
Pyrite	Dominant mineral. Abundant anhedral, subhedral and angular grains. Liberated and locked with (primarily) sphalerite, chalcopyrite and galena.	10-3000 (typically 400-800)	70-90
Sphalerite	Locked with (primarily) pyrite, to a lesser extent gangue and rarely galena and chalcopyrite. Not seen as fully liberated grains, more as pseudomorphic intergrowths and infill within pyrite grain fractures. Subhedral and anhedral grain shapes.	10-700 (typically 40-100)	5-10
Chalcopyrite	Locked and liberated grains with (primarily) pyrite, occasionally sphalerite and galena. Anhedral grains shapes with interstitial infilling of pyrite and gangue.	<10-100 (typically 30-60)	0,5-1
Galena	Locked within pyrite, usually in association with sphalerite and to a lesser extent chalcopyrite. Not seen as fully liberated grains, more as pseudomorphic intergrowths and infill within pyrite grain fractures.	<10-100 (typically 20-50)	0,5-1

TABLE 32 - MINERALS PRESENT IN MZ ORE TO THE PLANT FEED.

MZ sample has been used in bulk Cu / Pb flotation tests to determine optimal pH and reagent dosage conditions. The chemical analysis of the ore sample is presented in the next table. Based on this analysis, the sample is considered to include approx. 2% chalcopyrite, 1.8% galena, 12% sphalerite, 56% of pyrite and the remaining 28% are non-sulphide gangue minerals.

	Cu (%)	Pb (%)	Zn (%)	Fe (%)
MZ Ore Sample	0,69	1,56	7,50	32,63

TABLE 33 - CHEMICAL RESULTS OF MZ ORE SAMPLE USED IN THE FLOTATION TESTS.

MZP ore

The representative sample of Lombador South MZP assayed 0,28% Cu, 2,63% Pb and 9,47% Zn; a higher grade of zinc but also a much higher grade of lead, comparing with the sample from MZ ore. The MZP sample consists of the same minerals presented in the MZ ore so only the descriptive results for the grain size and percentage within the specimen are presented in next table.

	Grain Size Range (µm)	Percentage within specimen (%)
Pyrite	10-2200 (typically 150-400)	60-80
Sphalerite	10-300 (typically 40-100)	10-15
Chalcopyrite	10-60 (typically 20-50)	1-3
Galena	10-150 (typically 30-60)	<1

TABLE 34 - MINERALS PRESENT IN MZP ORE TO THE PLANT FEED.

Samples

In order for the pulp to not undergo chemical changes, the samples were withdrawn immediately before the start of each flotation test. The samples used in the flotation tests were collected using a cutter, in order to guarantee the homogeneity and representativeness of the sample, from the discharge of the pipe leading the pulp to the zinc DPR feed box in the production plant, where the product collected has not yet any reagent added.

The values of the feed contents presented next were calculated from the levels obtained by the analysis of the products of the flotation and the percentage of mass present in each product.

Since the samples used in the tests were collected on different days, due to the need to carry out the tests with "fresh", non-oxidized samples, there may be some disparity in the feed content, which is normal in an industrial environment. The next table shows the feed content in zinc, lead, copper and iron. The variability is lower for the tests performed at different temperatures with the same type of pH regulator since the samples used in the tests with the same type of pH regulator were withdrawn at the same time.

	Feed Grade DPR (%)								SUM GRADE (%)	
	Zn		Pb		Cu		Fe			
	(30 °C)	(60 °C)	(30 °C)	(60 °C)	(30 °C)	(60 °C)	(30 °C)	(60 °C)	(30 °C)	(60 °C)
W/o pH regulation	16,22	15,86	1,53	1,46	0,54	0,52	33,07	32,38	51,36	50,22
$Ca(OH)_2$	20,95	21,19	1,25	1,26	0,69	0,68	29,52	29,47	52,41	52,60
Na_2CO_3	18,49	---	1,38	---	0,58	---	31,39	---	51,84	---
NaOH	23,70	25,23	1,46	1,53	0,79	0,78	26,07	25,88	52,02	53,42

TABLE 35 - FEED GRADE OF SAMPLES USED IN TESTS, REGARDING THE INTEREST ELEMENTS.

In addition to the samples collected for the flotation tests, an additional sample of the feed and another of the tailings from the DPR should be collected and filtered with collection of the water, resulting from the process, for comparison purposes.

3.4.2 FACTORS AFFECTING ZINC FLOTATION

Lead grade

Since 2007, a correlation between the lead content in the feed to the zinc flotation circuit and zinc recovery in the concentrate has been identified. It was concluded that the higher the lead content in the feed to the zinc flotation circuit, the lower the recovery of the zinc carrier mineral in the final concentrate, as shown in the next figure.

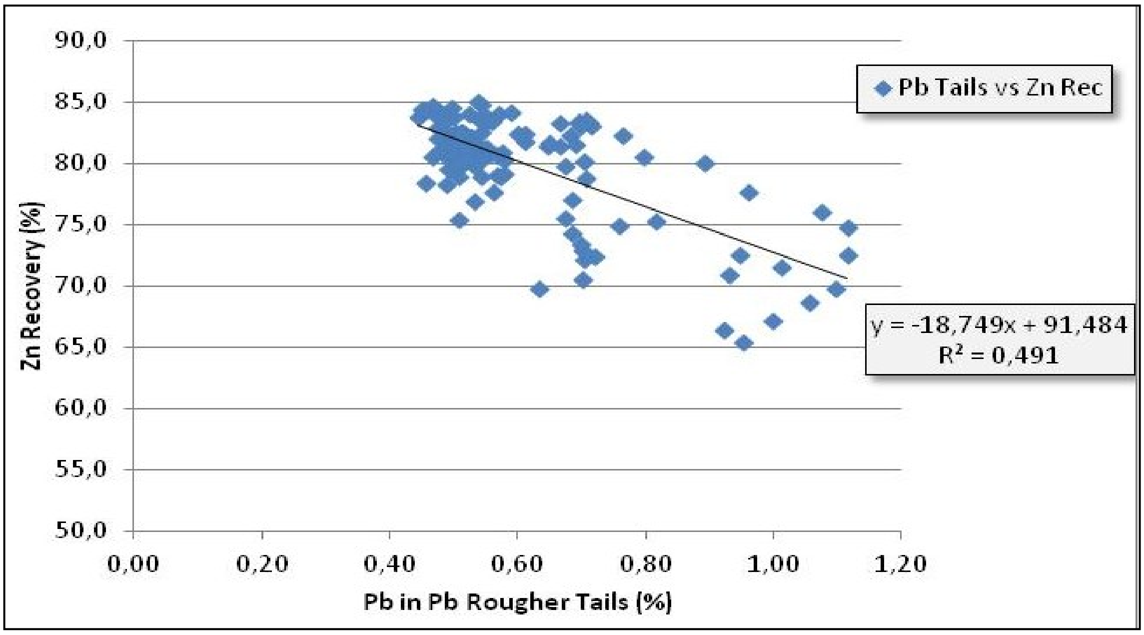


FIGURE 58 - EFFECT OF LEAD IN ZINC ROUGHER FEED ON MAIN ZINC CIRCUIT RECOVERY.

As seen from the mineralogical data, the galena at Neves Corvo is highly reactive. The working hypothesis was that following regrinding, at higher pH and temperatures, the precipitation of lead compounds such as PbOH on sphalerite surfaces were causing the depression of sphalerite.

Temperature

The studies carried out to understand the cause of the decrease in zinc recovery date back to 2008. In that year, a study was carried out at SOMINCOR in partnership with the international organization AMIRA. The aim of this study was to identify the causes of sphalerite depression through flotation tests with samples from the DPR feed, heated at different temperatures. Manouchehri et al. (2008), demonstrated the negative effect of temperature (> 60ºC) on the flotation of sphalerite in the concentrate of the DPR. Two main causes that could be at the origin of sphalerite depression were identified:

- Desorption of the collector, not allowing its action on the particles, making it impossible to create conditions for the flotation.
- Formation of insoluble lead and zinc hydroxides that prevent the flotation of the sphalerite particles because they cover them, not allowing the action of the collector.

As measures to mitigate the problem, it was suggested to decrease the pH from 11,5 to 10,8 and increase the dosage of activator (copper sulphate) added. To reduce the likelihood of pyrite flotation, which is potentiated at lower pH values, it was advised to create an aeration stage after regrind and prior to the addition of copper sulphate.

Lead hydroxides

The formation of lead hydroxides which coat sphalerite particles was shown to be a major problem. The decrease in flotation pH in the zinc circuit from approximately 11 to 10,5 following the 2008 work originated better results in terms of sphalerite recovery under certain conditions, however in Summer 2015, where pulp temperatures were again reaching 58ºC in the fine scavenger flotation, sphalerite recovery became highly unstable. During July 2016, as a result of laboratory flotation testwork at high and low temperature and high and low pH, the pH in the zinc regrind flotation section was further reduced to 6.5 – 7, with no lime addition. The decrease in pH to below neutral promoted the formation of lead sulphate crystals (Anglesite) instead of amorphous lead hydroxide, as shown in the Pourbaix Diagram below.

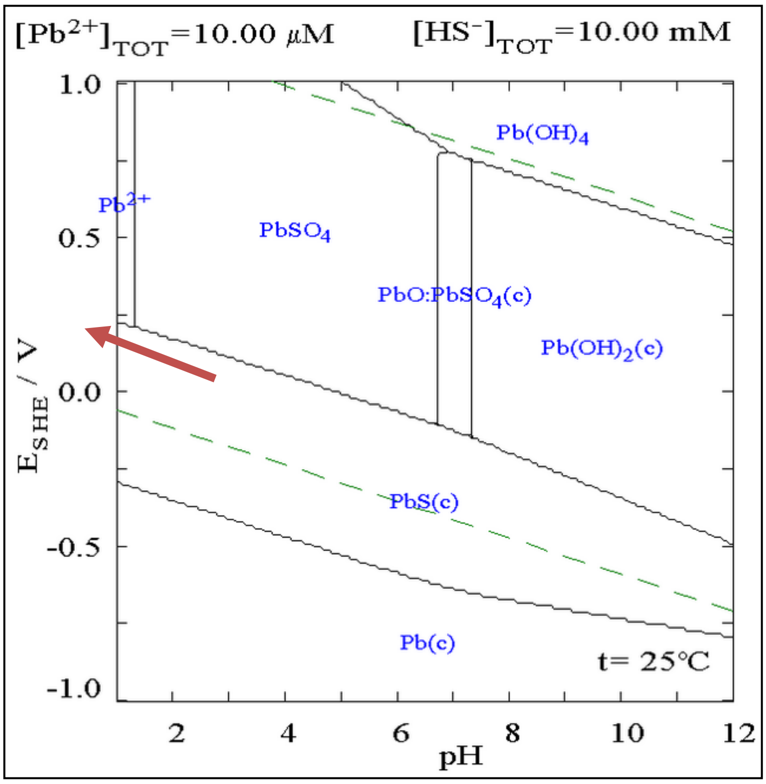


FIGURE 59 - POURBAIX DIAGRAM FOR LEAD IN SULPHATE MEDIA.

3.4.3 FLOTATION TESTWORK AND RESULTS

Zinc flotation conditions experimental work

The experimental work, regarding the INTMET project, was carried out with the purpose of testing the influence of temperature and pH regulation with lime, on the water used for flotation (process water) and ore exploited at Neves-Corvo mine. The effect of the temperature increase of the pulp was studied by conducting flotation tests without temperature manipulation, that is, by the temperature conditions of the pulp inside the flotation cell (≈30 °C), and heating the pulp up to 60°C.

The tests were performed with addition of 3 pH regulators and without addition of regulator. As regulators of pH, in addition to lime, currently used in the plant, sodium pH regulators were tested instead of calcium ones in order to verify if this type of regulators leads to better results when the pulp is at a temperature of 60ºC.

The collection of tailings water from the flotation tests enabled chemical analyses to be performed in order to identify the concentration of the dissolved ions in the water.

The principal equipment used is listed as follows.

Type of equipment	Brand	Specifications
Flotation Cell	Denver D-12	Equipped with a 2,4L tank
Heated water bath	Julabo ME	Equipped with container and pump
pH and Eh probes	HACH® HQ40D	Sensor pH: IntelliCAL™ PHC101 Sensor Eh: IntelliCAL™ MTC101

TABLE 36 - EQUIPMENT USED IN FLOTATION TESTS.

In the eight flotation tests performed with samples from the DPR feed pulp, the flotation operation parameters for the zinc DPR were used, so that the flotation conditions at the bench scale were similar to the flotation conditions at industrial scale. To this end, each test had a total duration of about 19 minutes and the reagents used in industrial flotation (KAX as a collector and $CuSO_4$ as sphalerite activator) were added, according to the concentration used in the industrial cell bank. In the tests in which the pH value was adjusted, this parameter was adjusted to the value used in the cell bank under study, at the time of the tests (9.5).

The total flotation time was 19 minutes determined based on the residence time of the pulp in the DPR cell bank, according to a scaling factor of 2,5 used in the laboratory tests performed at SOMINCOR.

In the first set of tests only the effect of increasing the pulp temperature from 30ºC to 60ºC, without pH manipulation, but with the addition of the remaining reagents (KAX and $CuSO_4$) was studied. Then, in the remaining tests, the effect of the addition of the following regulators: lime, sodium carbonate and sodium hydroxide were analysed in tests performed without temperature manipulation (≈30ºC) and heating of the pulp (60 ºC).

Test	Temperature
Without pH modification	30°C 60°C
pH regulation by lime ($Ca(OH)_2$)	30°C 60°C
pH regulation by sodium carbonate (Na_2CO_3)	30°C 60°C
pH regulation by sodium hydroxide (NaOH)	30°C 60°C

TABLE 37 - TESTS IDENTIFICATION.

The next table synthesizes the experimental procedure used in performing the flotation tests.

	Time (min)	**pH**	**Addition** (g/ton)		**Air** (L/min)
			KAX	$CuSO_4$	
Conditioning	1		30		
Float 1	1	9,5			5
Float 2	2				5
Float 3	3				5
Conditioning	1			120	
Conditioning	1		25		
Float 4	5	9,5			5
Float 5	8				5

TABLE 38 - EXPERIMENTAL PROCEDURE OF FLOTATION TESTS.

The next figure shows the values measured by the SOMINCOR chemical analysis laboratory in the waters from the flotation tests. The values for feed water (Alim) and tailings (Rej.) of the industrial cell bank (DPR), collected after filtration of samples from each of the streams, are also represented.

Only those elements that may be altered during the tests by the addition of reagents (such as calcium and sodium) and which are found in the solid phases of the ore, may be dissolved (zinc and lead) or which are indicative that oxidation reactions may be occurring in the pulp (sulphates and thiosalts). The thiosalt concentrations presented are the sum of thiosulphate and other polythionates analysed in the flotation liquors.

The result of the concentration of thiosalts, sulphates, calcium, sodium, lead and zinc dissolved in the waste water obtained after the flotation tests and in the water resulting from feed and DPR tailings samples are shown next. For better visualization, the results of the water resulting from flotation tests at different temperatures were joined.

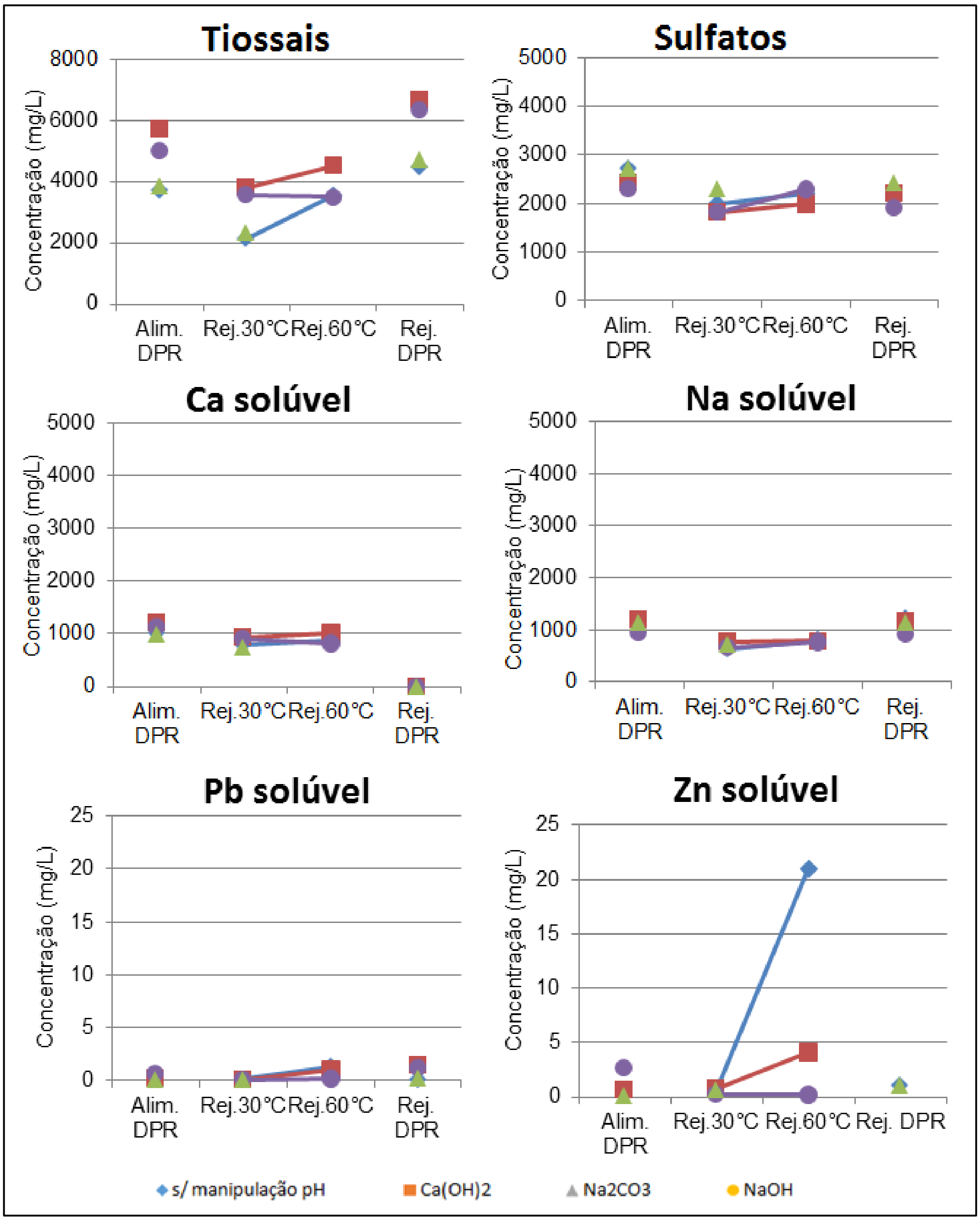


FIGURE 60 - CONCENTRATION OF VARIOUS ELEMENTS IN THE WASTE WATER FROM THE FLOTATION TESTS.

The increase in the concentration of thiosalts in solution is caused by the dissolution and / or oxidation of the ore as well as by the addition of reagents (Levay, 2015). In the laboratory results, thiosalt concentrations higher than those of the feed were not observed, however, a slight increase in thiosalt concentration was observed in the pulp tests heated at 60°C compared to the tests performed without pulp temperature manipulation.

The zinc plant flotation circuits contain a concentration of sulphates and calcium whose effect on flotation performance is not fully understood. However it is known that the increase of calcium ions together with a decrease of sulphate ions act in order to impair the conditions of flotation of the sphalerite (Levay, 2015). In terms of sulphate concentration, the tendency is for a decrease in the tests without manipulation of the pulp temperature, in relation to the DPR feed. At 60°C, the sulphate concentration value remains lower than that of the feed, although slight increases are noted relative to the concentration at 30°C. In the tails of the plant, the trend is always a decrease in relation to feed.

An excess of calcium ions (Ca^{2+}) in solution can lead to the adsorption of these to the surface of the mineral particles, affecting the surface charge, the adsorption of the collector, interactions between bubbles and particles, among others, causing adverse effects on the flotation of zinc (Levay, 2015). An increase in calcium concentration in the water, resulting from the lime addition, is expected due to the calcium nature of this regulator. In the tests carried out at 30ºC, the trend is always decreasing in relation to the feed water. At 60°C the calcium concentration does not undergo major changes as compared to the above data. There is no discrepancy in the concentration of soluble calcium in the tailings water when lime is used, so it is possible to state that the use of sodium regulators does not lead to better results with respect to a lower addition of Ca^{2+} ions to the system.

Sodium (Na) has a tendency to decrease in the tests carried out at 30ºC in relation to the feed water. Since the last two modifiers used are of a sodium nature, it would be expected to increase the concentration in the waste water of the tests in which they were used, but this is not the case. In the tailings, the solution concentration of Na is very close to the concentration values of this element in the feed water.

Due to the fact that the ore that forms the feed to the DPR has solid lead phases, there is a slight increase in lead concentration in the water due to the dissolution of the ore in the test at 60ºC. On the industrial scale, large concentrations of lead are found in DPR tailings water.

The concentration of zinc in the water can be explained by the dissolution of solid phases of the zinc ore, which is more pronounced in the flotation at 60ºC, especially when the pH is not manipulated (since there is no precipitation of ions promoted by the addition of pH regulators).

To conclude a higher concentration of lead and zinc ions in the water resulting from flotation tests at 60°C was observed, which points to the dissolution of the solid phases of the ore when the pulp is hot. The concentration of thiosalts and sulphates shows no evidence of increased oxidation of sulphur species from the ore, although this may be due to the rapid precipitation of calcium sulphate (gypsum) due to the saturation levels of SO_4^{2-} in the solution.

Bulk Cu / Pb flotation tests

A series of flotation tests were performed in order to determine the optimal condition, based on the pH and dosage of reagents, for bulk Cu/Pb flotation followed by zinc flotation. All tests were performed at P_{80}=60µm, which is in agreement with the primary grind size of the flotation plant.

Three tests were performed, under different conditions, in order to access the influence of the modified variables over the recovery of chalcopyrite, galena and sphalerite. Some of the operational conditions used in the tests were those seen at the plant at the time of the realization of the tests (pH=11,5 in the zinc circuit and KAX as sphalerite collector).

The operational conditions and the results obtained in each test are represented in this table:

Test Nº	Test Conditions	Mass Pull (%)	Grade (%)			Recovery (%)		
			Cu	Pb	Zn	Cu	Pb	Zn
FT1	MBS (500 g/t), pH 7.5, 3418A (30 g/t)	5.89	2.93	8.44	7.04	28.63	35.96	5.35
FT2	No MBS, pH 11.5, 3418A (30+20 g/t)	11.20	3.33	6.35	13.97	54.99	47.37	18.20
FT3	No MBS, pH 7.5 3418A (30 g/t)	7.21	2.53	4.62	37.32	30.64	23.40	35.72

TABLE 39 - IDENTIFICATION AND RESULTS OF THE FLOTATION TESTS (CU/PB BULK FLOTATION), TAKING IN CONSIDERATION THE INTEREST ELEMENTS.

Under standard conditions (FT1), chalcopyrite and galena recoveries were around 30-35%. Zinc was successfully depressed in this test although the recovery of the target minerals is low.

In the second test, the pH is increased in order to depress the zinc, in the absence of MBS. Both chalcopyrite and galena recovery increased but also the percentage of zinc loss to the bulk concentrate. The flotation selectivity was not satisfactory in this test.

In the third test at low pH and with no MBS, the copper and lead recoveries were no better than in test FT, while zinc losses were much higher without the MBS depressant.

Collector tests

The collector tests were conducted using MZP ore as it was classified as more problematic than MZ ore.

Different types of collectors and mixtures of collectors were tested. Aerophine 3418A, di-isobutyl dithiophosphinate type collector, was used as a standard collector in the Cu/Pb flotation stage. In this section, SIBX, which was the standard collector used in zinc flotation circuit, was used as single collector and in mixture (50:50 ratio) with Aerophine 208, a dithiophosphate type collector. Aerophine 7279 is a modified thionocarbamate type collector and used in place of 527e, which is used in the flotation plant. Considering slow flotation kinetics of galena, Aerophine 404 was also tested in mixtures with Aero7279 and 3418A (75:25 ratio). Aero 404 is a blend of mercaptobenzothiazole and dithiophosphate and widely used for flotation of tarnished galena and secondary copper minerals. This collector can also increase flotation of pyrite in acid and neutral circuits. In these tests, 500 g/t MBS was used as the standard depressant dosage. Pre-aeration was not applied.

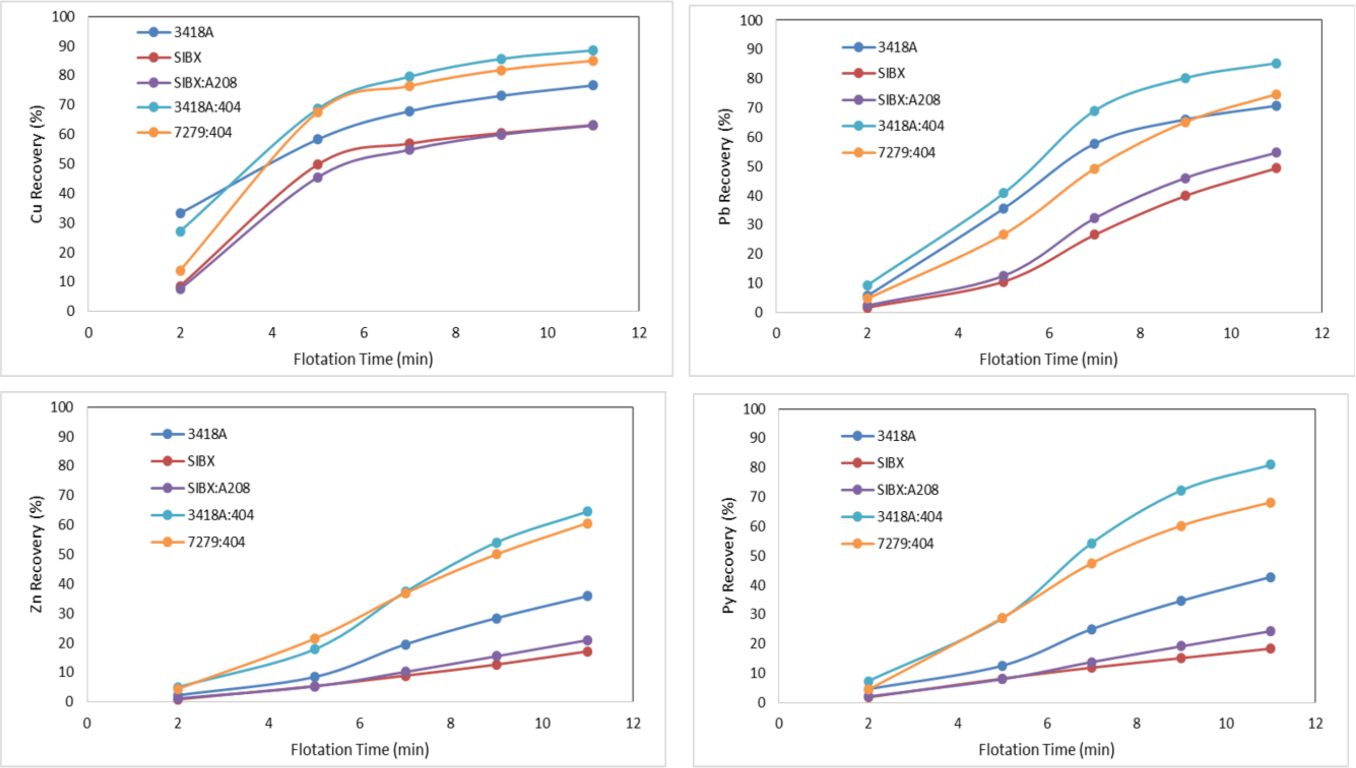


FIGURE 61 - FLOTATION KINETICS OF THE SULPHIDE MINERALS WITH DIFFERENT COLLECTOR TYPES.

The highest copper, lead, zinc and pyrite recoveries were obtained with 3418A:404 mixture. It is followed by Aero 7279:404 mixture and then 3418A. SIBX and its mixture with A208 were not effective collectors at this pH and presence of 500 g/t MBS.

It was clear that flotation kinetics of galena was lower than the copper minerals. Use of Aero 404 did not improve flotation kinetics of galena selectively due to high recovery of pyrite and sphalerite. 3418A was found to be the best collector for galena flotation.

The recovery curves of zinc and pyrite were identical. Recovery of these minerals was related to mass pull, not a selective recovery.

Previous tests showed that SIBX at pH 9,5 could be considered as a suitable collector for zinc flotation. In spite of that the following tests were conducted to better understand influence of pulp pH and type of collector. pH was tested at 6,5 (without addition of lime) and 9,5. Two more collectors, Aerophine 7279 and Aerophine 5100, were tested as alternative to SIBX, since these collectors are more effective for copper activated sphalerite and more selective against pyrite at moderately alkaline pH values.

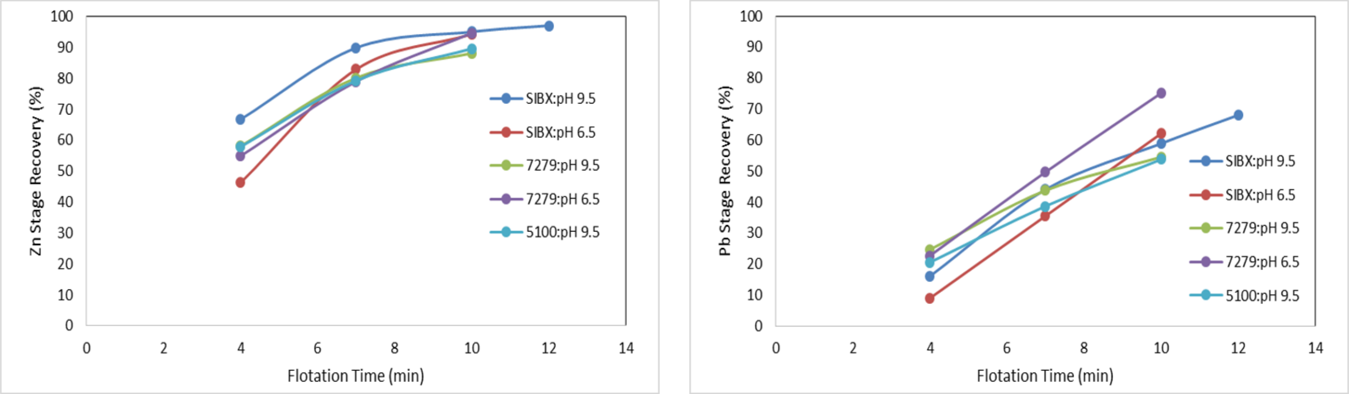


FIGURE 62 - STAGE RECOVERIES OF ZN AND PB AS FUNCTION OF FLOTATION TIME WITH DIFFERENT COLLECTOR TYPES AND PH.

The highest zinc flotation rate was obtained with SIBX at pH 9,5. Performance of Aero 7279 and Aero5100 was almost the same. Both flotation rate and cumulative recovery of zinc were lower than that of SIBX. Lower pH did not improve flotation rate.

The highest Pb recovery was obtained with Aero7279 at pH 6,5. The flotation rate of galena was higher with the thionocarbamate type of collectors in the beginning of flotation.

When the collectors and pH were compared for a given recovery value (e.g. 90%), higher grade values were obtained at pH 9,5 with all of the collectors. The highest grade was about 40% Zn (grade of the first concentrate in the kinetic flotation), and the highest recovery was obtained with SIBX at this point. It is clear that SIBX at pH 9.5 is the best collector option for zinc flotation.

3.5 BOR INSTITUTE LAB FLOTATION TESTWORK

It is known from literature that the polymetallic ore with barite is technologically very complex raw materials from which it is possible to extract more useful components but by the complicated technological schemes. These schemes usually involve several methods of concentration from physical methods, flotation and chemical methods, too. In addition they contain many useful components, their coalescence is very complicated and in a form of fine grained aggregates.

A test sample represents the typically polymetallic ore with barite. The sample was prepared in a manner which is described hereinafter.

3.5.1 ORE CHARACTERIZATION

The following table shows the chemical analysis of the samples used in tests.

Element	Content	Analytical method	Element	Content	Analytical method
Au g/t	1.4	FA	S %	25.09	ACS
Hg g/t	605	A-Hg	Cd ppm	105	ICP-AES
SiO_2 %	28.74	G	Co ppm	11	ICP-AES
Al_2O_3 %	0.21	ICP-AES	Cr ppm	20	ICP-AES
Ag g/t	110.4	ICP-AES	Mo ppm	56	ICP-AES
Pb %	5.26	ICP-AES	Ni ppm	15	ICP-AES
Zn %	5.63	ICP-AES	Se ppm	< 40	ICP-AES
Cu %	1.84	ICP-AES	Sn ppm	24	ICP-AES
As %	0.32	ICP-AES	Ti ppm	102	ICP-AES
Sb %	0.16	ICP-AES	CaO %	0.036	AAS
Mn ppm	319	ICP-AES	MgO %	0.025	AAS
Fe(Fe^{2+}) %	24.79(3.17)	V	Ba %	15.72	XRF Semiquantitative analysis

TABLE 40 - CHEMICAL ANALYSIS OF SAMPLES.

These are the analytical methods used:

G – Gravimetric analysis
V – Volumetric analysis
ICPAES - Atomic emission spectrometry with inductively coupled plasma
ACS - Analyzer of carbon and sulfur
FA – Fire assay
FAAS – Flame atomic absorption spectrometry
XRF - X-Ray fluorescence

XRD – X-Ray difraction.

Natural pH of the ore samples is determined by measuring the pH value of ore and tap water (pH = 7,17) in the ratio 1:1 after 30 minutes of standing. The result is pH=5,73.

Density of the ore sample was determined by the method of glass pycnometers with vacuuming. The mean value of density from three measurements is ρ=4480 kg/m^3.

Bulk density was determined on the ore size class of -12,7mm and -3,35mm.

$\Delta_{-12.7}$= 2,531 t/m^3
$\Delta_{-3.35}$= 2,619 t/m^3

3.5.2 GRINDING

The entire sample was comminute to the size class of >12.5 mm in the following way: the product of crushing was control screened by a sieve with mesh size of 12.5 mm, wherein the sieve oversize was again returned to crushing to achieve >12.5 mm. After homogenisation of the sample by the cone ring method, sampling was carried out to determine the Bond Index in a rod mill. Sample was crushed to the size class of >3.35. Crushing product was control screened by a sieve with mesh size of 3.35 mm wherein the sieve oversize was again returned to crushing to achieve >3.35 mm. The samples were separated to determine the Bond Index in a ball mill for characterization, chemical analysis and technological tests. Next figures show sampling for technology tests and the sampling for mineralogical analysis and the scheme of sample preparation, respectively.

FIGURE 63 - SAMPLING TECHNOLOGY TEST. SAMPLING FOR MINERALOGICAL ANALYSIS.

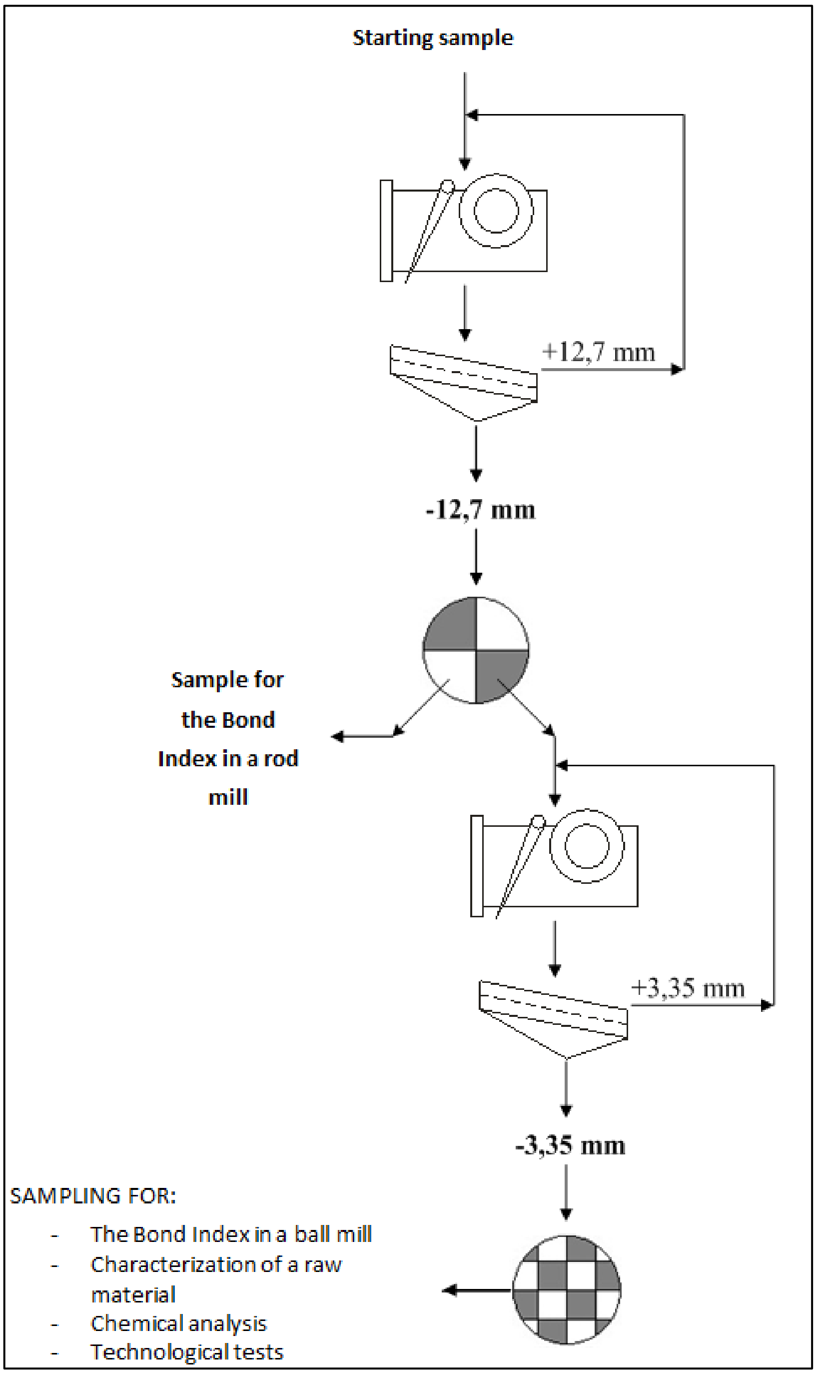


FIGURE 64 - SAMPLE PREPARATION SCHEME.

The Bond Index was determined on a sample in a rod mill and ball mill.

W_{ir} = 13,5 kWh/t
W_{ib} = 8,7 kWh/t

Grinding kinetics was done on a sample for the needs of further research. All grinding experiments were carried out in an ellipsoidal ball mill, volume of 14,6 l and batch of balls with weight of 13,45 kg. The solid content in the mill was of 75%. Next table shows the dependence of particle size distribution of sample on grinding time, and next figure shows the dependence of class content of >0,075 mm on grinding time.

	4 min		7 min		10 min	
	m %	**D %**	**m %**	**D %**	**m %**	**D %**
-0.600+0.425	1.80	100.00				
-0.425+0.300	1.00	98.20				
-0.300+0.212	4.40	97.20				
-0.212+0.150	9.20	92.80	1.80	100.00	0.40	100.00
-0.150+0.106	11.60	83.60	6.20	98.20	2.60	99.60
-0.106+0.075	13.00	72.00	12.20	92.00	7.80	97.00
-0.075+0.053	4.80	59.00	6.20	79.80	5.20	89.20
-0.053+0.038	6.80	54.20	9.80	73.60	9.20	84.00
-0.038+0	47.40	47.40	63.80	63.80	74.80	74.80

TABLE 41 - DEPENDENCE OF PARTICLE SIZE DISTRIBUTION OF SAMPLE ON GRINDING TIME.

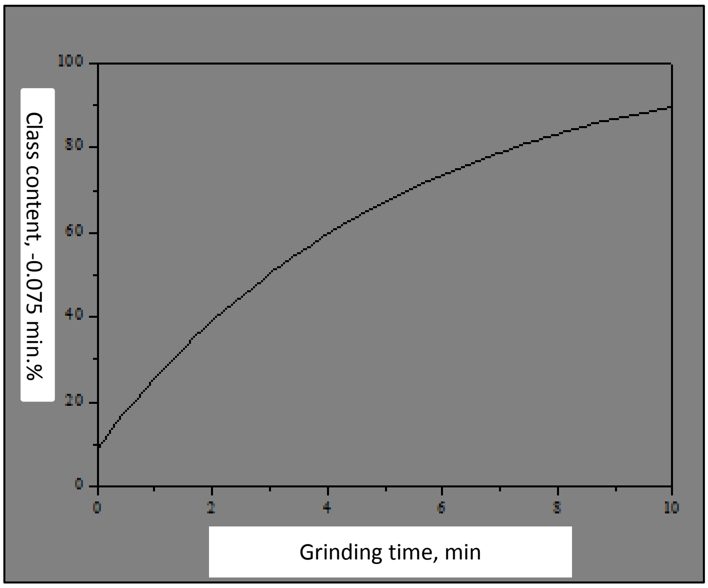


FIGURE 65 - DEPENDANCE THE CLASS CONTENT -0,075MM ON GRINDING TIME.

3.5.3 FLOTATION TESTWORK

Laboratory flotation tests were carried out in order to obtain the selective concentrates of lead, zinc and copper. Gained results showed that selective concentrates cannot be obtained. Due to this reason, the experiments were carried out on polymetallic ore sample in order to obtain the bulk sulphide concentrate and barite concentrate.

Conditions, under which laboratory tests were implemented, were adopted on the basis from experience in this field. The scheme according to which the several typical experiments were performed is shown in next figures.

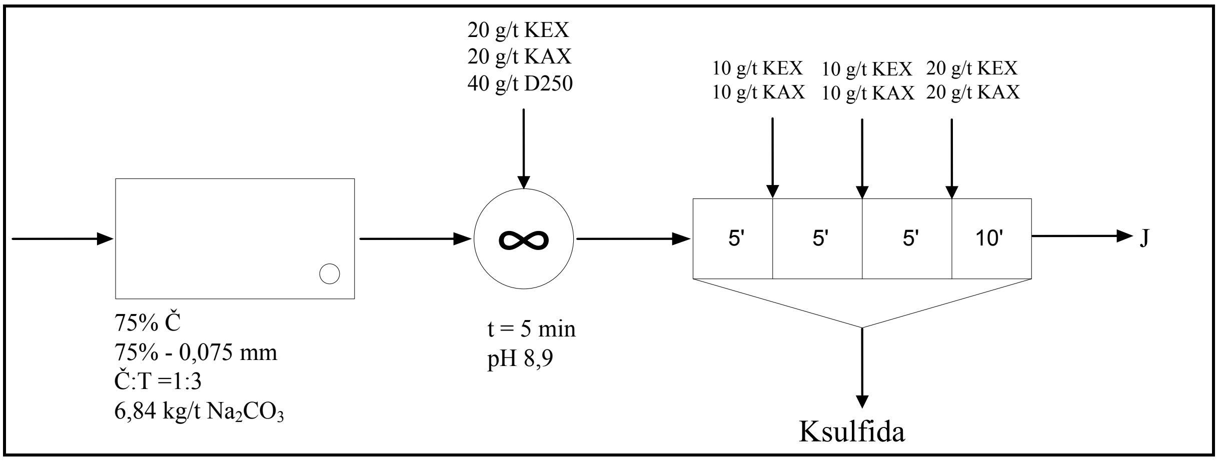


FIGURE 66 - FIRST EXPERIMENT SCHEME.

	m %	Zn %	I_{Zn} %	Pb%	I_{Pb} %	Cu %	I_{Cu} %	Au g/t	I_{Au} %	Ag g/t	I_{Ag} %	$BaSO_4$ %	I_{BaSO4},%
U	100.00	5.77	100.00	5.05	100.00	1.80	100.00	1.47	100.00	109.29	100.00	14.98	100.00
K	67.56	7.39	86.56	5.46	73.00	2.22	83.47	1.7	78.65	133.2	82.34	6.18	83.11
J	32.44	2.39	13.15	4.20	27.00	0.92	16.53	1.0	21.35	59.5	17.66	33.30	16.89

TABLE 42 - CONCENTRATION BALACE IN THE FIRST EXPERIMENT.

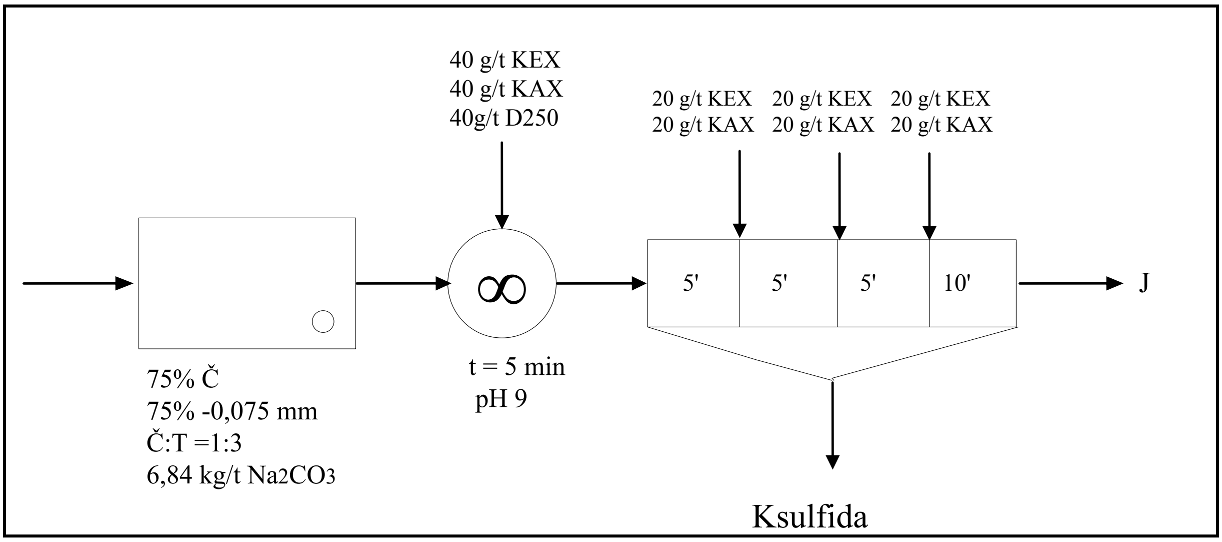


FIGURE 67 - SECOND EXPERIMENT SCHEME.

	m %	Zn %	I_{Zn} %	Pb %	I_{Pb} %	Cu %	I_{Cu} %	Au g/t	I_{Au} %	Ag g/t	I_{Ag}, %	BaSO4 %	I_{BaSO4} %
U	100.00	5.59	100.00	3.11	100.00	1.69	100.00	0.92	100.00	121.24	100.00	62.93	100.00
K_S	73.78	6.04	99.09	3.20	75.83	2.10	91.77	1.10	88.30	151.40	92.13	58.80	68.93
J	26.22	0.62	0.91	2.87	24.17	0.53	8.23	0.41	11.70	36.40	7.87	74.56	31.07

TABLE 43 - CONCENTRATION BALANCE IN THE SECOND EXPERIMENT.

In the next experiment, the grinding fineness was 85% >0.075 mm. The scheme, according to which the experiment was carried out, is presented in the next figure, and the results of concentration in the following table.

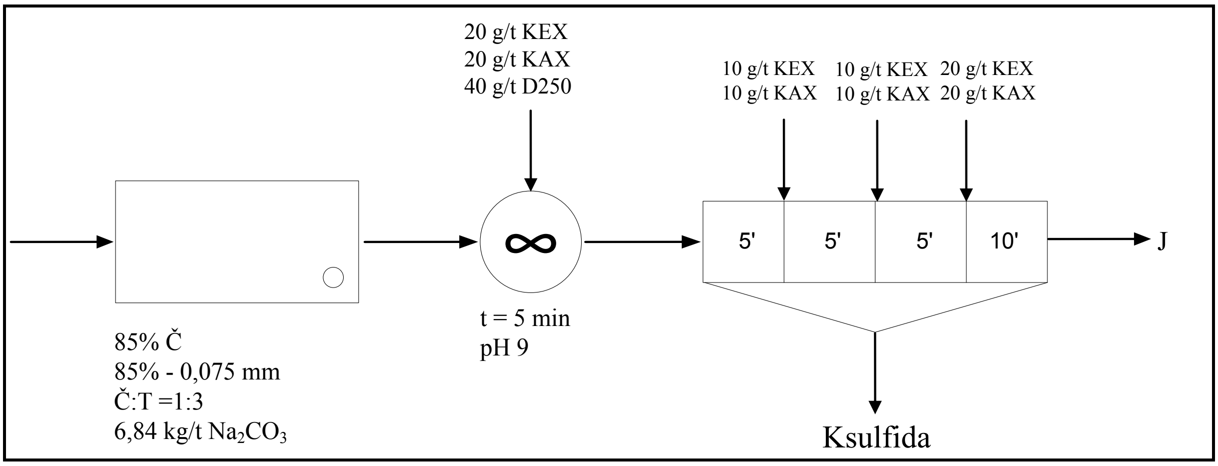


FIGURE 68 - THIRD EXPERIMENT SCHEME.

	m %	Zn %	I_{Zn} %	Pb%	I_{Pb} %	Cu %	I_{Cu} %	Au g/t	I_{Au} %	Ag g/t	I_{Ag} %	$BaSO_4$ %	I_{BaSO4},%
U	100.00	5.70	100.00	4.68	100.00	1.93	100.00	1.49	100.00	100.51	100.00	13.83	100.00
K	47.05	6.66	54.96	4.94	49.69	2.79	67.94	1.6	50.38	120.0	56.17	3.82	13.00
J	52.95	4.85	45.04	4.45	50.31	1.17	32.06	1.4	49.62	83.2	43.83	22.72	87.00

TABLE 44. CONCENTRATION BALANCE IN THE TIRD EXPERIMENT.

After the obtained results in the previous present experiments, the following can be concluded:

- Samples have high content of coper, lead, zinc, silver and gold.
- Masses of sulphide concentrate are high.
- Better metal recoveries in sulphide concentrate were obtained in the experiments with the grinding fineness of 75% >0.075 mm, and greater distribution of barite in the underflow of sulphide flotation of sulphides was in the grinding fineness of 85% >0.075mm.
- In the underflow of sulphide flotation, the barite content is insufficient in relation to the market requirements for use, so it is necessary to separate it into separate concentrate.

Next figure shows laboratory sulphide flotation.

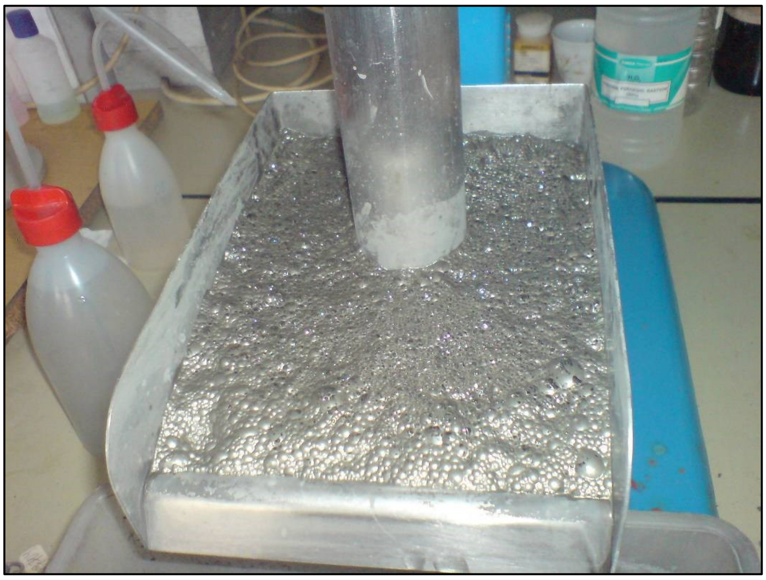


FIGURE 69 - SULPHIDE FLOTATION.

The next series of experiments are planned so that the selected grinding fineness of 75% >0,075 mm is one that is more favourable for flotation of sulphide minerals due to the value of such concentrates. From the underflow of sulphide flotation, the barite concentrate was floated with three different reagent regimes on both samples. From collectors for barite, recommended in the literature, the A845 was applied. Two doses of this collector were tested as well as the one using the barite activator $BaCl_2$. Next figures show the schemes according to which the experiments were carried out and the realized concentration balances in the following tables.

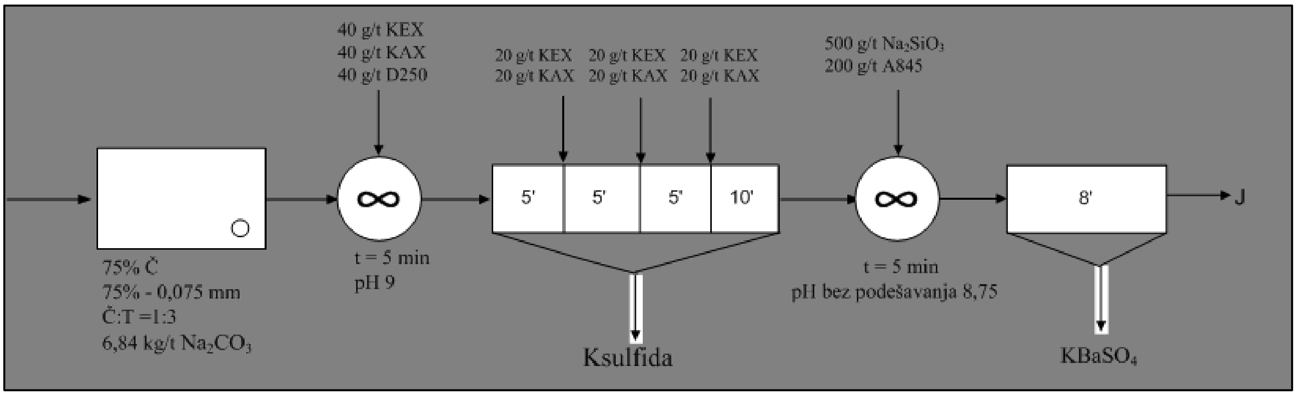


FIGURE 70 - FOURTH EXPERIMENT SCHEME.

	m %	Zn %	I_{Zn} %	Pb%	I_{Pb} %	Cu %	I_{Cu} %	Au g/t	I_{Au} %	Ag g/t	I_{Ag} %	$BaSO_4$ %	I_{BaSO4},%
U	100,00	5,53	100,00	5,36	100,00	1,80	100,00	1,30	100,00	110,70	100,00	14,76	100,00
K_s	81,50	6,61	97,44	6,20	94,19	2,12	96,10	1,0	59,63	47,50	34,98	7,09	39,14
K_{Ba}	14,67	0,78	2,08	1,64	4,48	0,40	3,28	3,1	35,57	471,5	62,48	59,06	58,69
J	3,83	0,69	0,48	1,86	1,33	0,29	0,62	0,9	2,80	73,4	2,54	8,35	2,17

TABLE 45 - CONCENTRATION BALANCE IN THE FOURTH EXPERIMENT.

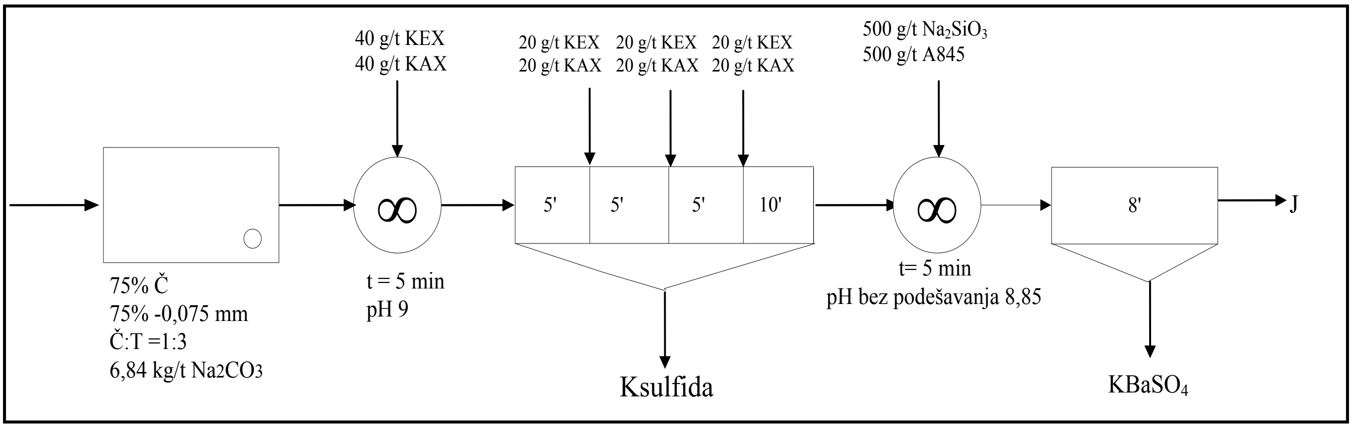


FIGURE 71 - SCHEME OF THE FITH EXPERIMENT.

	m %	Zn %	I_{Zn} %	Pb%	I_{Pb} %	Cu %	I_{Cu} %	Au g/t	I_{Au} %	Ag g/t	I_{Ag} %	$BaSO_4$ %	I_{BaSO4},%
U	100.00	5.73	100.00	5.56	100.00	1.89	100.00	1.61	100.00	107.14	100.00	14.65	100.00
K_s	80.22	6.96	97.39	6.39	92.14	2.27	96.38	1.7	92.81	114.9	94.13	5.75	31.49
K_{BaSO4}	16.32	0.73	2.09	2.32	6.80	0.37	3.17	0.5	5.05	26.3	4.38	60.06	66.92
J	3.46	0.86	0.52	1.70	1.06	0.25	0.45	1.0	2.14	42.1	1.49	6.75	1.59

TABLE 46 - CONCENTRATION BALANCE IN THE FITH EXPERIMENT.

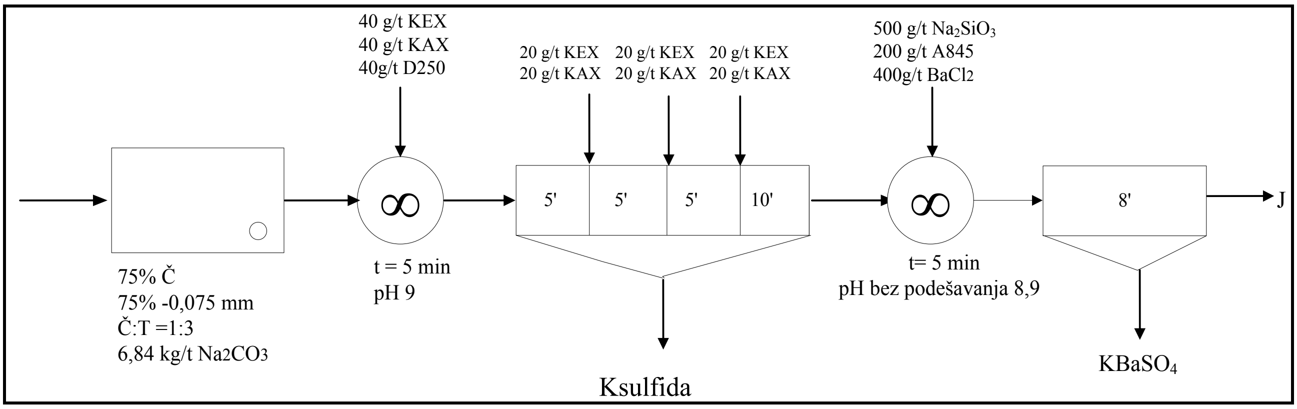


FIGURE 72 - SIXTH EXPERIMENT SCHEME.

	m %	Zn %	I_{Zn} %	Pb%	I_{Pb} %	Cu %	I_{Cu} %	Au g/t	I_{Au} %	Ag g/t	I_{Ag} %	$BaSO_4$ %	I_{BaSO4},%
U	100.00	5.24	100.00	5.48	100.00	1.80	100.00	1.6	100.00	100.20	100.00	13.97	100.00
K_s	79.77	6.37	96.96	6.29	91.82	2.17	95.94	1.2	60.60	40.8	32.50	5.78	33.01
K_{BaSO4}	16.78	0.78	2.50	2.35	7.19	0.38	3.51	3.4	36.12	374.8	62.74	54.76	65.79
J	3.45	0.82	0.54	1.57	0.99	0.29	0.55	1.5	3.28	138.5	4.76	4.86	1.20

TABLE 47 - CONCENTRATION BALANCE IN THE SIXTH EXPERIMENT.

These flotation expirements demonstrate that polymetallic ore (Cu, Pb, Zn, Au, Ag) with barite is a very complex raw material with coalescenced very fine size minerals and aggregates which are not possible enough to open for flotation. So, only a collective sulphide concentrate can be obtained with weight of approximately 75-80% compared to the entrance, with recovery of over 90% on copper, zinc, lead, gold and silver. That contribute to small increasing concentration of metals.

3.6 BRGM LAB FLOTATION TESTWORK

Considering the low impact of the microwave treatment on the ores grindability, the work upon beneficiation through flotation trials only focused on Cobre Las Cruces ore. Moreover, in order to stay in the range of the Bond ball mill work index value (12.5 kWh/t regarding CLC), the tested samples were microwave treated up to 10 kWh/t.

3.6.1 FEED SULPHIDE GRAINS CHARACTERIZATION

A non-treated ore sample of CLC ground to about d80 = 110 microns as a product of the Bond Ball mill was separated into several size fractions: +100-160 microns; +80-100microns; +63-80microns; +40-63microns; +20-40microns; minus 20 microns.

Each fraction had been observed under light transmitted microscope to characterize sulphides grains liberation size. Unlocked Zn-, Pb- or Cu- sulphides grains are barely present in size fractions above 63 microns (Figure 73) except from some chalcopyrite grains (

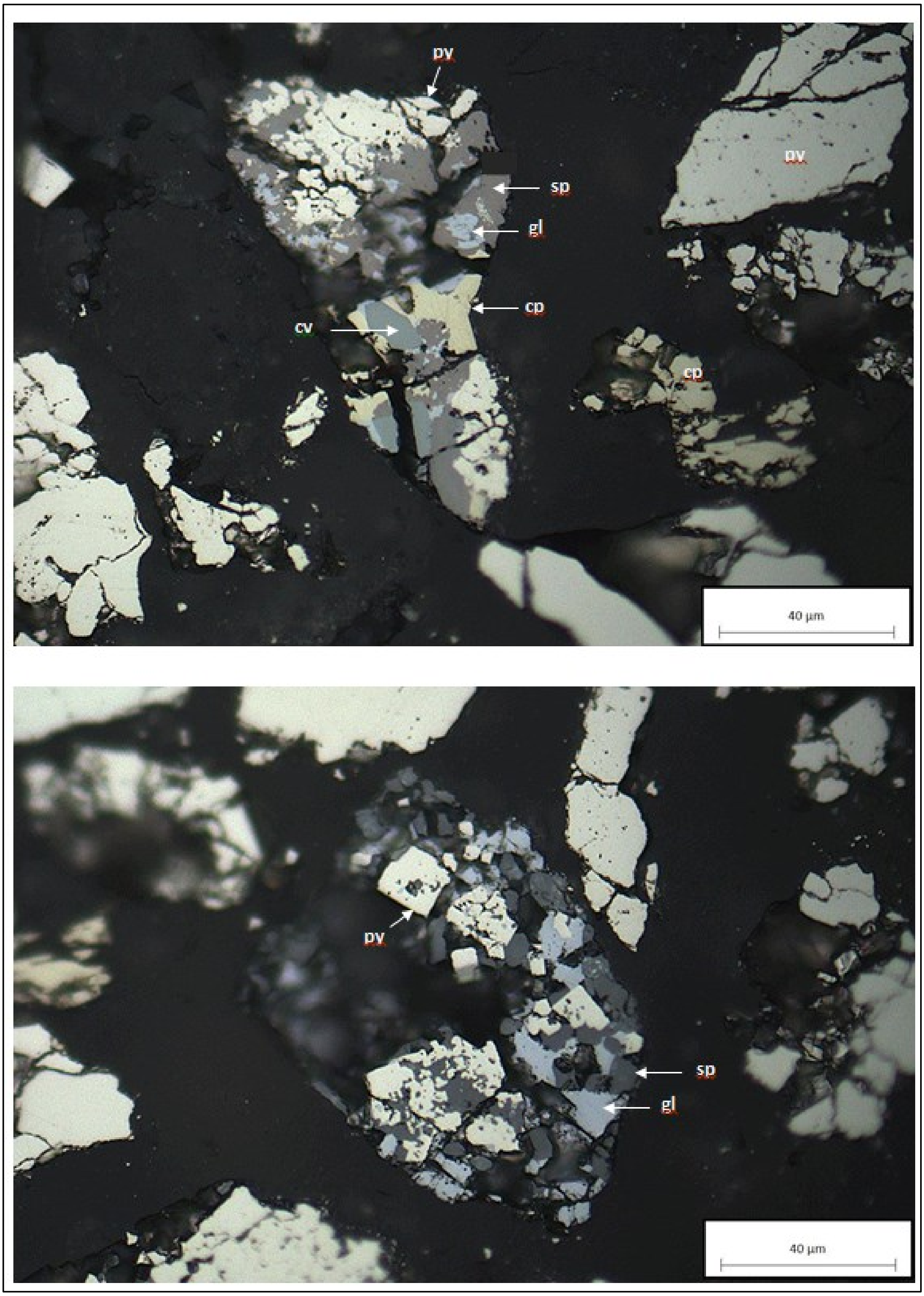


Figure 74).

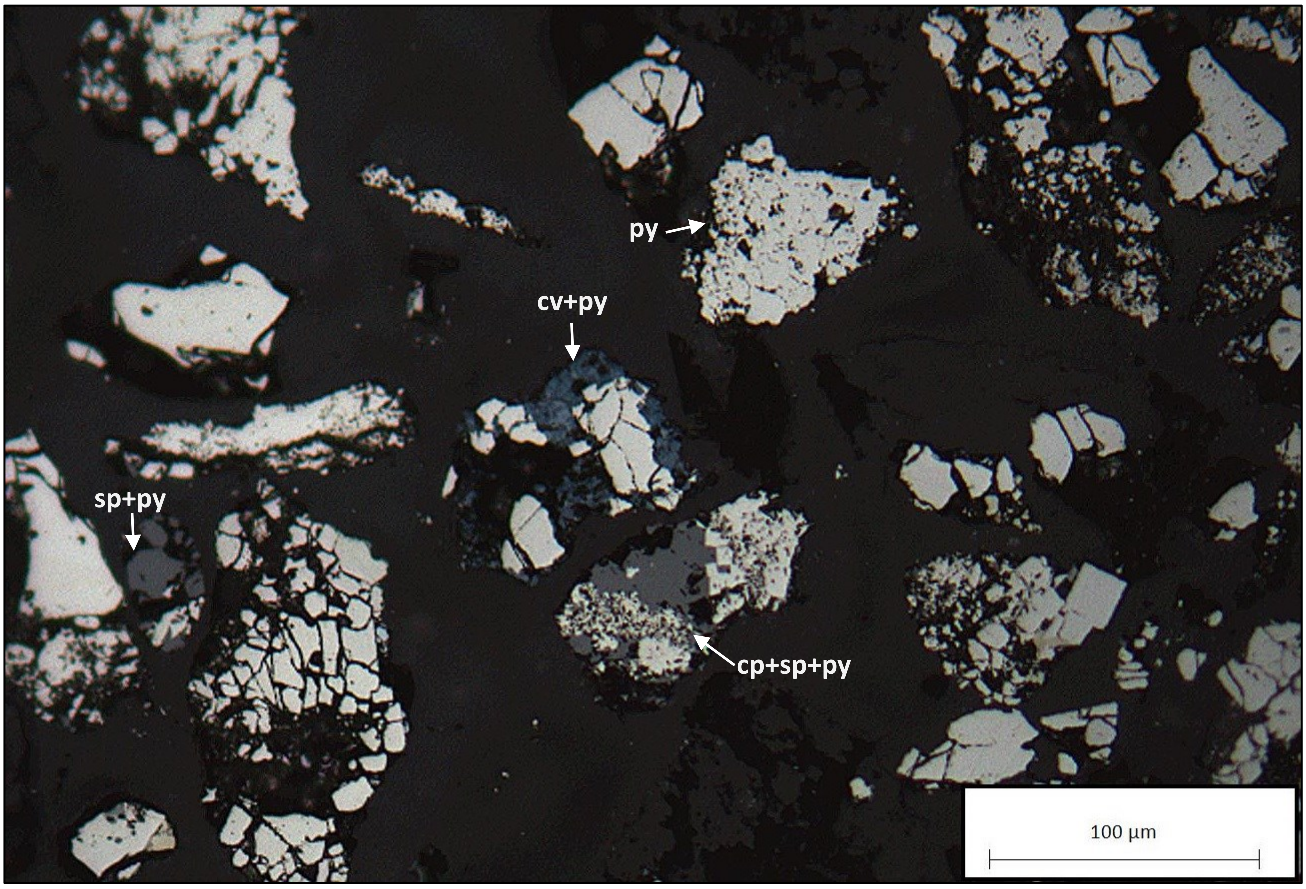


FIGURE 73 - PICTURES OF LIGHT TRANSMITTED MICROSCOPE OBSERVATION OF A 100-160 MICRONS FRACTION FROM A GROUND CLC SAMPLE.

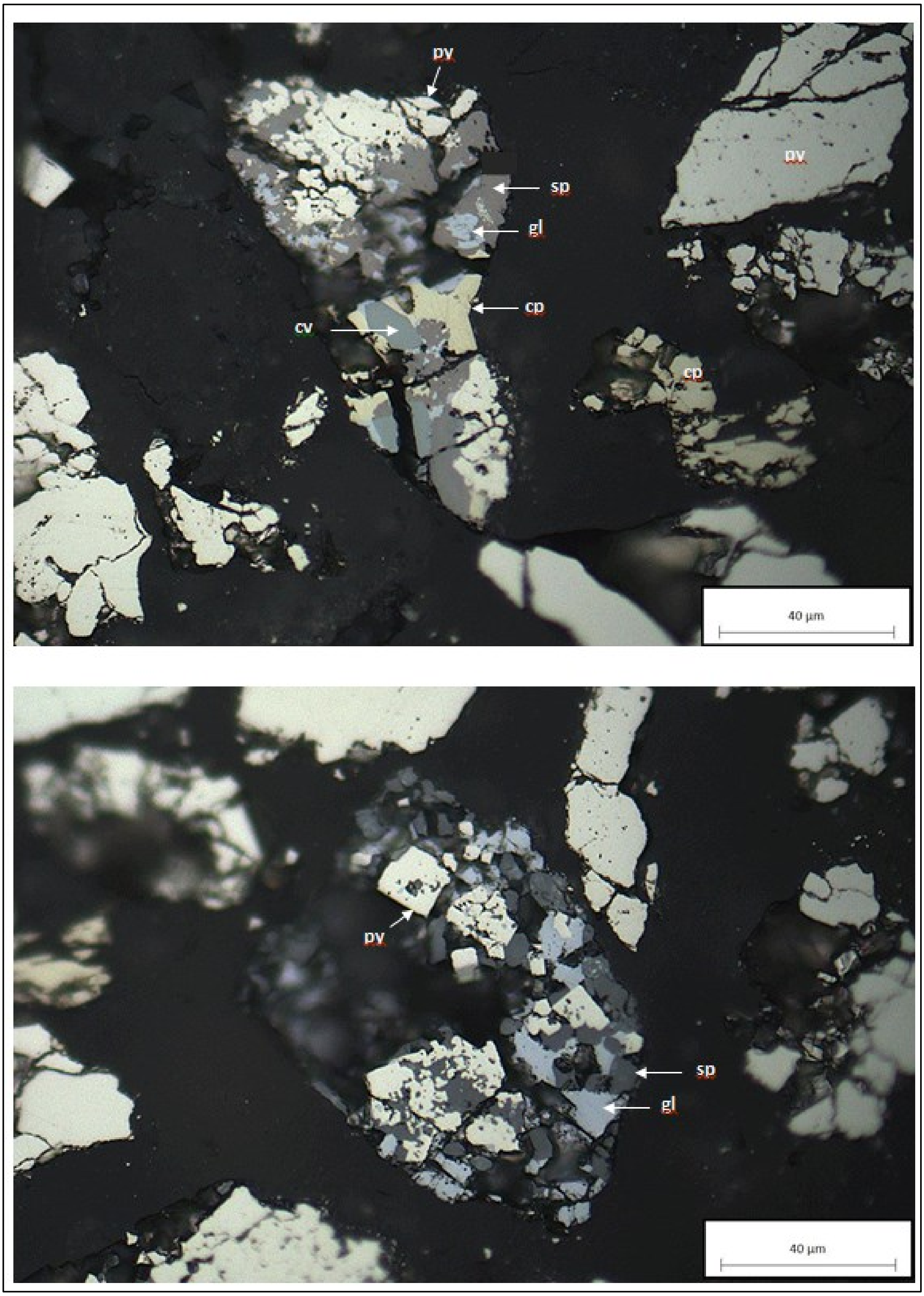


FIGURE 74 - PICTURES OF LIGHT TRANSMITTED MICROSCOPE OBSERVATION OF A 63-80 MICRONS FRACTION FROM A GROUND CLC SAMPLE.

Liberated Zn-, Pb or Cu- sulphides occurs mostly at size fractions under 40 microns (Figure 75 & Figure 76).

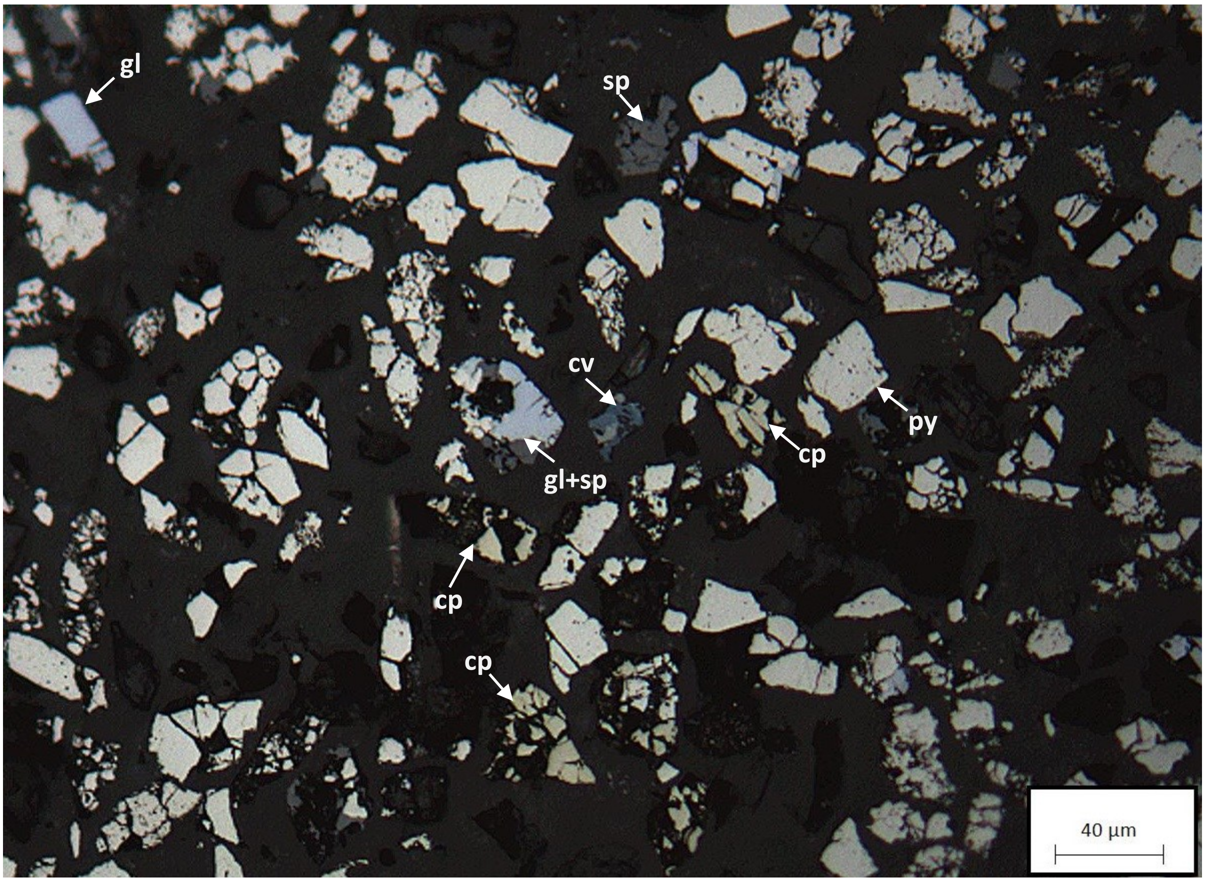


FIGURE 75 - PICTURES OF LIGHT TRANSMITTED MICROSCOPE OBSERVATION OF A 20-40 MICRONS FRACTION FROM A GROUND CLC SAMPLE (GL: GALENA; SP: SPHALERITE; PY: PYRITE; CP: CHALCOPYRITE; CV: COVELLITE)

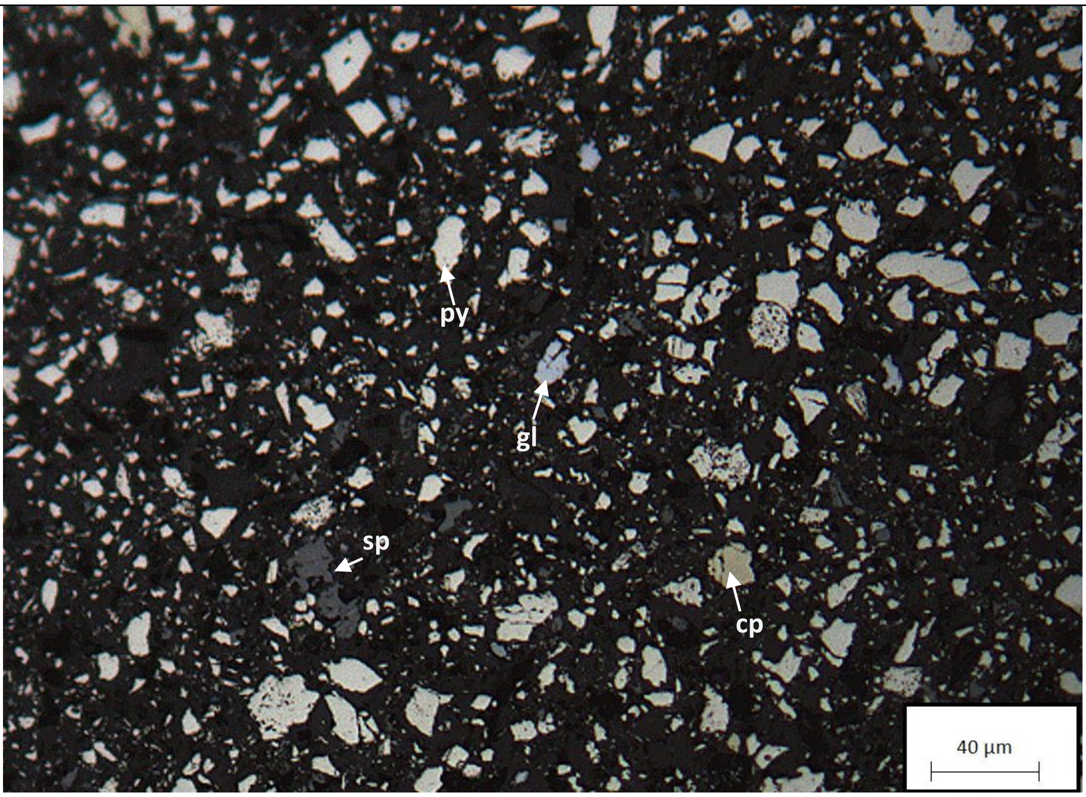


FIGURE 76 - PICTURES OF LIGHT TRANSMITTED MICROSCOPE OBSERVATION OF A MINUS 20 MICRONS FRACTION FROM A GROUND CLC SAMPLE (GL: GALENA; SP: SPHALERITE; PY: PYRITE; CP: CHALCOPYRITE).

3.6.2 FLOTATION MATERIAL AND PROCEDURE

Flotation trials had been carried out at a laboratory scale using a 2.5 L Denver cell, at 1500 rpm with air tap fully open for bubble generation (see Figure 77).

FIGURE 77 - FLOTATION TRIAL UNDER WAY WITH A 2,5L DENVER CELL.

The cell was filled with the sample and water considering a solid content of 25 wt%. The reagents used for flotation trials were as follows:

- Dispersant:
  - Sodium silicate (Na_2SiO_3), with a dosage of 300 g/T.
- Depressant:
  - Sodium sulphate (Na_2SO_3), with a dosage of 300 g/T.
  - Lime (CaO), used as a pH regulator and pyrite depressant, dosage around 2000-2500 g/T.
- Collector / Promoter:
  - AEROPHINE 3418A (30 g/t per dose for each conditioning step).
- Frother:
  - AEROFROTH 70.

Flotation trials were undertaken using a sequential procedure as described below (see Figure 78).

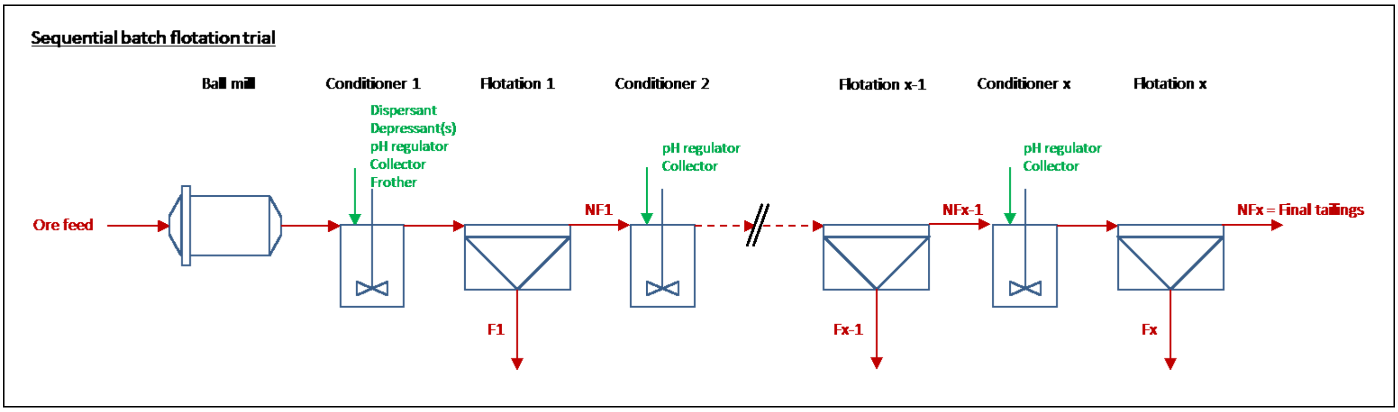


FIGURE 78 - PROCEDURE APPLIED FOR FLOTATION TRIALS.

3.6.3 METALLURGICAL ASSAYS

In order to calculate mass balances around each flotation trial, metallurgical assays had been conducted using a FPXRF (Field Portable X-Ray Fluorescence) device (Niton XL3t980, see Figure 79).

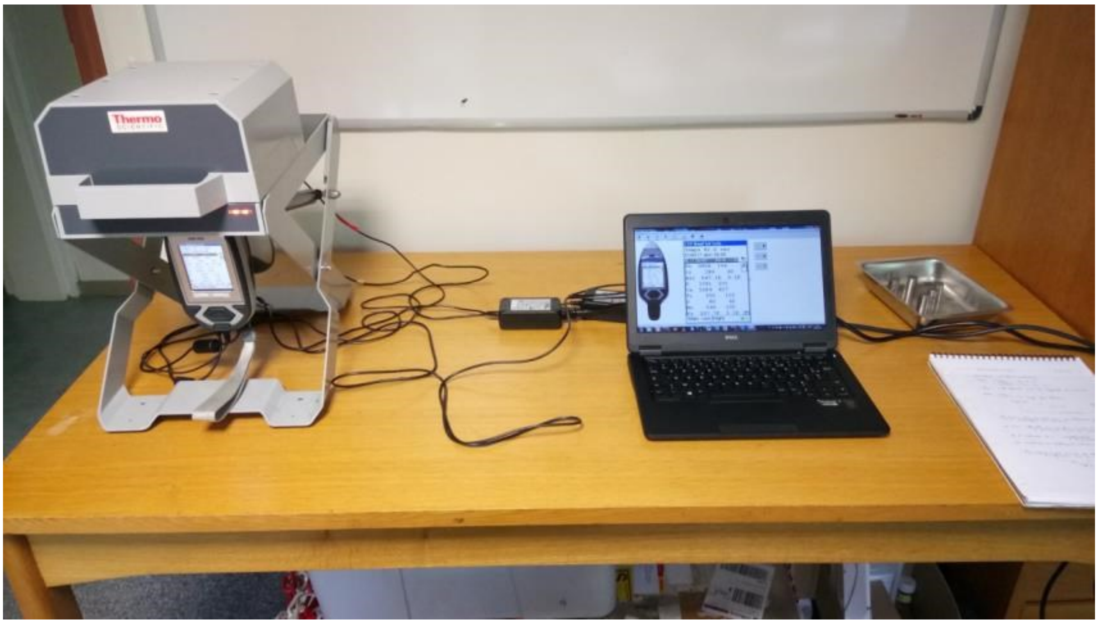


FIGURE 79 - FPXRF STATION USED TO PERFORM METALLURGICAL ASSAYS OF FLOTATION TRIALS PRODUCTS.

FPXRF ensures fast and non-destructive elementary analysis (from Mg to U) in solid matrix such as ores, with contents from ppm to several percent. XRF technique consists in emitting an X-ray beam upon the material which is submitted to three physical phenomena: absorption, dispersion and fluorescence. Fluorescence is a secondary emission of electrons characterizing the atomic elements that constitutes the material.

The XRF device, portable or not, is made of two parts:

- An excitation source which produces an X-ray beam towards the material to analyse.
- A detector and a spectre analyser identifying the rays of the secondary emission of electrons, based on Moseley law. Integrated software calculates then the content of atomic elements.

Regarding each assays, the FPXRF had been used systematically with the “Industrial Cu/Zn” pre-calibrated mode ensuring analysis of metals within heavy matrix.

3.6.4 FLOTATION TESTWORK

3.6.4.1 METAL DISTRIBUTION BY SIZE FRACTIONS

Metallurgical assays by size fractions upon CLC samples ground with the Bond Ball mill at d80 around 110 microns (see Figure 80) were performed using FPXRF. The results of these assays are reported as metal distributions by size fraction respectively for samples of CLC untreated (Figure 81), CLC microwave treated at 3.3 kWh/t (Figure 82) and CLC microwave treated at 10 kWh/t (Figure 83).

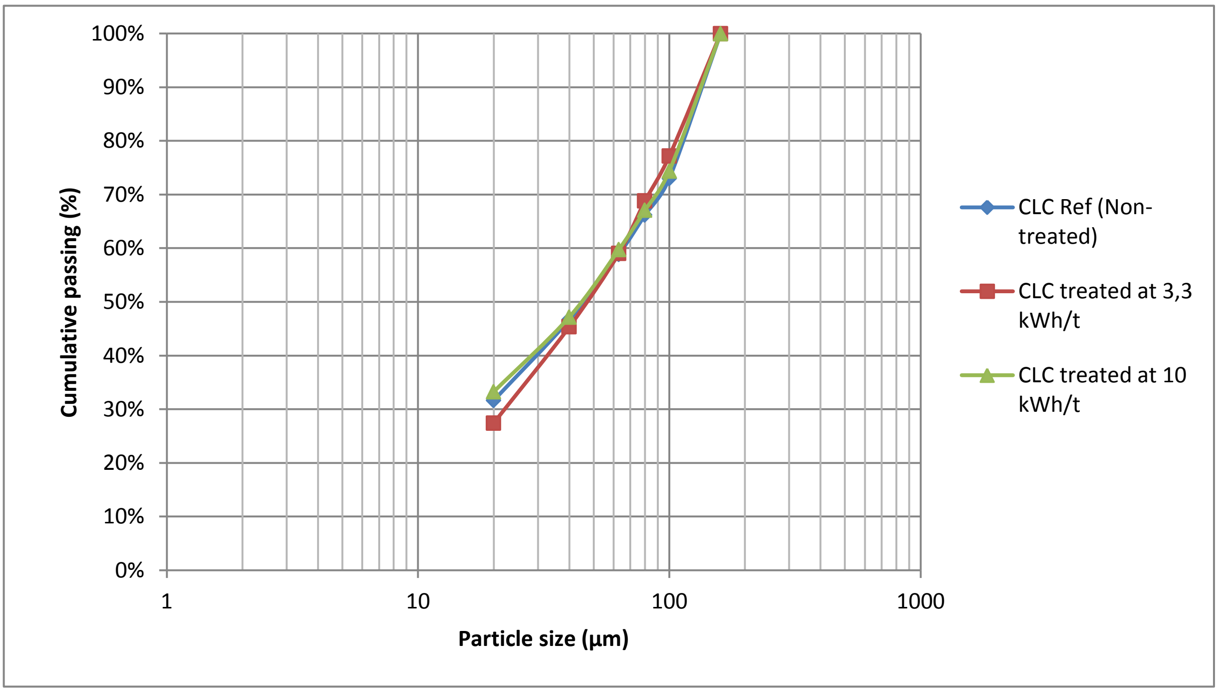


FIGURE 80 - PARTICLE SIZE DISTRIBUTIONS OF GROUND SAMPLES OF CLC MICROWAVE TREATED AND UNTREATED.

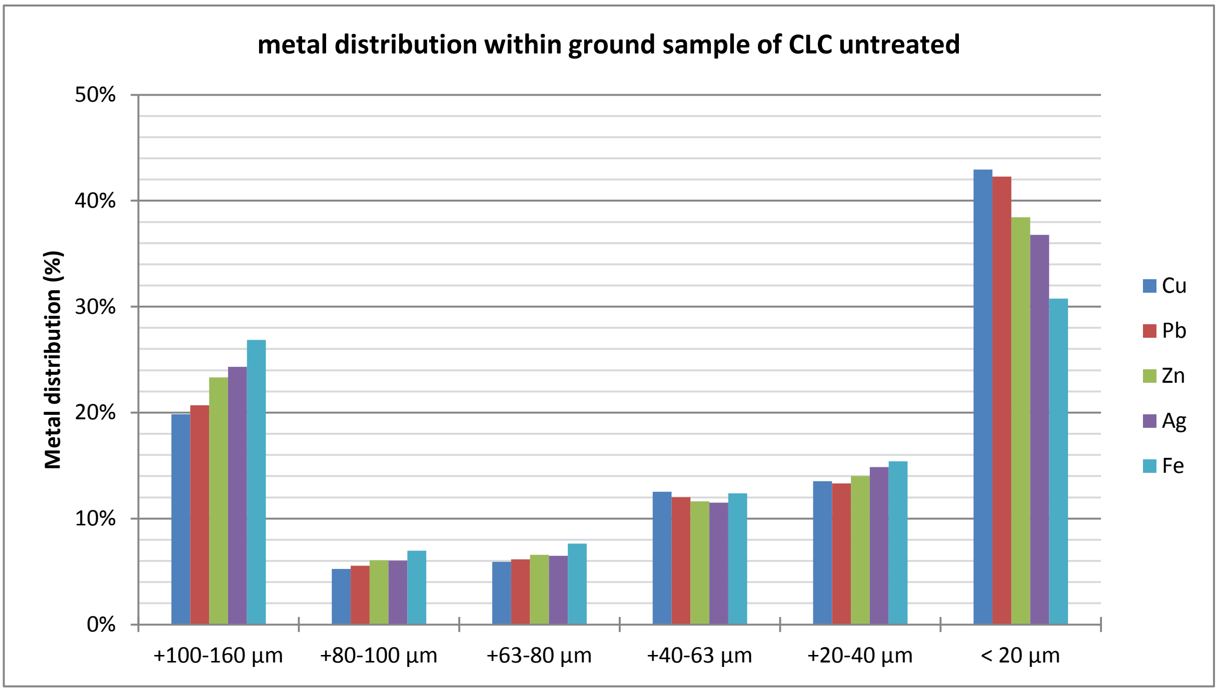


FIGURE 81 – METAL DISTRIBUTIONS BY SIZE FRACTION WITHIN GROUND SAMPLE OF CLC UNTREATED.

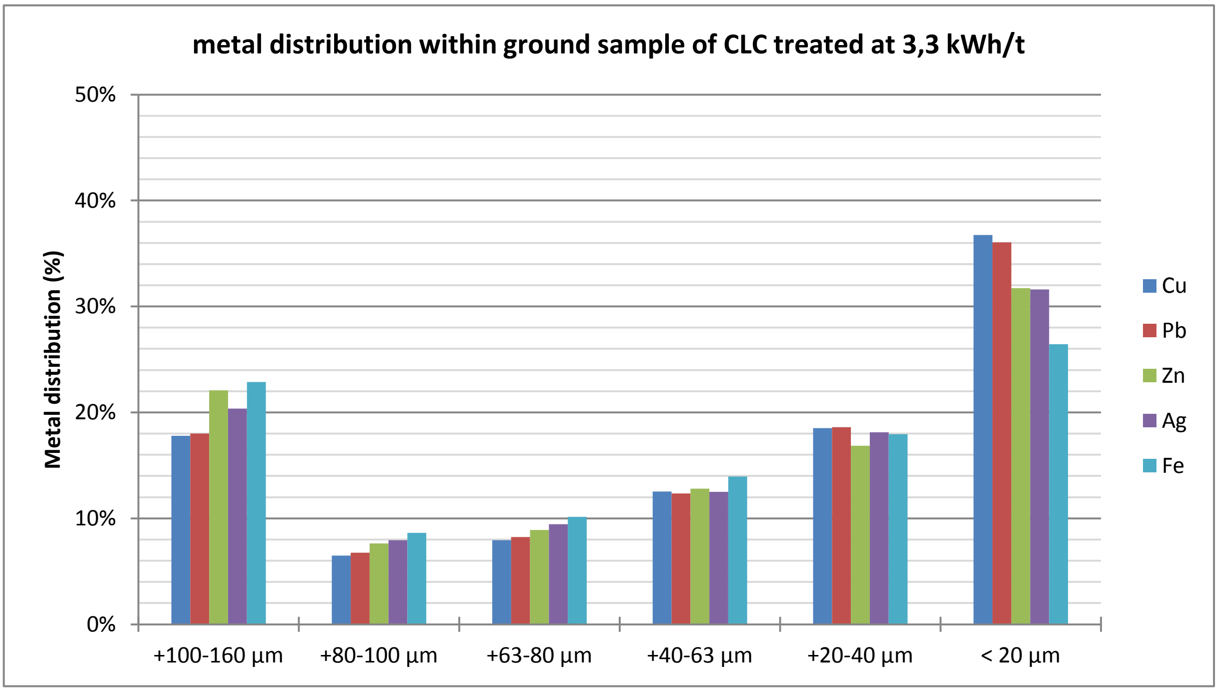


FIGURE 82 - METAL DISTRIBUTIONS BY SIZE FRACTION WITHIN GROUND SAMPLE OF CLC TREATED AT 3.3 KWH/T.

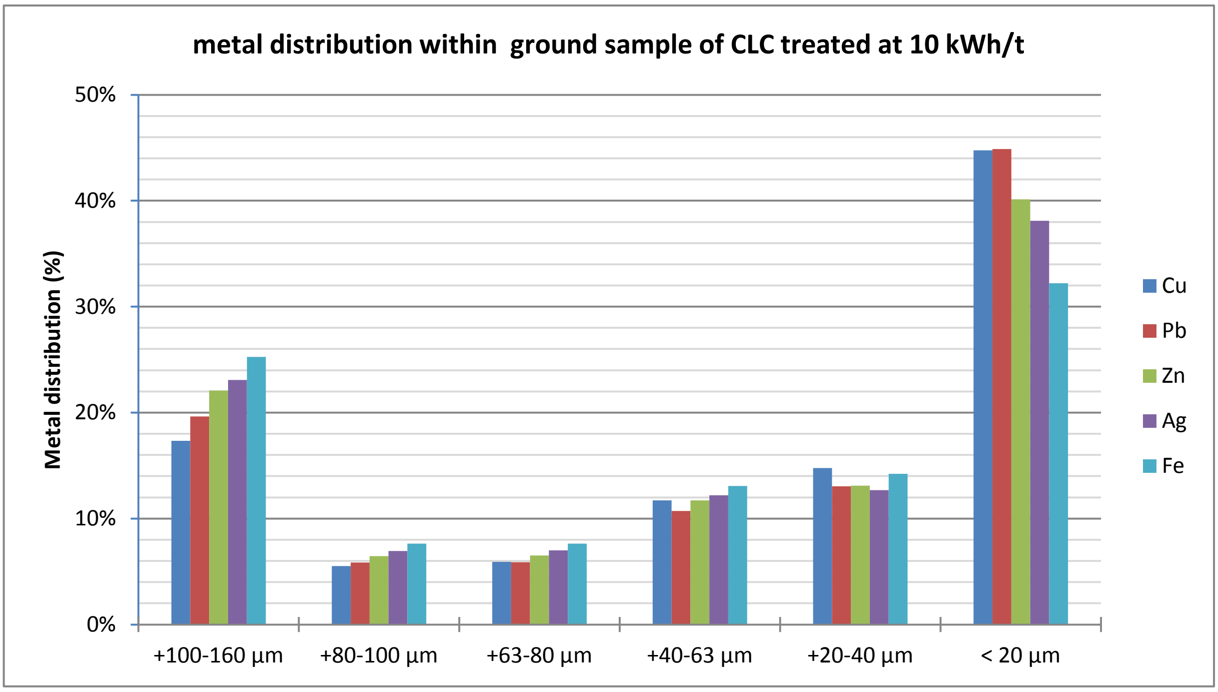


FIGURE 83 - METAL DISTRIBUTIONS BY SIZE FRACTION WITHIN GROUND SAMPLE OF CLC TREATED AT 10 KWH/T.

Mass and metal repartitions of Cu, Pb, Zn, Ag, and Fe are very similar regarding each size fraction to another between CLC microwave treated and untreated ground samples (Appendix).
Then, the microwave treatment up to 10 kWh/t of CLC samples seems not to have led to any Cu-, Zn- or Pb-bearing sulphides liberation at higher size than without it.

3.6.4.2 FLOTATION TRIALS

Flotation trials had been undertaken on the previous CLC ground samples (to d80 = 110 microns) using AEROPHINE 3418A as collector, sodium silicate (Na_2SiO_3 or “waterglass”) as dispersant and AEROFROTH 70 as frother.

A sequential flotation procedure (Figure 78) had been selected to carry on these tests applied to a non-treated sample and two micro-wave treated samples, respectively at 3.3 and 10 kWh/t.

The kinetics results are reported as cumulative mass and metals cumulative recoveries.

Mass and metal recoveries are similar one test to another, which tends to confirm that no Cu, Pb or Zn sulphide liberation at higher size occurred due to the microwave treatment up to 10 kWh/t.

Mass recovery goes up to 20%, while metal recoveries of Cu, Pb, and Zn vary from 38.7 to 52.4%, and Ag recovery ranges from 31.4 to 35.7%. The test carried on the CLC treated sample at 10 kWh/t shows even less recovery of Zn with 38.7%, while the two other ones are around 44%.

Metal recoveries are quite low and out of the objective range targeted: the global objective will be to recover over 90% of the valuable metals. However, most of the liberated grains of valuable sulphides minerals were present within size fraction below 40 microns.

The metals upgrades by size fraction of the flotation tailings had been investigated and the results are reported respectively for the tailings of CLC untreated (Figure 84), CLC microwave treated at 3.3 kWh/t (Figure 85) and CLC microwave treated at 10 kWh/t (Figure 86) and with detailed comparison.

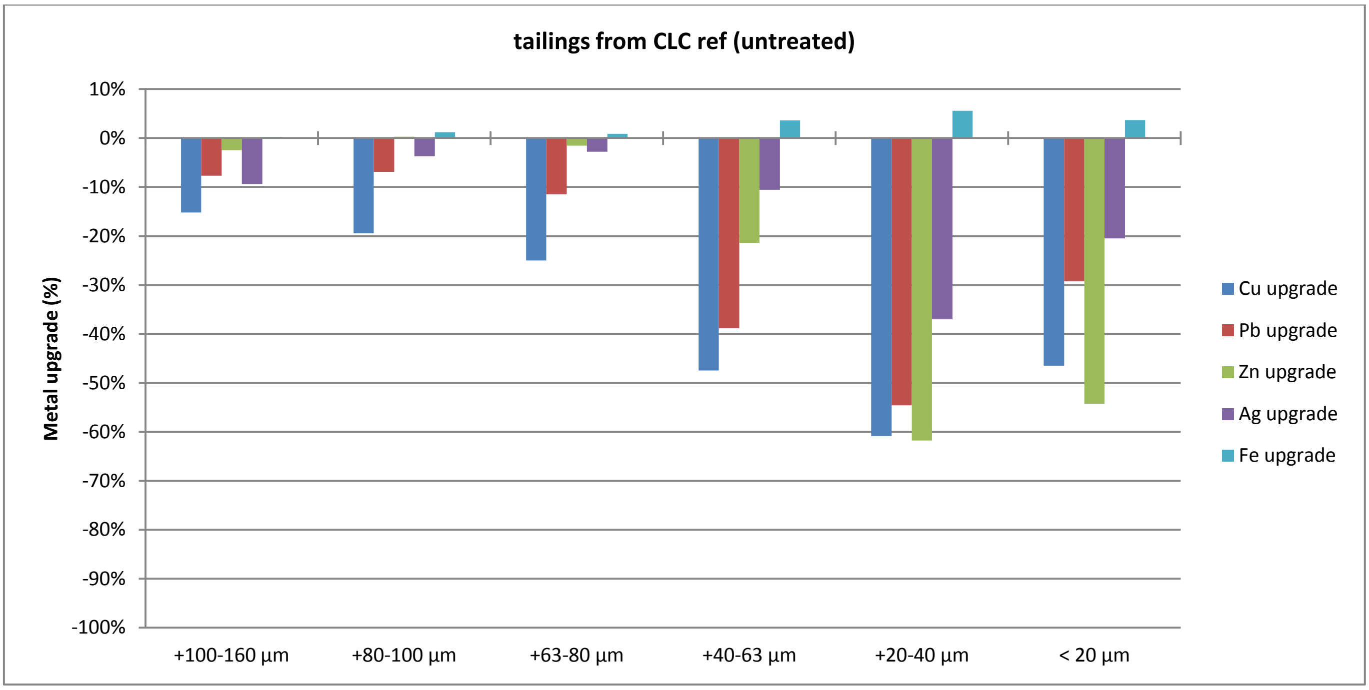


FIGURE 84 - METAL UPGRADE WITHIN THE TAILINGS OF THE FLOTATION TRIAL FROM CLC UNTREATED SAMPLE.

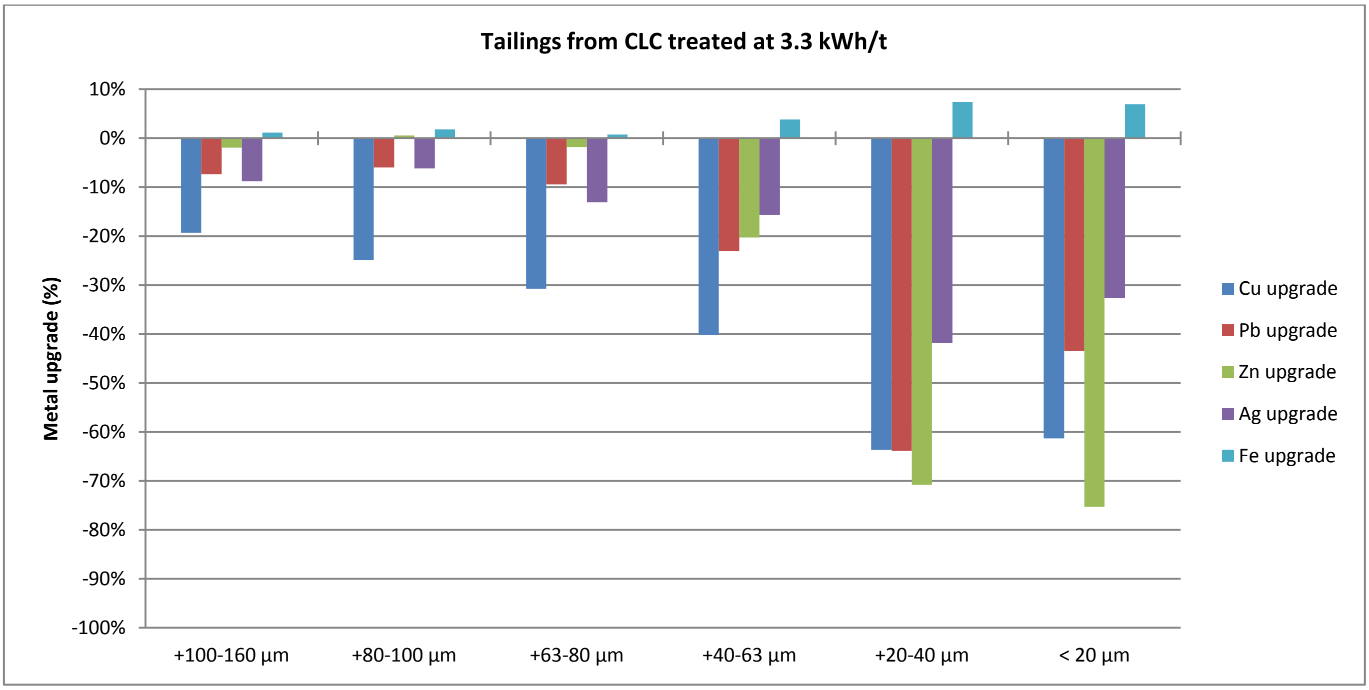


FIGURE 85 - METAL UPGRADE WITHIN TAILINGS OF FLOTATION TRIAL FROM CLC MICROWAVE TREATED SAMPLE AT 3.3 KWH/T.

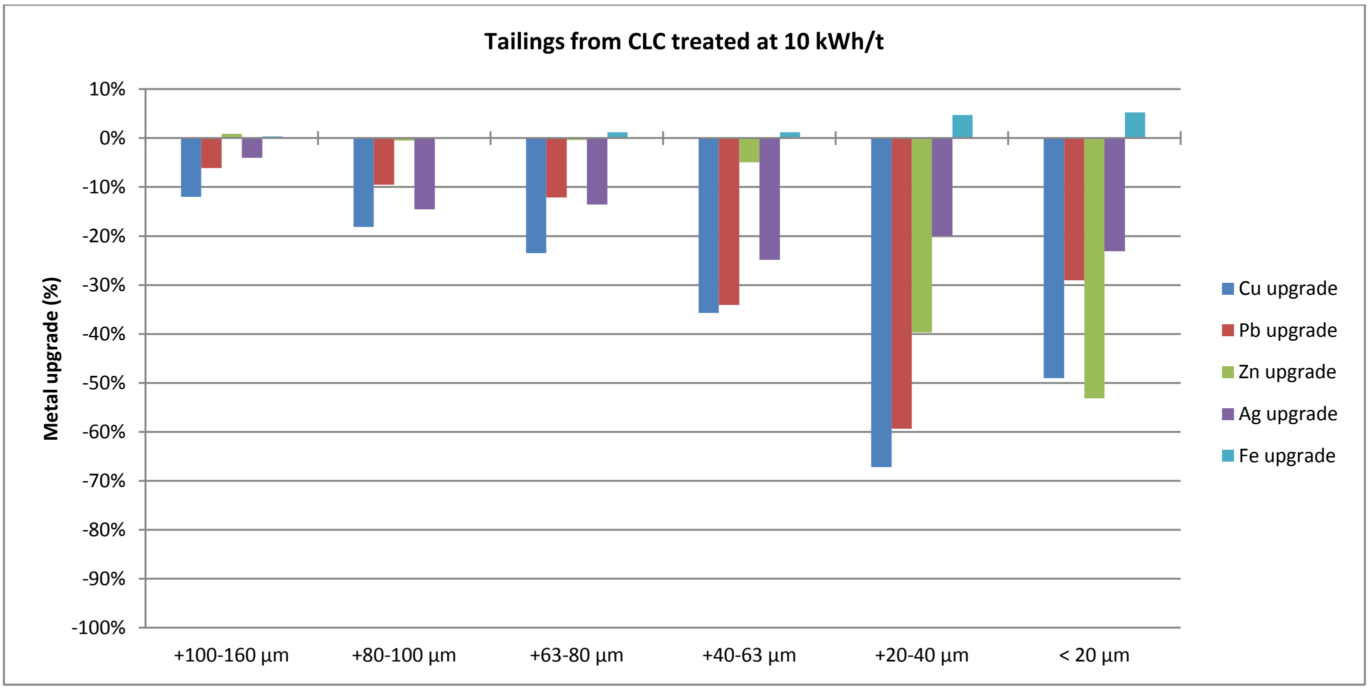


FIGURE 86 - METAL UPGRADE WITHIN TAILINGS THE FLOTATION TRIAL FROM CLC MICROWAVE TREATED SAMPLE AT 10 KWH/T.

Scavenging in Cu, Pb and Zn is more efficient within fraction sizes below 40 microns of the tailings where these metals upgrade goes down to -70%. However, Ag seems quite difficult recover in the concentrate since this metal upgrade is above -40% in the tailings. On the other hand, Fe tends to be concentrated within the tailings with small but positive metal upgrades in each fraction sizes.

The metals recoveries by size fraction of the flotations concentrates had been investigated and the results are reported respectively for Cu (Figure 87), Pb (Figure 88), Zn (Figure 89) and Ag (Figure 90).

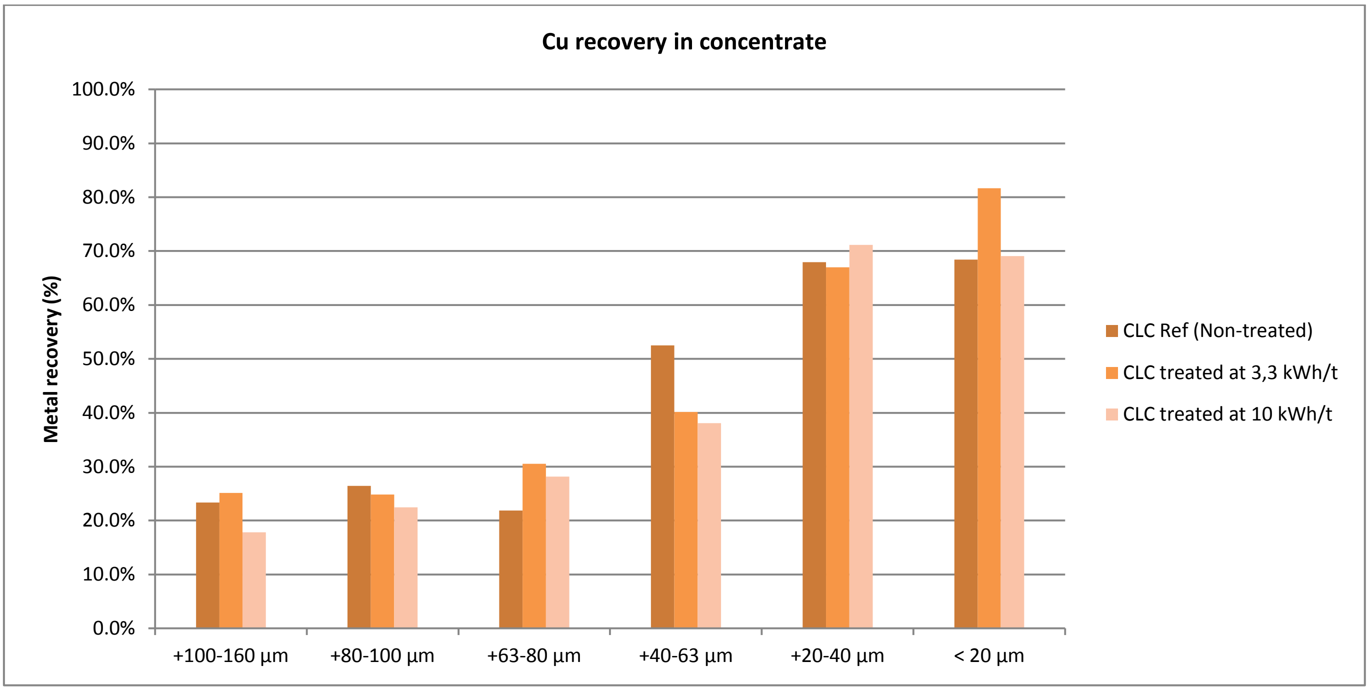


FIGURE 87 - CU RECOVERY PER SIZE FRACTION IN FLOTATION CONCENTRATE OF CLC TREATED AND UNTREATED SAMPLES.

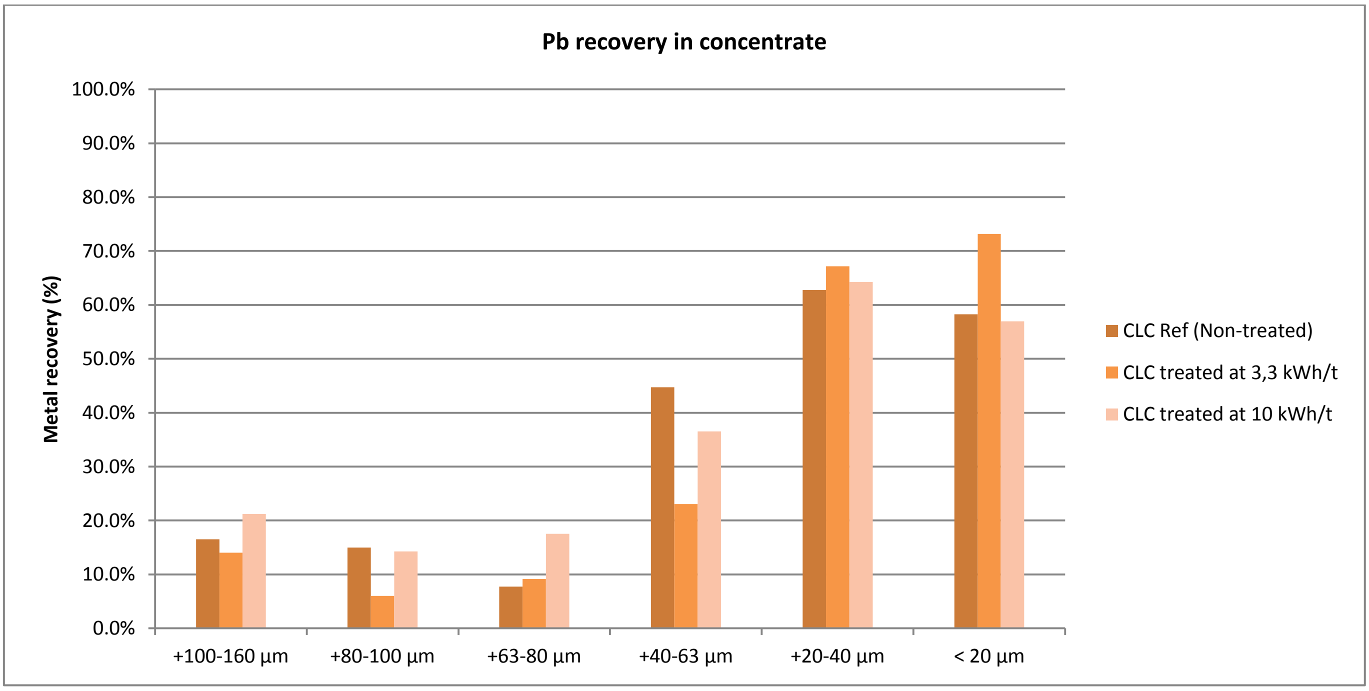


FIGURE 88 - PB RECOVERY PER SIZE FRACTION IN FLOTATION CONCENTRATE OF CLC TREATED AND UNTREATED SAMPLES.

Low recoveries (below 50%) occur within higher size fractions (above 40 microns) as a consequence of still present locked valuables minerals. Moreover, microwave treatment up to 10 kWh/t didn’t lead to significant better metal recoveries in these higher size fractions.

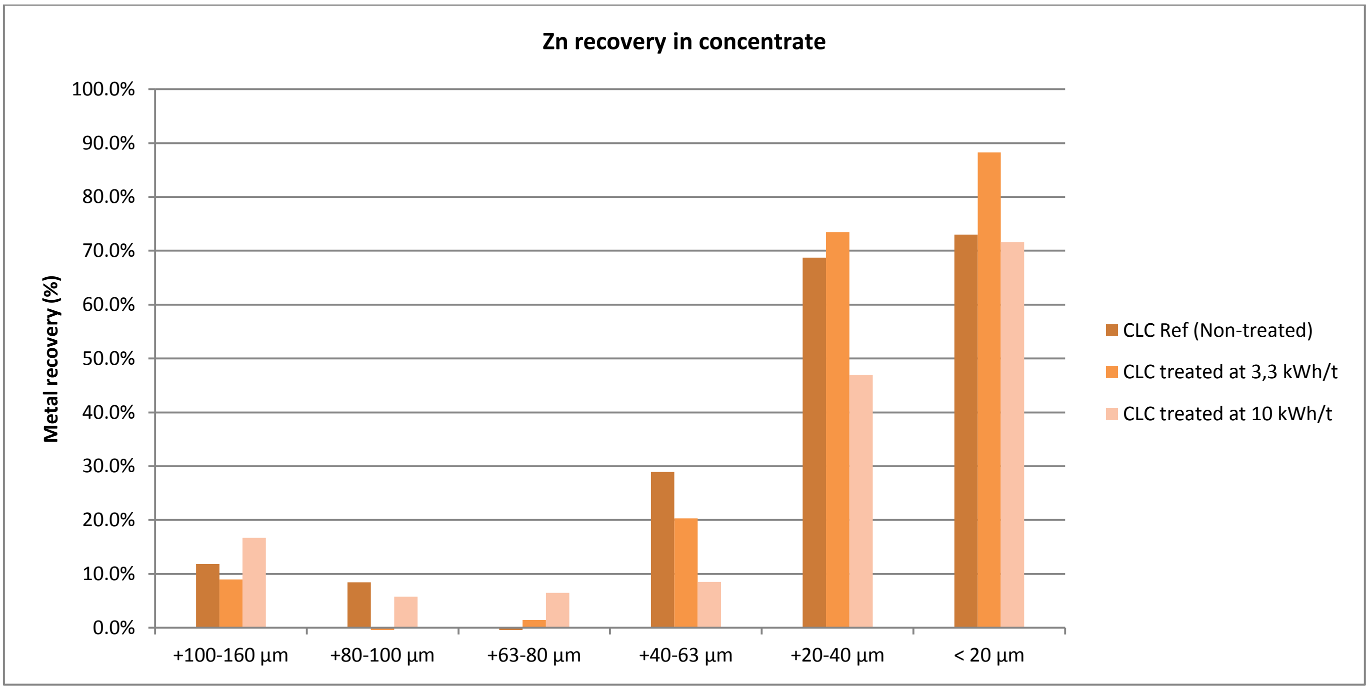


FIGURE 89 - ZN RECOVERY PER SIZE FRACTION IN FLOTATION CONCENTRATE OF CLC TREATED AND UNTREATED SAMPLES.

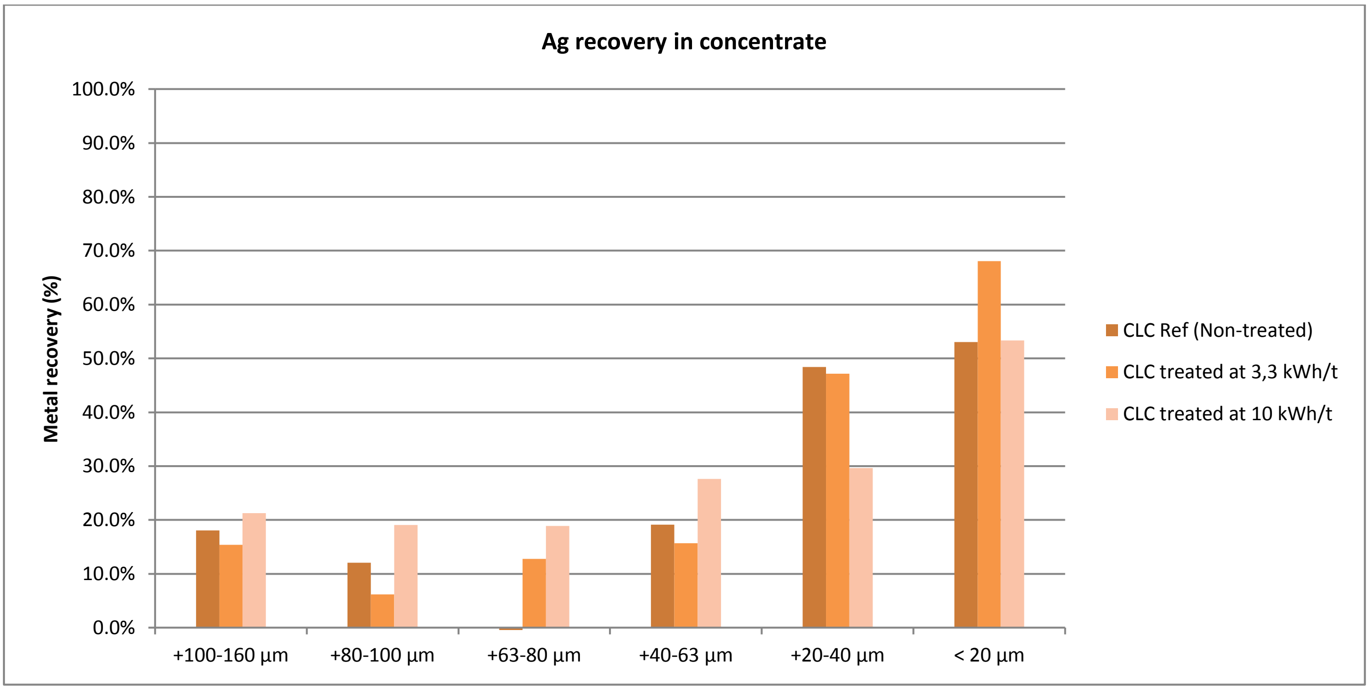


FIGURE 90 - AG RECOVERY PER SIZE FRACTION IN FLOTATION CONCENTRATE OF CLC TREATED AND UNTREATED SAMPLES.

Maximum recoveries in Cu, Pb, Zn and Ag had been reached in +20-40 and below 20 microns size fractions with the CLC sample treated at 3.3 kWh/t, while the range of recovery considering every test is:

- Between 67.0 and 81.7% recovery of Cu.
- Between 57.0 and 73.2 % recovery of Pb.

- Between 47.0 and 88.3% recovery of Zn.
- Between 29.6 and 68.1% recovery of A.

Considering only the size fractions below 40 microns, the recoveries of the valuables metals (Cu, Pb, Zn and Ag) stand still below the global objective to recover 90% of them.

4. FLOTATION PILOT PLANT OPERATION AND CONCENTRATES PRODUCTION

Currently, selective flotation is usually applied to deal with pollymetallic ores aiming to produce separated concentrates of copper, zinc and lead to be marketed and then treated in smelting plants. Nevertheless, the selective flotation process is strongly affected by complex mineralogy of massive sulphides ores, and also by other factors such as ore grade, liberation degree, surface properties, operating conditions, etc. as a result, the selective flotation proces is sometimes inefficient when processing polymetallic ores, and producing qualified commercialconcentrates is difficult and contains high level of detrimental impurities, incurring penalties in toll smelting contracts.

In accordance with the objectives of the INTMET project the high recovery of metals from polymetallic and complex ores are needed.

Producing separate commercial concentrates, as current technology does, metals recovery are low and, at the same time, processing cost are high. For that reason bulk concentrate production is the best option and the flotation pilot plant has been designed with this final aim.

4.1 BOR INSTITUTE PILOT PLANT

For further technological testings and necessity of IntMet project, for delivery of necessary amount samples of polymetallic concentrate to the other partners, and, on the base preliminary BOR flotation tests shown in this deliverable, due to small amount of separated tailings, about 26%, in the experiments and metal content in the concentrate, which was almost the same as in the ore, (whereas the metal content in the concentrate was very slightly increased , compared with metal content in the ore, see above experiments and chemical analysis of the ore), it was decided that do not flotate that ore.

Due to these reasons, it will be better to reduce the ore grain size class to the concentrate grain size class, and as such, it will represent a law grade polymetallic concentrate, which will be used for further testing within the Project IntMet.

For this purpose, the old flotation pilot plant had to be reconstructed in prototype, for two reasons:

1. First, for the preparation of low grade polymetallic concentrates, i.e. the ore grinding to the fineness of flotation concentrate.

2. Second, to provide a sufficient amount of pyrite concentrate.

4.1.1 BOR INSTITUTE PILOT PLANT ADAPTATION

The task of the project was to revitalize and adopt the old flotation pilot plant, which for a long time was not in use, and which is located in the Institute area. The aim was to get prototype existing pilot plant, for preparing and obtaining samples for further testing in the IntMet project.

Predicted budget for adaptation and revitalization flotation pilot plant prototype was 30.000 €. According to Serbien law procurements, below 40.000 € are considered as a procurements of small worths. So to realise it, we asked for three offers and got three prices from three SMEs. We decided for the SME with lower price, which was finished all works in time and correctly.

Adapted plant should have to obtain:

- A low grade polymetallic concentrate (Cu, Zn, Pb, Au, Ag) of smaller quantities, for further laboratory tests in the project. The rich polymetallic ore (raw material), after drying, crushing and grinding, corresponded with metal content to the low grade polymetallic concentrate with grain size (65-75% >74 microns).
- Pyrite concentrate was obtained by flotation concentration from the overflow of industrial copper flotation. Basic pyrite concentrate was purified three times what gave the definitive concentrate.

For this purpose it was necessary first, to do old pilot plant defectation, and second to prepare the "Project of adaptation and revitalization of the flotation pilot plant" with the following specific requirements and contents:

- Adaptation for primary grinding mill to work on wet and dry conditions.
- Installation of the system to add lime.
- Installation of dosing system of raw material, flotation tailings, flotation flow, for the concentration of pyrite.
- Installing the missing filter units for filtering the concentrate and tailings.
- Installation of vacuum pumps and compressor for filter units.

The project should have contained the following parts:

1. Reasons for adaptation and revitalization.
2. Description of the scheme and the existing old flotation pilot plant.
3. Do the plant defectation.
4. Description of necessary works in order to adapt and revitalize.
5. The specification and layout of existing equipment and new equipment.
6. Description and scheme of adapted flotation plants.
7. The description further treatment of flotation tailings and waste water.
8. Safeguarding living and working environment.
9. Cost estimate of work.

After finishing the mill reconstruction and adaptation for dry and wet milling (to produce low grade polymetallic concentrate) and the reconstruction and adaptation of the whole old flotation pilot plant (for pyrite concentrate production), the appropriate quantity of samples was provided.

4.1.2 BOR INSTITUTE PILOT PLANT OPERATION

Production of polymetallic low grade concentrate was performed only by crushing and milling of rich polymetallic ore.

The scheme according to which the pyrite flotation was carried out is shown in next figure. Production of pyrite concentrate was performed according to ordinary technology scheme and reagent regime.

Pyrite concentrate was obtained by flotation concentration of the overflow of industrial flotation of copper. The overflow from copper flotation was set with sulfuric acid up to pH 9. For Pyrite flotation was used Sodium isopropyl xanthate with dose of 50 g/t and frother Dowfroth 250 with dose of 20 g/t. Basic pyrite concentrate was purified three times what gave the definitive concentrate, see principal scheme on the figure. From conditioner, the pulp went gravitationally to the basic flotation and the basic concentrate on three purifications. The underflow of basic flotation and the first purification were the definitive tailings and it was deposited in a sedimentation tank. The precipitated tailings were deposited in the tailings basin for collection of tailings and return water. The resulting concentrate was the definitive pyrite concentrate. It was filtered on press filters and such concentrate, in the form of pulp, was manually poured into presses. After a few pulp filtering it was got appropriate quantity of pyrite concentrate, it was got as samples for delivery for further testings.

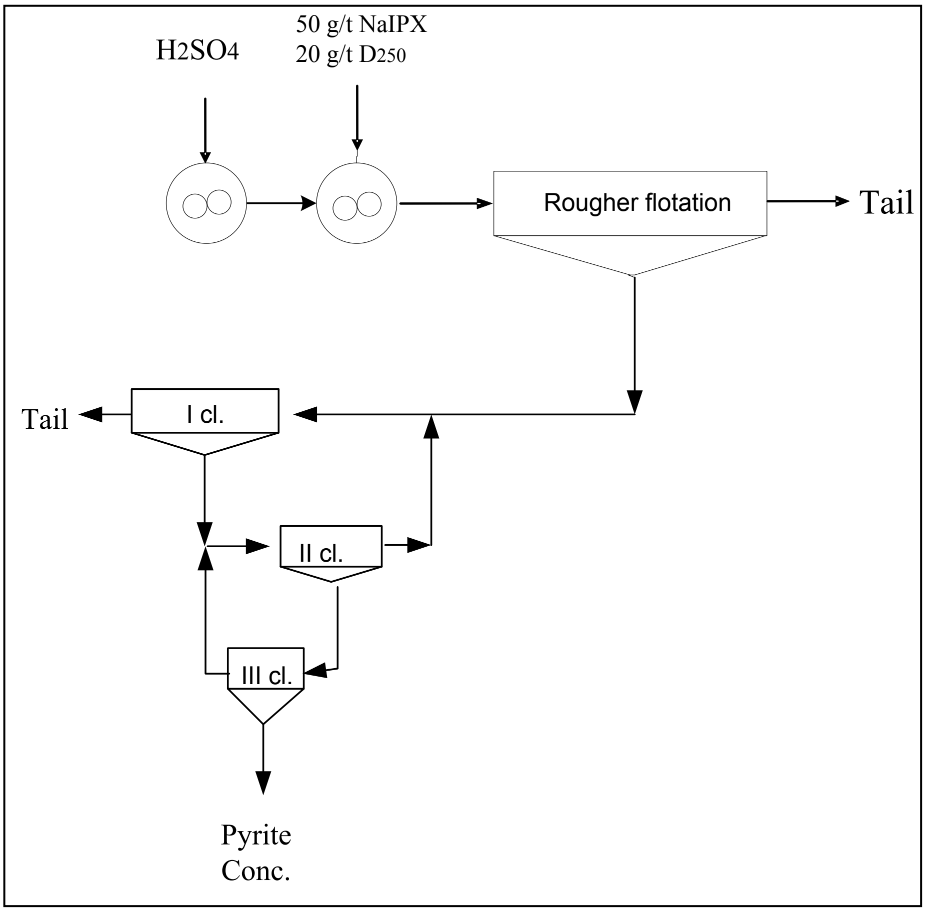


FIGURE 91 - FLOWSHEET FOR PRODUCTION PYRITE CONCENTRATE.

Some pictures of the pilot plant are shown bellow:

FIGURE 92 – LEFT: BINS AND FEEDERS FOR ORE AND LIME; RIGHT: MILL RECONSTRUCTION.

FIGURE 93 - LEFT: RECONSTRUCTION ALL FLOTATION CELLS; RIGHT: OVERHAUL MOTORS.

FIGURE 94 - LEFT: OVERHAUL POWER INSTALATIONS ; RIGHT: FLOTATION CELLS READY FOR USES.

FIGURE 95 - LEFT: FILTRATION PARTS BEFORE; RIGHT: FILTRATION AFTER.

FIGURE 96 - PRODUCED PYRITE.

FIGURE 97 - LEFT: ORE SAMPLES DELIVERING; RIGHT: POLYMETALLIC AND PYRITE SAMPLES DELIVERING.

All those samples were sent, on schedule, to foreseen participants, for further research tests.

4.2 CLC PILOT PLANT

To overcome the deficiencies exposed above related to metal recuperation from pollymetallic ores, INTMET project is developing an innovative technological solution to make possible explotation.

The new technology approach includes a suitable combination of two stages: Bulk flotation and Hydroprocessing.

This workpackage nº 2 is focused on Bulk flotation. The main objectives pursued by the proposed thecnology implemented in the flotation pilot plant are:

- To collect all valuable metals from the polymetallyc ore into a bulk concentrate containing Cu + Zn + Pb.
- To achieve maximum metals recovery over 90% in flotation process.
- To run a low cost operation thanks to design and install a simplified bulk flotation circuit.

After covering successfully the laboratory test works and getting metal extractions above 90% , CLC designed and constructed the Pilot Plant facility having a capacity of one tonne per hour of feed polymetallic ore to produce a bulk concentrate containing approx. 12% - 15% Cu + Zn + Pb.

The Pilot Plant has been running in continuous mode during several months aiming to achieve design parameters an get technical information to undertake finally a feasibility study of the future commercial plant implementation.

In the following figure, the simplify block diagram of the pilot plant is presented.

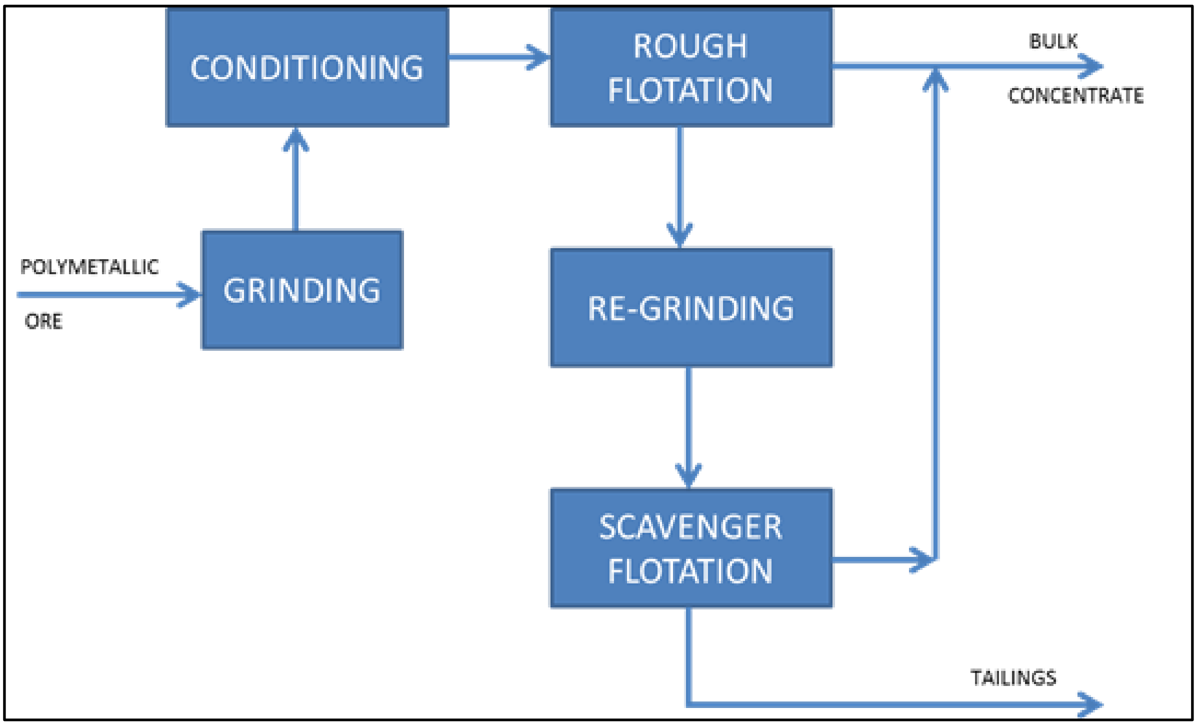


FIGURE 98 - PILOT PLANT BLOCK DIAGRAM.

The flotation pilot plant includes these main stages:

- Feed material: a large ore sample having 5.000 tonnes of primary polymetallic ores was prepared and crushed to achieve 100% <10 mm particle size.
- Grinding: a ball mill having a capacity of 1 t/h feed ore was installed combined in closed circuit with a hydrocyclone to get ground ore with P_{80}= 30-75 microns.
- Rougher flotation: four cells (0.5 m^3) running in serial were installed to achieve a first high grade bulk concentrate. Produced tailings were sent to regrinding stage.
- Regrinding: a ball mill having a capacity of 0.5 t/h feed ore was installed combined in closed circuit with a hydrocyclone to get a ground material with P80= 25-50 microns.
- Scavenger flotation: four cells (0.5 m^3) running in serial were installed to achieve a second bulk concentrate. Final exhausted tailings were obtained in this stage.
- Concentrate handling: the two mixed flows of initial and second bulk concentrates goes to a thickener, and then, the underflow pulp is fed to a horizontal press filter to produce bulk concentrate wet cake ready to be further treated through hydrometallurgical processing.

In next figure is presented a simplified flowsheet of the flotation pilot plant.

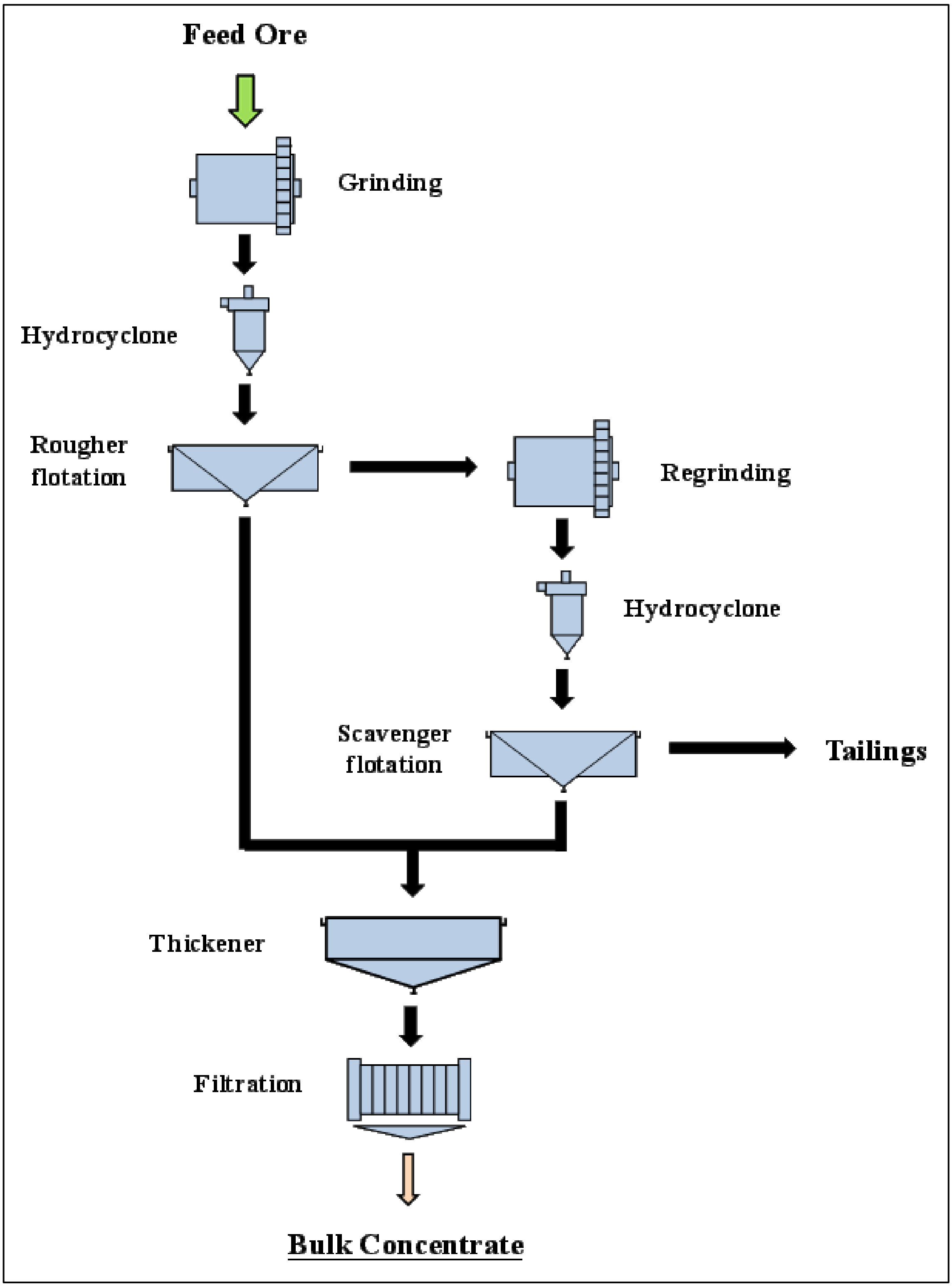


FIGURE 99 - CLC FLOTATION PILOT PLANT FLOWSHEET.

The flotation pilot plant is arranged in two main levels, ground level contains mainly bins, tanks, mills and pumps. In the second level flotation machines and reagents are installed.

4.2.1 COMMISSIONING & START-UP

The cold and hot commissioning of the flotation pilot plant was performed in July-August 2016. At the beginning of the period the personnel was trained to be ready for continuous operation of the facilities.

For this purpose the internal manuals prepared for every task were deeply studied and revised.

CLC	**PUESTA EN MARCHA MOLINO REMOLIENDA PMS 30010-ML-002**	**ITOP PMS 30010-06**	3 ¿Cómo?
		Revisión: 02	Fecha: 28/06/2016
	ÁREA 30010	30010-ML-002 MOLINO REMOLIENDA	

Riesgos asociados a la Instrucción

Medidas obligatorias para la operación

Alcance de la instrucción técnica de operación

- Afecta las personas que realizan la tarea (operador del área).
- El responsable de la operación será el operador asignado al área de molienda y flotación de la planta piloto.

Procedimiento

La presente instrucción establece la metodología a seguir para la puesta en marcha del molino de remolienda 30010-ML-002 de la planta piloto PMS.

NOTA: ANTES DE PONER EN MARCHA EL MOLINO DEBE SER PUESTO EN FUNCIONAMIENTO SIN CARGA DURANTE 4 HORAS PARA CONTROLAR LA TEMPERATURA EN LOS RODAMIENTOS.

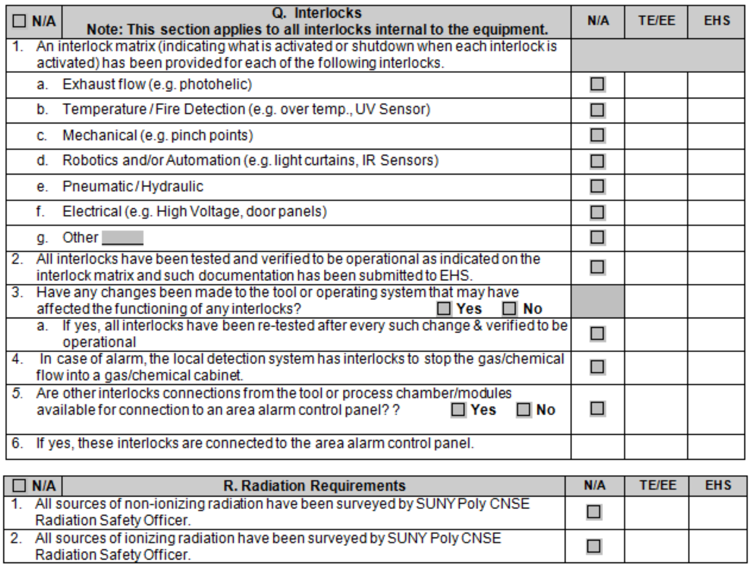
Para el **arranque** del molino deben tenerse en cuenta las siguientes **consideraciones**:

1. Resetear los botones de control remoto y los pulsadores de parada de emergencia del panel de control.
2. Comprobar las alarmas contempladas en el dispositivo HMI (Human Machine Interface → Interfaz máquina-operador).

FIGURE 100 - RE-GRINDING START UP PROTOCOL.

FIGURE 101 - FLOTATION CELL.

During the cold commissioning all the equipment were tested with water separately, pumps, tanks, flotation cells, mills, thickener and filter checking its status and repairing any leaks of any other problem found during the activity. After that, the period for hot commissioning started, the ore was gradually fed to the equipment and after confirming this task the pilot plant was ready for start-up.



☐ N/A	Q. Interlocks Note: This section applies to all interlocks internal to the equipment.	N/A	TE/EE	EHS
1.	An interlock matrix (indicating what is activated or shutdown when each interlock is activated) has been provided for each of the following interlocks.			
	a. Exhaust flow (e.g. photohelic)	☐		
	b. Temperature / Fire Detection (e.g. over temp., UV Sensor)	☐		
	c. Mechanical (e.g. pinch points)	☐		
	d. Robotics and/or Automation (e.g. light curtains, IR Sensors)	☐		
	e. Pneumatic / Hydraulic	☐		
	f. Electrical (e.g. High Voltage, door panels)	☐		
	g. Other ____	☐		
2.	All interlocks have been tested and verified to be operational as indicated on the interlock matrix and such documentation has been submitted to EHS.	☐		
3.	Have any changes been made to the tool or operating system that may have affected the functioning of any interlocks? ☐ **Yes** ☐ **No**			
	a. If yes, all interlocks have been re-tested after every such change & verified to be operational	☐		
4.	In case of alarm, the local detection system has interlocks to stop the gas/chemical flow into a gas/chemical cabinet.	☐		
5.	Are other interlocks connections from the tool or process chamber/modules available for connection to an area alarm control panel? ? ☐ **Yes** ☐ **No**	☐		
6.	If yes, these interlocks are connected to the area alarm control panel.			

☐ N/A	R. Radiation Requirements	N/A	TE/EE	EHS
1.	All sources of non-ionizing radiation have been surveyed by SUNY Poly CNSE Radiation Safety Officer.	☐		
2.	All sources of ionizing radiation have been surveyed by SUNY Poly CNSE Radiation Safety Officer.	☐		

FIGURE 102 - COMMISSIONING CHECK LIST.

Simultaneously the SCADA system was checked and re-programmed to ensure the proper control of the pilot plant.

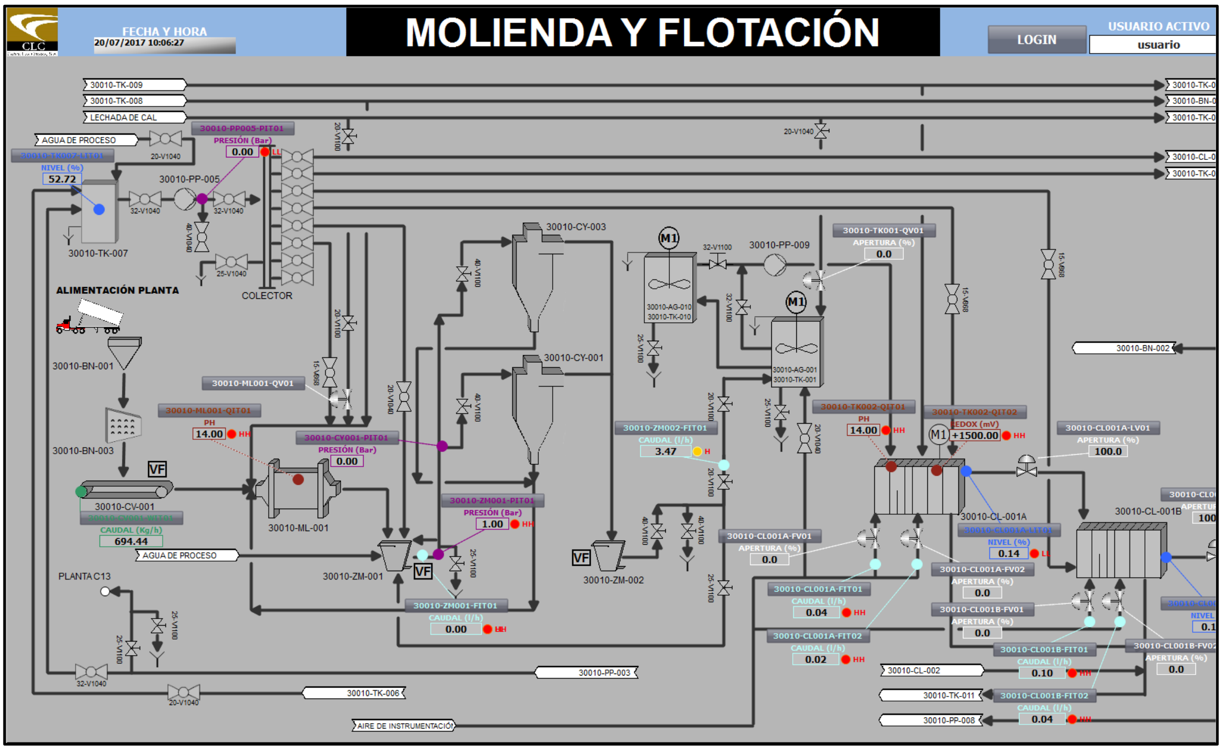


FIGURE 103 - GENERAL SCADA SCREEN.

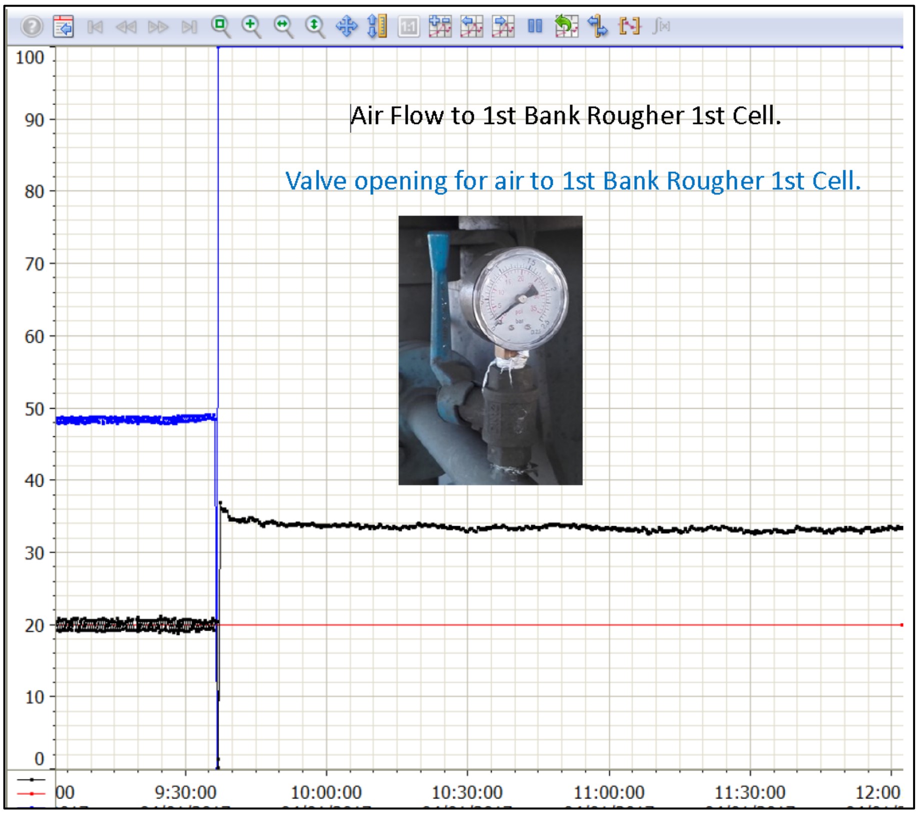


FIGURE 104 - CONTROL SYSTEM CHECKINGS.

After commissioning, the pilot plant start-up took place and mechanical adjustment and flowrates adjustment were done according to design specifications.

Following is shown a couple of photos of the flotation pilot plant.

FIGURE 105 - CLC FLOTATION PILOT PLANT. GENERAL VIEW OF THE FLOTATION CELLS.

FIGURE 106 - CLC FLOTATION PILOT PLANT. REGRINDING BALL MILL.

4.2.2 TUNING. PROCESS VARIABLES SET UP & INSTRUMENT CALIBRATION

Once commissioning and start-up activities were finished, tuning stage started.

Feed ore and grinding step was initially running at design process conditions and the following tasks were performed:

- Feeder: calibration curve and outlet adjusting for the fine control of the ore inlet to the ball mill.
- Pressure gauges of the complete stage: checking and adjusting for the proper operation pressure.
- Flowmeters: checking and adjusting to needed process conditions.
- Ball mill: the ball mill includes an integrated control system that measure the different running parameters, critical speed and alignments are the main variables checked and adjusted.

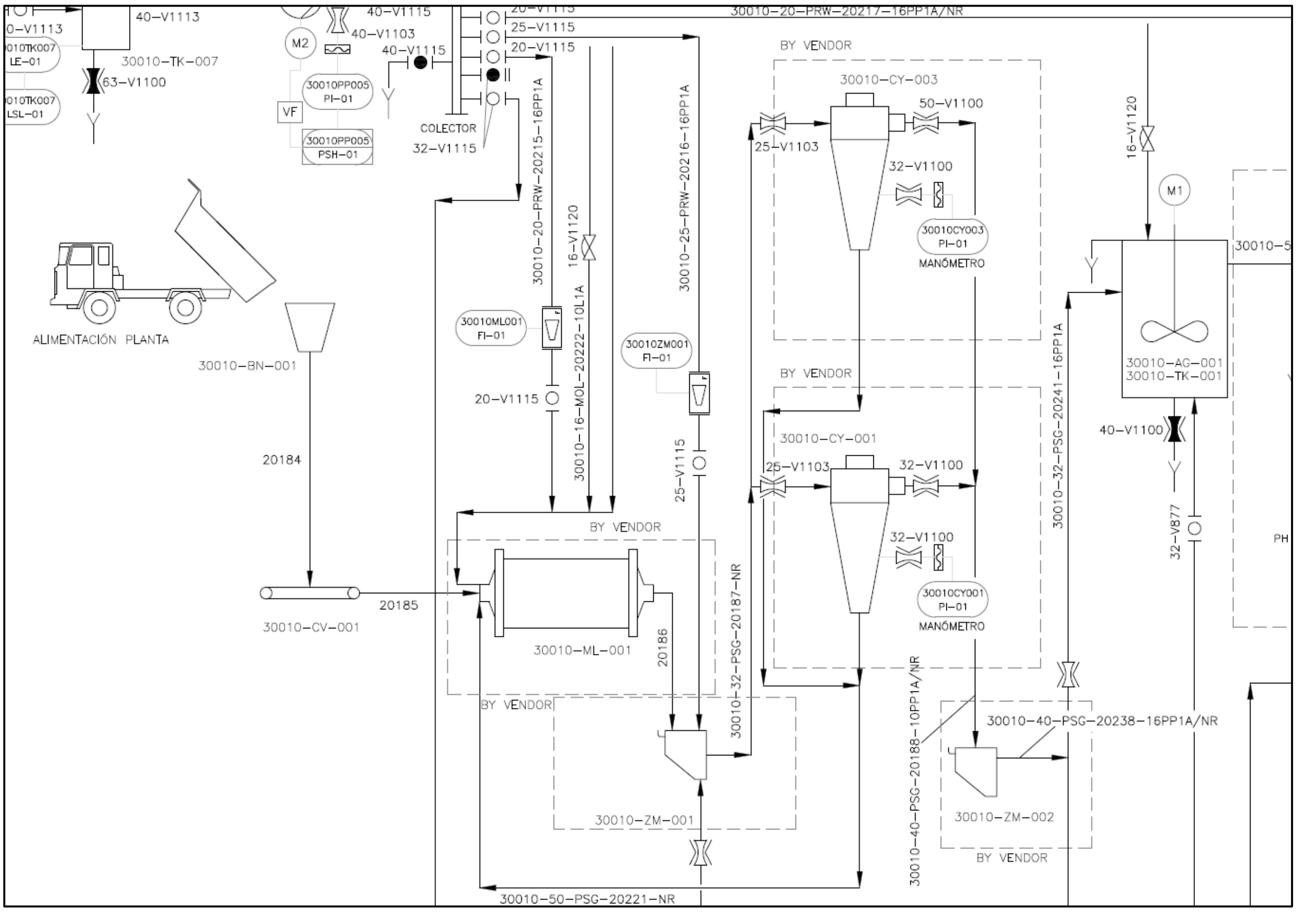


FIGURE 107 - P&ID VIEW OF GRINDING STAGE.

After that complete flotation step was initially running at design process conditions and the following tasks were performed:

- Reagents Pumps: calibration and adjusting for the fine control of the chemicals to be dosed to the process .
- Level gauges of the flotation cells: checking and adjusting for the proper operation of the cells.
- Air Flowmeters: calibration, checking and adjusting to needed process conditions.
- Regriding Mill: the mill includes an integrated control system that measure the different running parameters, critical speed and alignments are the main variables checked and adjusted.
- Pressure gauges of the complete stage: checking and adjusting for the proper operation pressure.

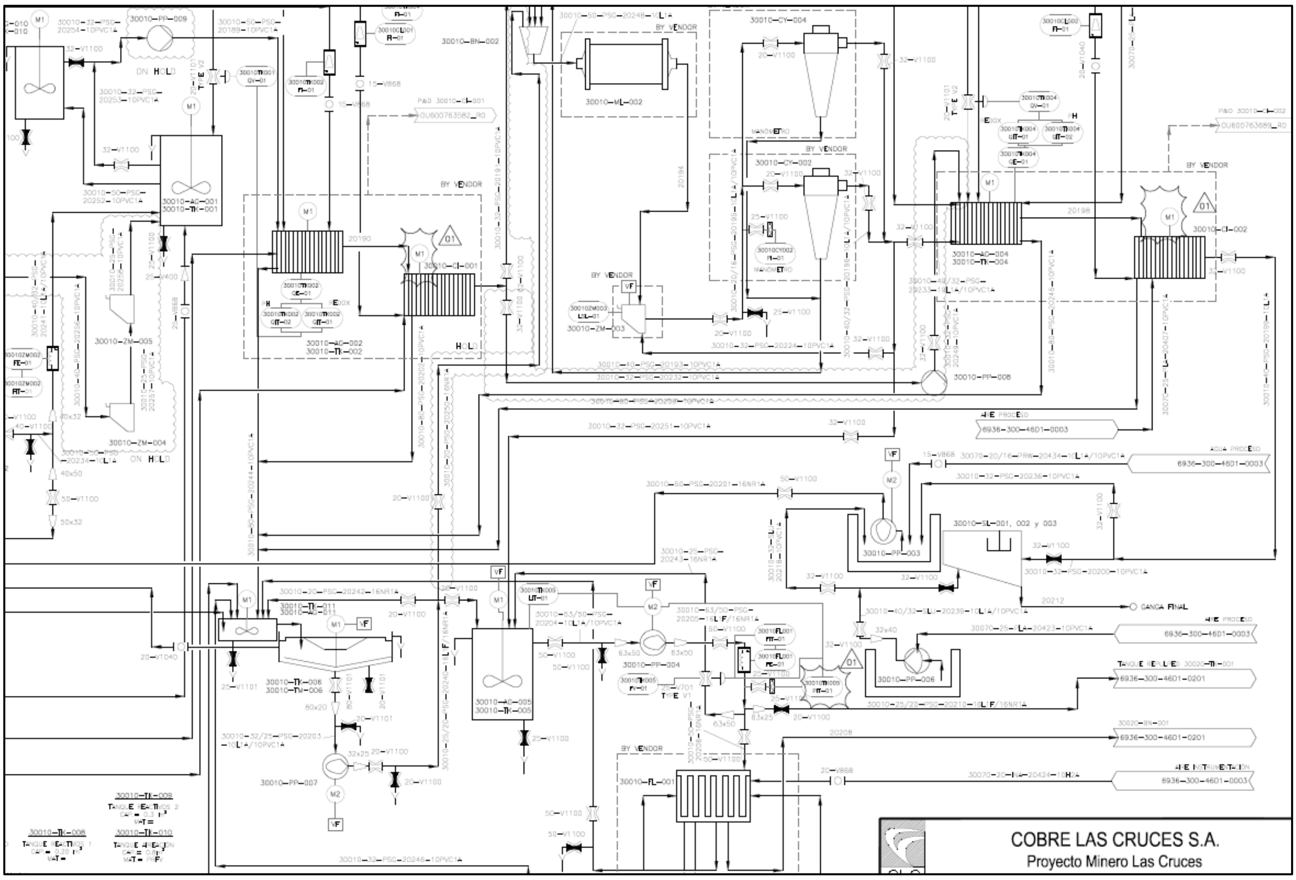


FIGURE 108 - P&ID VIEW FOR FLOTATION.

Finally after this extensive work the pilot plant was totally ready for continuous operation.

4.2.3 CONTINUOUS OPERATION UNDER STEADY STATE CONDITIONS

The crushed ore coming from mine was sent to a grinding stage in order to produce the first liberation of the mineral for rough flotation, as described before the particle size could be adjusted to fine tune the flotation process. After grinding, a conditioning stage was used, where flotation additives and air were used to promote an effective flotation of desirable metals.

In the rough flotation stage, major part of metals was recovered in the froth and the tailings were re-grinded in order to produce the proper size for further recovery of the metals. Finally the froth stream from scavenger flotation was sent with the previous froth stream producing the bulk concentrate.

Variables setting up were based on results obtained in flotation laboratory test, but the tuning stage was the key to scale-up the process and to optimize the process variables values and the reagents dosage to enhance pilot plant flotation and obtaining a bulk concentrate rich on valuable desired metals.

FIGURE 109 - CONCENTRATE PRODUCED IN A PILOT PLANT FLOTATION CELL.

Following it is described the main outcomes of the flotation pilot plant after running for concentrate production in continuous operation.

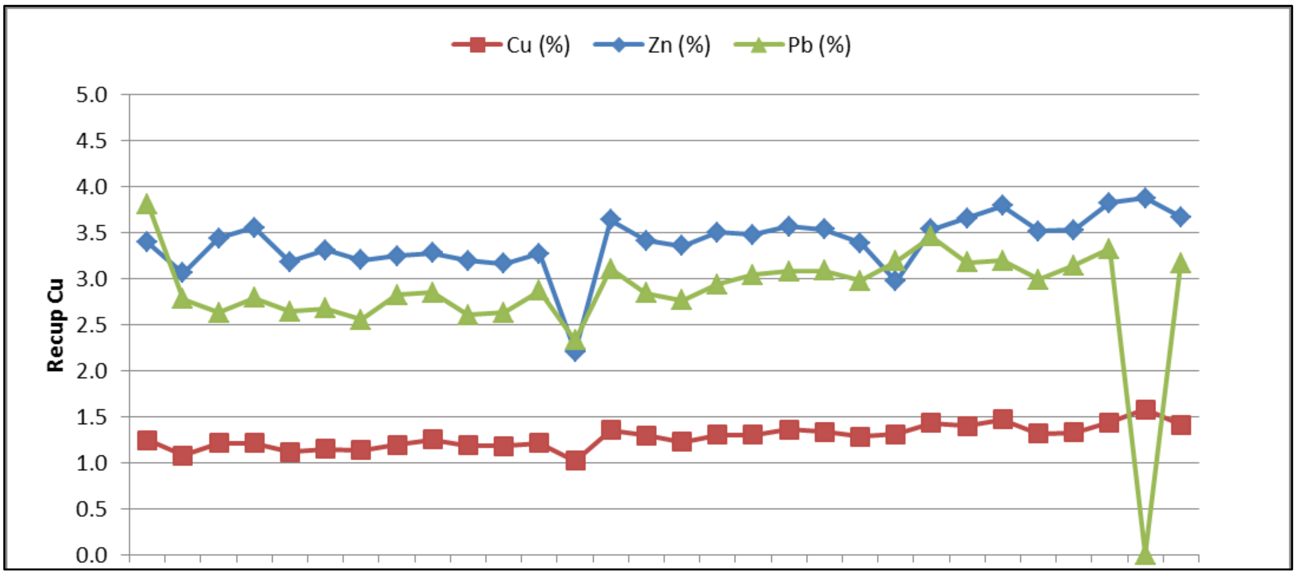


FIGURE 110 - PILOT PLANT FEED ORE.

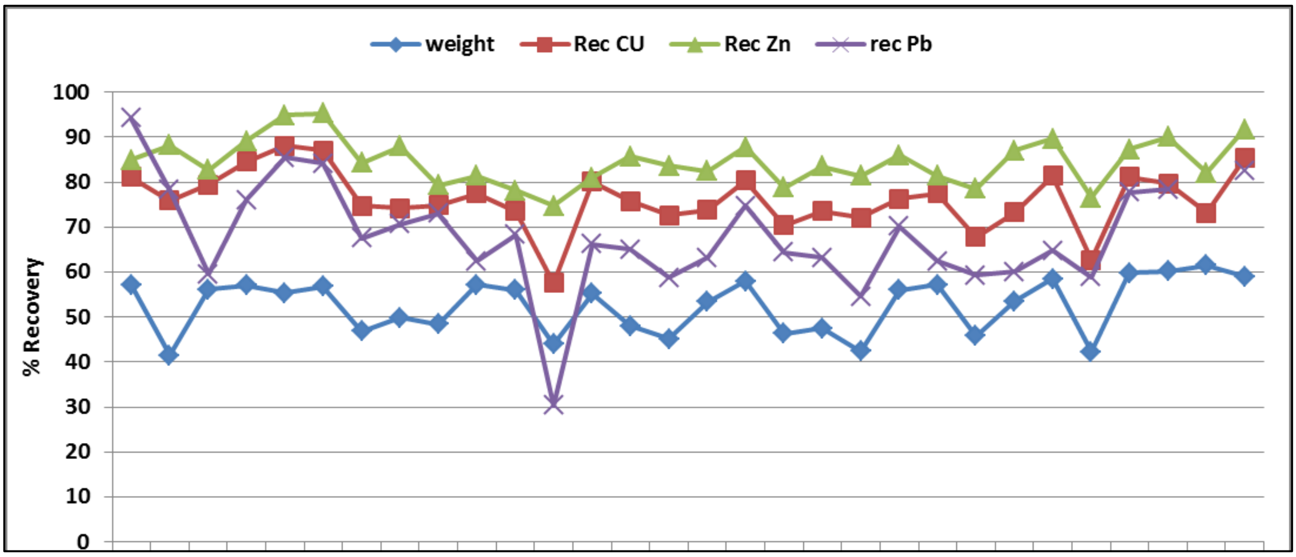


FIGURE 111 - PILOT PLANT RECOVERIES.

The range of feed ore grade is shown in the next table.

Cu %	Zn %	Pb %	Ag ppm
1.0-1.5	3.0-3.5	2.5-3.0	50-70

TABLE 48 - MAIN COMPONENTS RANGE OF THE FEED ORE.

Mineralogical composition range of the feed ore is presented in the next table:

- Pyrite is the major component accounting 82%.
- Sphalerite and galena are the only zinc and lead mineral species respectively.
- Main copper specie is chalcopyrite, and next, covellite, chalcocite, tetrahedrite and enargite.

Mineral Species	%
Pyrite	82.0
Sphalerite	5.0
Galena	3.2
Chalcopyrite	1.5
Covellite, Chalcocite	0.6
Tetrahedrite, Enargite	0.7
Others	7.0

TABLE 49 - MINERALOGICAL COMPOSITION OF FEED ORE.

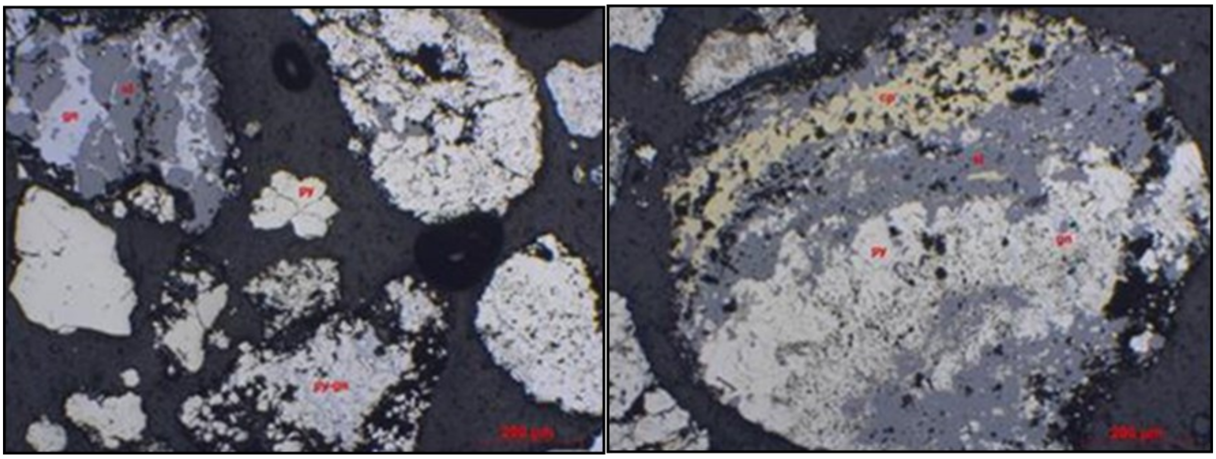


FIGURE 112. MICROSCOPE IMAGE OF FEED ORE.

The milling and flotation pilot plant has been running accordingly to the process configuration shown, aiming at:

- Maximise overall metals recovery to the bulk concentrate.
- To get suitable ratio bulk concentrate mass pull vs overall metals recovery.
- To work under proper liberation size in order to maximise pyrite depression rate.

The following tables show average results obtained during the bulk concentrate production of the pilot plant operation.

	Composition					**Metals Distribution**			
	Weight %	**Cu %**	**Zn %**	**Pb %**	**Ag ppm**	**Cu %**	**Zn %**	**Pb %**	**Ag %**
Bulk concentrate	52	1.83	6.34	4.23	108	93	95	80	90
Tailings	48	0.16	0.36	1.12	13	7	5	20	10
Feed	100.0	1.13	3.48	2.68	62	100	100	100	100

TABLE 50 - FLOTATION PILOT PLANT OPTIMUM METALLURGICAL RESULTS.

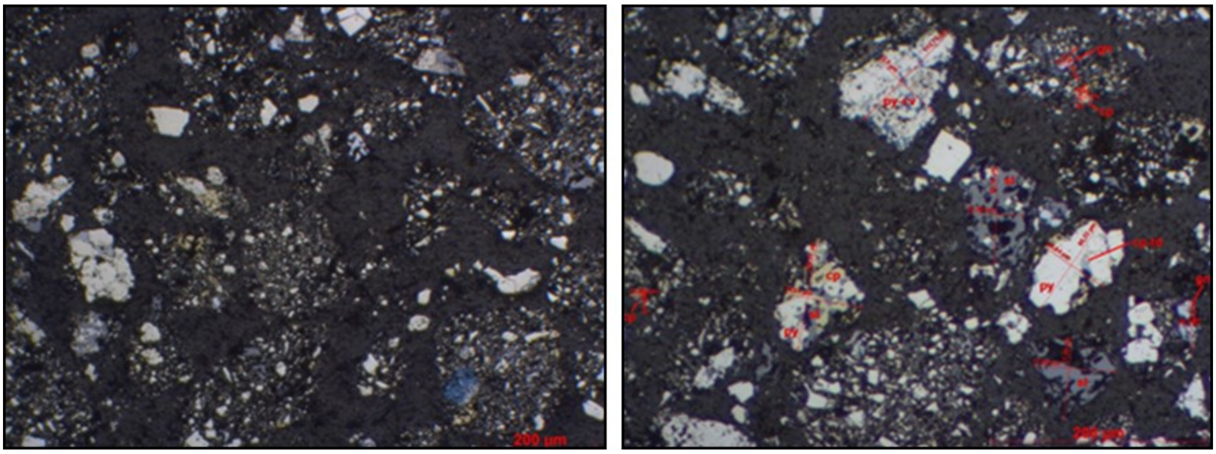


FIGURE 113 - BULK CONCENTRATE MICROSCOPE IMAGE.

Relevant highlights of flotation pilot plant operation are as follows:

- Processed ores: over 1.500 tonnes of primary polymetallic ores.
- The plant was operating in continuous 24 hours a day, 7 days a week.
- During pilot plant running the relevant target grinding size (P_{80} close to 35 microns) and the operating conditions were steadily maintained.

Next points are remarkable:

- Obtained metals recovery (Cu, Zn and Pb) into the bulk concentrate is rather satisfactory; for instance:
    - Copper recovery ranges from 65% to 92% when concentrate mass pull raises from 35% to 65%.
    - Zinc recovery ranges from 75% to 95% when concentrate mass pull is increased from 35% to 65%.
    - Lead recovery ranges from 50% to 98% when concentrate mass pull raises from 35% to 65%.
    - Still there is some room to improve pyrite depression, and consequently, decreasing concentrates mass pull after finer grinding.

In next figure is shown the relationship of bulk concentrate overall grade (Cu + Zn + Pb) versus metals recovery:

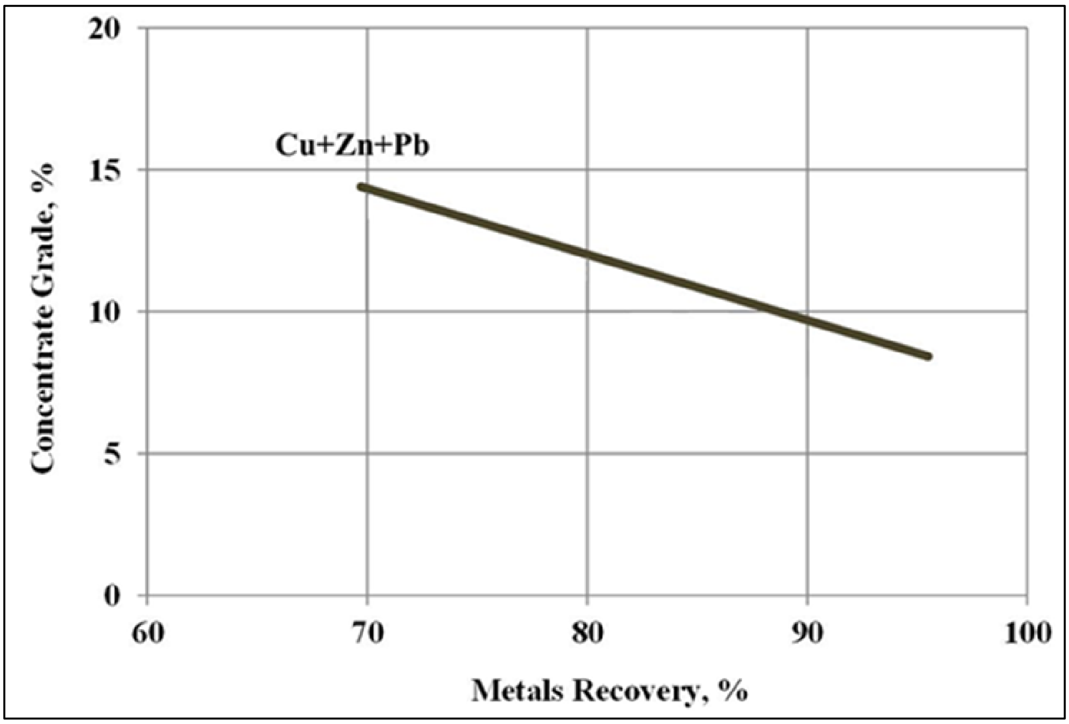


FIGURE 114 - RELATIONSHIP OF BULK CONCENTRATE OVERALL GRADE VS METALS RECOVERY.

After the research activities completed in the pilot plant the next points can be highlighted:

- Produced bulk concentrate overall grade (Cu+Zn+Pb) varies from 9% to 14%, which may be acceptable for further hydrometallurgical processing considering, for example, that actual CLC industrial leaching plant is treating feed ore containing around 5% Cu. During the pilot plant operation enough fresh concentrate was produced and delivered to be used as feed material for the other workpackages research tasks.
- Process performance achieve highly efficient metals recovery, that is one of the main advantages of the bulk flotation process versus conventional selective flotation process. Metals recovery from 85-95% was obtained, depending on flotation process conditions and producing bulk concentrate able to be futher processing by means of an hydrometallurgycal route.

5. CONCLUSIONS

After the extensive work performed by CLC, SOMINCOR, BRGM, BOR INSTITUTE and OUTOTEC on the mineral processing stage of the different ores the initial general and specific objectives of the research activities have been achieved:

> “Increasing raw materials efficiency and valuable metals recovery from polymetallic and complex orebodies by means of enhanced flotation techniques and flotation pilot/demonstration trials to produce concentrate samples for further hydro-processing”
>
> ”Developing enhanced flotation techniques including energy efficient comminution and more specific reagents”
>
> “Raising base metals extraction efficiency through bulk flotation in comparison to conventional selective flotation”
>
> “Development and implementation at pilot plant scale of process flowsheets and flotation protocols aiming to
>
> Maximise valuable metals recovery and obtaining concentrates containing Cu, Zn, Pb, Ag, which continue to be treated by hydrometallurgical ways”

Finally it must be highlighted that the promising results obtained in WP2 processing the polymetallic complex ores reinforce INTMET project as an efficient route to develop a Mine to Metal process devoted to complex orebodies.