Influence of temperature on sulphide ore flotation

Applied to the rougher regrind circuit of the zinc flotation plant of Neves-Corvo mine

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Abstract

The present work aims to study the influence of the temperature on the flotation of zinc sulphide ores with the addition of different pH regulators after documentation of temporary decreases of sphalerite recovery in the final concentrate since 2008. These occurrences were associated predominantly to the summer period.

The study was applied to the DPR cell bank since this is the circuit with the most variability in the recovery of sphalerite in the floated product.

The study began with the statistical analysis of the variable indicating the success of the flotation operation, the recovery of sphalerite in the final concentrate of the plant, and other variables such as maximum ambient temperature and the dosage of lime used in the zinc plant. This analysis allowed concluding that there is no observable correlation between the maximum ambient temperature and the recovery of zinc. However, it has been found that the pH regulator dosage is increased at times when higher maximum temperatures occur although the correlation coefficient between these two variables is quite small (0.2612).

An entalphy balance, applied to the DPR cell bank, was elaborated. Quantification of the theoretical temperature associated with the tailings of the bank cells showed that the model underestimates the value of this variable, in comparison with the practical values. This may be an indicator that not all factors, that influence the temperature of the pulp, were taken in consideration.

The experimental plan consisted in 8 floatation tests. These tests were performed at 30°C and 60°C without pH modification or with modification of this variable using calcium or sodium based regulators. The results showed that at 30°C the sphalerite flotation has favoured results. At 60ºC there is a reduction in the recovery of sphalerite between 30 and 70%. Sodium based pH modifiers lead to better results in terms of sphalerite recovery at 30°C (54,6% of sphalerite recovery). In turn, at 60°C the best recovery is obtained without addition of any pH regulator (33,4% sphalerite recovery).

At 60°C it's possible to observe disruptions in the oxidation-reduction potential to less positive values, as pH regulators are added to the pulp, suggesting that the reactions promoted by the addition of these regulators to the pulp are unfavourable to the sphalerite, galena, chalcopyrite and pyrite flotation given the low recovery of these minerals under the mentioned conditions.

1. Introduction

Froth flotation is one of the techniques of metal concentration, widely used in the mining industry, which consists of a physical separation of particles based on the selective adherence of mineral surfaces to air bubbles. Although it is a process that is more than 100 years old, it is still widely used for the separation of minerals since it is possible to chemically alter the surface of the minerals using reagents, in order to give them the properties necessary for flotation, namely hydrophobicity. (Feuerstenau et al., 2007)

Phenomenon of temporary reductions in sphalerite recovery accompanied by difficulties in raising the pH value have been recorded since the start of the operation in the zinc plant situated at Neves-Corvo mine. These phenomenons are prevalent during the summer period suggesting that the temperature may be a factor capable of influencing the pH regulation, during froth flotation of the zinc sulphide ores exploited at the Neves-Corvo mine. The present work aims to study the influence of temperature on the froth flotation of the zinc sulphide ores. The study was applied to the rougher regrind flotation circuit (DPR) since this is the flotation stage in which greater losses in sphalerite recovery are registered.

In studies carried out in the company in order to characterize the problem, two phenomena were identified in the zinc fluctuation circuit in periods of decreased sphalerite recovery, these being:

- Increase in temperature by 10 °C from the first to the fourth cell of the DPR, this increase in periods of normal operation is only 1,5 °C.
- Atypical pH value reduction with consequent increase in pH regulator consumption.

The study began with the historical analysis of the recovery of sphalerite and some other variables whose information is available and which were considered to be related to the recovery of sphalerite in the final concentrate of the plant.

To determine the effect of temperature on an industrial scale in the cell bank under study, an entalphy balance was elaborated with the purpose of quantifying the theoretical temperature of the waste and comparing this value with the actual values observed in the in the DPR cell bank, in order to determine the possible occurrence of exothermal reactions.

In turn, at bench scale the effect of the temperature on sphalerite, galena, chalcopyrite and pyrite flotation, with addition of different pH regulators, was studied in order to test the influence of these parameters on the pulp that feeds the DPR cells.

2. The DPR circuit

The zinc DPR circuit is composed of 4 cells with 40 m^3 of volume, making a total of 160 m^3. The flows rougher concentrate, coarse scavenger concentrate and fine scavenger concentrate as well the tailings of the 1^{st} cleaner feed a battery of 20 hydrocyclones so that the particles are classified according to their size. The DPR feed consists of the overflow of the hydrocyclones.

The underflow feeds the regrind stage. The wet grinding is performed in a mill designated by VertiMill whose charge is composed of 25mm balls of an iron and chromium alloy, where the reduction of the size of the particles is made by impact. The residence time in the DPR cell bank is approximately 59 minutes. The tails of this circuit are conducted to the flotation stage designated by fine scavenger.

The addition of reagents is done on the first and third cells of this flotation stage. The addition of the sphalerite collector, KAX, is preceded by the activation of this mineral with copper sulphate ($CuSO_4$) to promote the flotation. The lime is added during the grinding of the material and in the second flotation bank cell in order to achieve a pH value of approximately 9,5.

The DPR is fed on average with a flow rate of 220 ton/hour containing 30% of solids in weight. The results of the mineralogical analysis performed by Petrolab, with samples collected from the DPR between the 28th of January and the 2nd of February, are presented in Table 1.

Table 1 – Composition of the DPR feed based on samples collected between 28th of January and 2nd of February 2016 (Adapted from: Petrolab, 2016).

Mineral	Weight in the sample composition (%)
Pyrite	68,3
Sphalerite	26,5
Fe-rich Sphalerite (Marmatite)	1,7
Galena	1,0
Arsenopyrite	0,6
Chalcopyrite	0,4
Silicate Gangue	0,8
Carbonate Gangue	0,4
Fe oxides	0,1
Acessory Minerals	0,1
SUM	99,9

The sphalerite comprises 76,1% of all the zinc, which is the element of interest in this study, present in the feed of the flotation stage under study. (Petrolab, 2016)

3. Historical analysis of some variables

To analyze the relation of the maximum ambient temperature with the variables recovery of zinc in the final concentrate and the lime dosage used throughout the zinc plant as well as the latter variable and the recovery of sphalerite in the final concentrate, the graphs of the FXX were elaborated. In the case of recovery of zinc in the final concentrate as a function of the maximum ambient temperature, the graph was elaborated with the daily values while in the case of the remaining graphs, since only the average monthly value of the lime dosage is known, the graphs were elaborated with the average monthly values. The line of the linear trend of the values under study with the correlation coefficient between them is shown.

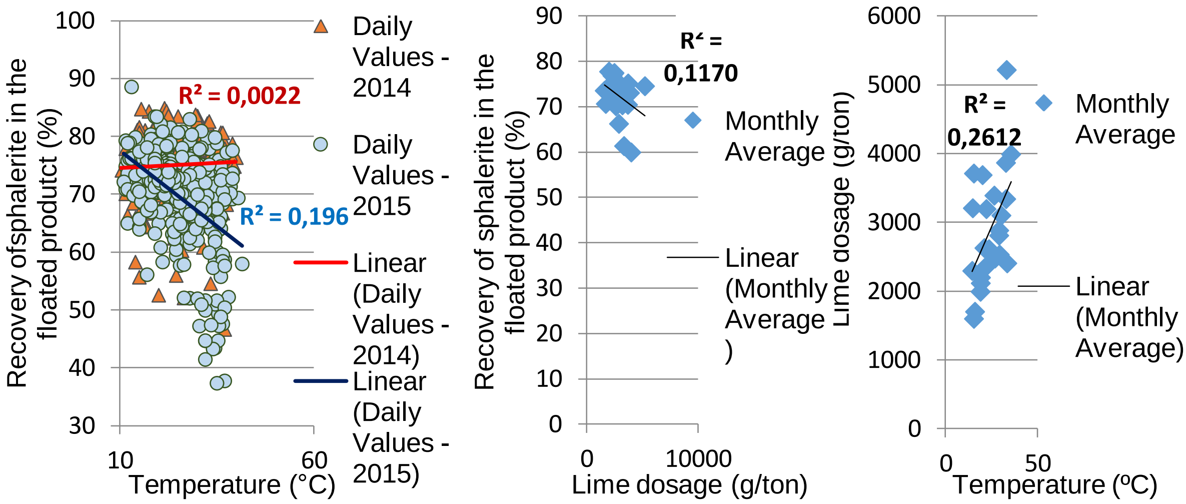

Figure 1 - Recovery of sphalerite in the final concentrate as a function of maximum ambient temperature (left) and lime dosage (middle) and lime dosage as a function of maximum ambient temperature (right).

In the historical analysis of available information there is no correlation between the recovery of zinc in the final concentrate and the variables maximum ambient temperature and lime dosage. There is, however, a direct correlation although it is quite small between the dosage of lime used throughout the zinc wash and the maximum ambient temperature.

4. Entalphy Balance

The balance is made from the assumption that the energy that enters the system (Feed Energy (**EF**)) is equal to the energy that comes out (Concentrate Energy (**EC**) and Waste Energy (**EW**)). Since the system has an input power caused by the addition of water and air and the heat dissipation due to the rotor stirring (Energy Variation (∆**E**)), it is possible to formulate the following expression:

$$EF + \Delta E = EC + EW \qquad (1)$$

The energy of each flow was determined by the following expression:

$$E = m \times Cp \times \Delta T \qquad (2)$$

Where:

- E - Energy (Joule);
- m - Mass (g);
- Cp – Specific Heat (J/g°C);
- ∆T - Temperature variation (°C)

In order to calculate the energy in question, only the contribution of pyrite and sphalerite was considered since these two minerals make up 94,8% of the DPR feed. It was considered the average summer temperature associated with the streams, presented in the Figure 2.

Table 2 – Mass composition of the solid (pyrite + sphalerite) and liquid phases present in each product

	Feed composition		Concentrate composition		Waste composition	
	(%)	(ton/h)	(%)	(ton/h)	(%)	(ton/h)
Pyrite (FeS_2)	16,83	36,50	21,19	18,84	16,32	21,48
Sphalerite (ZnS)	12,03	26,07	22.32	19,84	1,86	2,45
Water	70	152	55	49	81	107

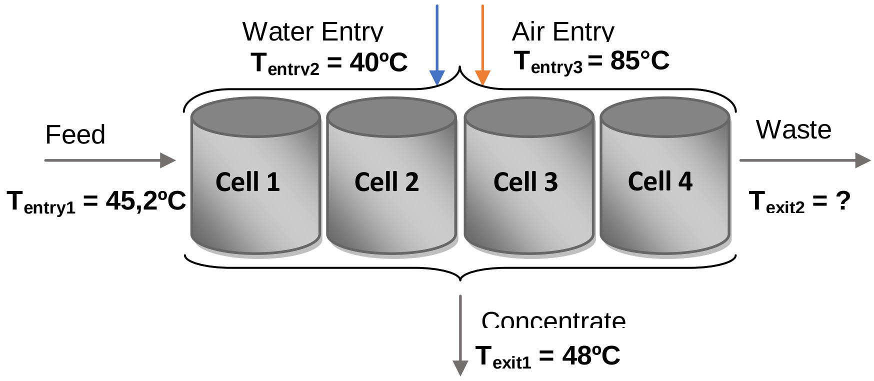

Figure 2 – Maximum mean temperature in and out of the DPR circuit in the summer period.

The specific heat values of each of the substances considered in the energy balance calculation are shown in Table 3.

Table 3 – Specific heat of the principal elements considered. (Adapted from: Bailey, 1997)

	Cp (J/(g°C))	**Cp_{pulp}** (J/(g°C))
Pyrite	1,93	
Sphalerite	2,11	3,55
Water	4,19	
Air	1,02	

Each flotation cell is equipped with a rotor that allows the air to enter the system and prevents the sedimentation of the particles, which prevents the existence thermal preference zones. There is a percentage of energy that is transferred to the engine of the equipment in the form of heat and another that is transferred to the pulp. Assuming an efficiency of each rotor of 85% and that of the energy being dissipated 30% is transferred as heat to the pulp, and also knowing from the cell catalogs, that the power of a rotor is 51 kW, it is possible to calculate the energy that is dissipated. It is estimated that the energy dissipated is $3,3 \times 10^4$kJ.

The specifications concerning the flow rate ($Q_{entry\ air}$) as the mean temperature of the air that enters the cells (T_{entry3}), in the summer period, are shown in the following table.

Table 4 – Temperature and flow rate of the air entering the DPR cell bank.

	1st Cell DPR	2nd Cell DPR	3rd Cell DPR	4th Cell DPR
$Q_{entry\ air}$ (ton/hora)	0,4	0,4	0,3	0,3
T_{entry3} (°C)	85			

The energy associated with each of the streams was possible to calculate (Table 5). Considering an addition of water to the DPR stage of 4 ton/h for levelling the cells at a temperature indicated by the water entry in Figure 2, it was possible to determine the **ΔE.**

Table 5 – Energies corresponding to the flows of the DPR.

	E(kJ)			
ΔE	Air	Water	Rotor	**∑(ΔE)**
	$1,2\times10^5$	$6,0\times10^5$	$3,3*10^4$	$6,8\times10^5$
Feed Energy (EA)	$3,7\times10^7$			
Concentrate Energy (EC)	$1,4\times10^7$			

It is now possible to calculate the value of the theoretical temperature of the tails.

$$FE+\Delta E=CE+WE \qquad (1)$$

$$\rightarrow (3,7\times10^7)+(8,3\times10^5)=(1,4\times10^7)+(4,9\times10^5)\times\left(\text{Temperatura}_{\text{rejeito}}\right)$$

$$\rightarrow\left(\text{Temperature}_{\text{tails}}\right)=47^\circ C$$

The temperature value obtained for the tails of 47°C is lower than the average summer temperature value of the waste to the DPR flotation stage which is 53,1°C (Figure 2).

Using the values obtained through temperature measurements in the bank cells under study, it is possible to calculate the theoretical temperature of the tails and the energy difference that allows increasing the temperature of the system from the theoretical temperature until to the value that was measured using probes in an attempt to quantify this energy.

There are factors that were not considered in the energy balance and that contribute to the temperature variation of the DPR tailings pulp.

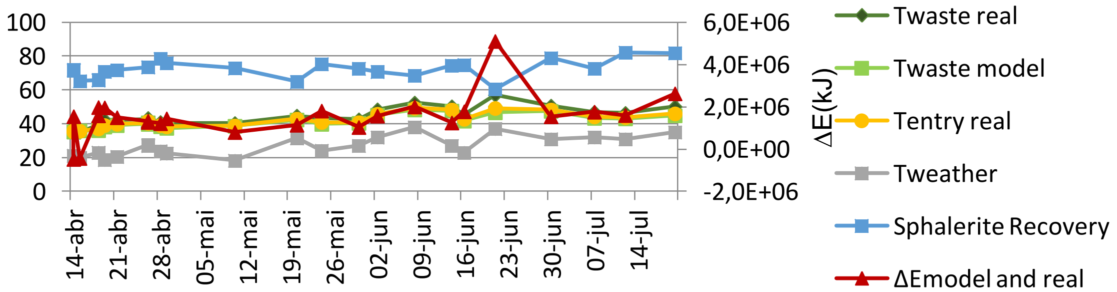

Figure 3 – Variation of energy calculated according to the energy balance temperatures and the real values and respective daily recovery of zinc in the plant.

It is noticeable that on days when the temperature of the waste in the plant is higher than the temperature calculated by the model, the energy variation varies between 1×10^6 and 3×10^6 kJ. However, an anomalous increase, which is an isolated occurrence whose analysis must be careful, in the difference between the estimated temperature and the actual DPR waste temperature is observed on the same day as the lowest sphalerite recovery in the final concentrate. This is also the day when a maximum weather temperature peak occurs. The increase in pulp temperature may be due to exothermic reactions whose contribution has not been taken into account in the energy balance and which are promoted by the addition of lime in which the dosage increases in the days of higher weather temperature.

5. Flotation Tests

The experimental work was carried out with the purpose of testing the influence of the temperature on the flotation of the zinc ore exploited in Neves-Corvo; with addition of different pH regulators.

The tests were performed in the laboratory at the natural pulp temperature within the flotation cell (≈30°C) and with heating of the pulp using a water bath equipment (60°C) (Table 6).

Table 6 – Description of the flotation tests.

	Temperature of the pulp
Without pH manipulation	30°C and 60°C
With pH regulation by lime ($Ca(OH)_2$)	30°C and 60°C
With pH regulation by sodium carbonate (Na_2CO_3)	30°C and 60°C
With pH regulation by sodium hydroxide (NaOH)	30°C and 60°C

4.1 The sample

To avoid undesired oxidation of the particles surface, the samples were collected before the beginning of each flotation test. The samples used in the flotation tests were collected using a cutter, in order to ensure homogeneity of the sample, in the discharge pipe of the pulp to the zinc DPR feed box, where the collected product does not yet has any reagent added.

4.2 Reagents

The collector and activator were the ones used in the industrial scale for flotation of sphalerite, manufactured by the company FloMin. The amount of reagent added was determined based on the collector dosage on the first and third DPR cells of 30 g/ton and 25 g/ton, respectively. The same reasoning was followed for the addition of copper sulphate. Addition of the KAX sulphide collector at a 1% dilution was preceded by the addition of the sphalerite activator, $CuSO_4$, at a 5% dilution.

The regulation of the pH value was done by addition of bases with the aim of raising the pH value. Lime is the reagent used in the plant for pH regulation. Lime was one of the pH regulators tested as an aqueous solution with a 5% dilution. Sodium carbonate and sodium hydroxide were the sodium type regulators tested.

4.3 Equipment

The type of equipment as well as the brand and specifications thereof are given in Table 7.

Table 7 – Type and brand of the equipment used in the flotation tests.

Type of Equipment	Brand	Specifications
Flotation cell	Denver D-12	Equipped with a 2,4 L tank
Water bath equipment	Julabo ME	Equipped with a proper container
Probe	HACH® HQ40D	pH sensor: IntelliCAL™ PHC101 Eh sensor: IntelliCAL™ MTC101

4.4 Methodology

In the 8 flotation tests performed with samples from the DPR feed pulp, the flotation operation parameters for the zinc circuit 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 CuSO4 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 industrial cell bank, at the time of the tests (9.5), recording the amount of reagent used.

Table 8 – Flotation scheme with indication of operational variables.

	Operation (mins)	**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

Before each flotation step, the pH and Eh values were recorded as these parameters can provide indications of the reactions that may be occurring in the pulp.

6. Results and discussion

In the flotation tests, the analysis of the system response to the imposed modifications was made in terms of recovery of sphalerite, mineral of economic interest, and galena, pyrite and chalcopyrite, considered penalizing elements.

It was not possible to record the amount of product required to raise the pH to the desired value since the entire product was spent in the first pH adjustment, which did not allow the analysis of the behaviour of this regulator at 60°C.

The results of measurements of the chemical parameters, pH and Eh are represented Figure 4 and Figure 5 respectively.

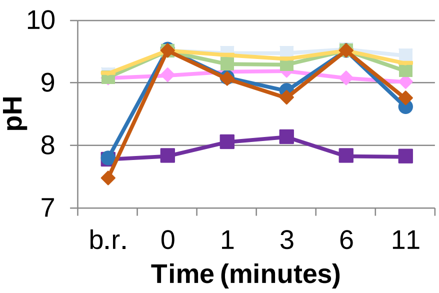

Figure 4 - pH registered at the beginning of each float.

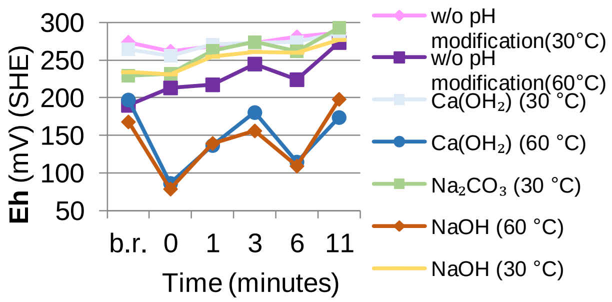

Figure 5 - Eh registered at the beginning of each float.

From Figure 4 it is possible to observe that the pH is slightly decreasing from the beginning of the flotation, in which the pH was adjusted to a value of 9,5, until the new pH regulation at minute 6 of the flotation. This effect is most pronounced when the temperature of the pulp is higher, resulting in an increase in the regulator consumption. At 60°C, the pH regulation proved to be quite difficult (given the resistance of the pulp to increase the value of this parameter). The lowering of the pH value may be due to the oxidation of the minerals, which is promoted at a higher temperature and, being this an acidic reaction, lowers the pH value of the pulp (Williams, 2016).

With respect to the values of Eh, it is possible to observe a discrepancy between the tests carried out at different temperatures. In the tests where the pulp wasn't heated, the Eh values are between 200 and 300 mV. On the other hand, with manipulation of the temperature in the tests in which the pH was regulated by different bases, the recorded Eh values are much lower decreasing sharply (for values between 50 to 150 mV) when the pH regulator is added to the pulp. This means that the addition of pH regulators at 60°C enhances the reducing action of the solution and may lead to the oxidation of the minerals.

At 60°C, in the test in which the pH was not manipulated the Eh values approximate the values for the tests performed at 30°C. In this test, performed with temperature manipulation, the same reagents, added in the remaining tests, were added, except for the pH regulator. This fact suggests that the values of Eh are dependent on the interaction of the pH regulators with the pulp being this interaction influenced by the temperature.

The influence of the manipulation of the temperature of the pulp, with the addition of different pH regulators, was also studied through the recovery of each mineral after 19 minutes of flotation.

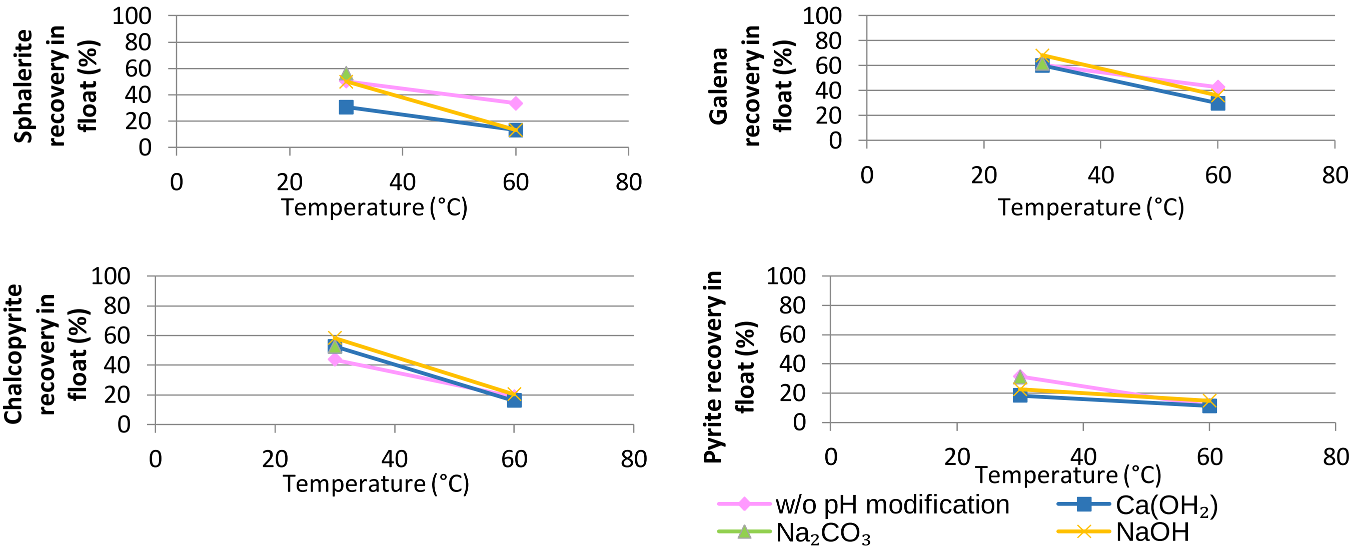

Figure 6 – Recovery of sphalerite, galena, chalcopyrite and pyrite vs. temperature

It was observed that the recovery of any of the minerals under study is lower when the temperature is manipulated (see Figure 6). Sodium carbonate leads to the best results at 30°C with regard to the recovery of sphalerite in the floated product. In turn, at 60°C, the highest recovery of sphalerite in the floated product occurred in the test without pH manipulation. In relation to galena recovery, the highest recovery at 30 °C is obtained with the use of sodium hydroxide and at 60°C without pH modification. As regards to chalcopyrite and pyrite, at 30°C there is a greater recovery of the first mineral with addition of sodium hydroxide and a greater recovery of the second mineral in the test without pH modification and with sodium carbonate. At 60°C the above elements exhibit similar recovery values for any of the added pH regulators.

7. Conclusions

In order to study the problem in two different strands (industrial and laboratory), theoretical and practical studies were carried out.

With the theoretical study no relation was observed between the recovery of sphalerite in the final concentrate and the maximum ambient temperature. It has been found however, that the pH regulator dosage is increased when higher maximum temperatures occur, although the correlation coefficient between these two variables is quite small. This increase may be due to the decrease in the solubility of lime with temperature, which leads to a larger dosage of reagent applied to the system in order to regulate the pH value up to the desired value.

To study the problem at an industrial level a theoretical model was elaborated that allows quantifying the energy associated to the DPR waste. Temperature measurements in this cell bank allowed the calculation of the estimated temperature values of the tailings for several days and their comparison with the actual values recorded on an industrial scale. It was found that the temperature of the industrial bank tailings is higher than the temperature calculated by the model. There is an anomalous increase in the difference between the estimated temperature and the actual temperature of the DPR tailings, about 200% higher than the average variation, in the same day when the lowest recovery of sphalerite in the final concentrate is recorded. This is also the day when a maximum ambient temperature peak occurs. The increase in pulp temperature may be due to exothermic reactions that are promoted by the addition of lime, which increases in periods of higher temperature.

In turn, the effect of pulp temperature on flotation was studied through laboratory flotation tests. The obtained results showed that the temperature has influence on the flotation process. At 60°C there is a reduction between 30 to 70% of the recovery of sphalerite, being this recovery higher without pH manipulation.

It was possible to prove, by the experimental work, the existence of a relation between the temperature and the recovery of sphalerite and penalizing minerals in the concentrate. This relation is amplified by the addition of pH regulators.

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