

ELECTROCHEMICAL ASPECTS IN THE FLOTATION OF LEAD-ZINC SULFIDES IN BRAZILIAN SILICATE ORE – USE OF Na₂S AS MODULATOR

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Abstract

Sodium sulfide plays a multifunctional role in sulfide minerals flotation. The restorative action of minerals surface is its main function. As pH regulator, it reacts on surface and provides the conditions for interactions between minerals-collectors. However, changes in pulp composition can affect the electrochemical conditions desirable for flotation. Thus, the purpose this study was the evaluation of electrochemical state established in flotation, involving a willemite ore bearing zinc and lead sulfide minerals, when Na₂S was used as pH regulator. So, the electrochemical potential established in the pulp, the recoveries and contents of Zn, Pb, and Ag were considered as criteria for assessing the process. The pH equal to 9 yielded the best results for recovery (95.33% Zn; 61.24% Pb; 79.01% Ag) and content (12.96% Zn; 1.54% Pb; 307.33 ppm Ag), due to the smaller interference that occurred in the electrochemical conditions of systems when compared to pH 11, also included in the evaluations. However, larger dosages of Na₂S were counterproductive due to depressant action. Decrease in the potential can be related to the excessive amount of HS⁻, impairing the sulfides flotation.

Keywords: Electrochemical potential; Sodium sulfide; Sulfide minerals; Flotation.

ASPECTOS ELETROQUÍMICOS NA FLOTAÇÃO DE SULFETOS DE ZINCO-CHUMBO PRESENTE EM MINÉRIO SILICATADO BRASILEIRO – USO DO Na₂S COMO MODULADOR

Resumo

O sulfeto de sódio possui um papel multifuncional na flotação de minerais sulfetados. A restauração da superfície sulfetada dos minerais é a sua principal função. Como regulador de pH, este age na superfície mineral e oferece condições para as interações entre mineral-coletor. Contudo, mudanças na composição da polpa podem afetar as condições eletroquímicas necessárias à flotação do sulfeto. Assim, o propósito deste estudo foi avaliar o estado eletroquímico estabelecido em flotação, envolvendo um minério willemítico portador de sulfetos de zinco e chumbo, quando o Na₂S foi usado como regulador de pH. Portanto, o potencial eletroquímico estabelecido na polpa mineral, as recuperações e teores de Zn, Pb e Ag foram considerados como critérios para a avaliação do processo. O pH igual a 9 permitiu os melhores resultados de recuperação (95,33% Zn; 61,24% Pb; 79,01% Ag) e teor (12,96% Zn; 1,54% Pb; 307,33 ppm Ag), devido às menores interferências nas condições químicas do sistema quando comparado ao pH 11, também incluso nos parâmetros de avaliação. Contudo, maiores dosagens de Na₂S podem ter sido deletérias como ação depressora para os sulfetos. Quedas no potencial eletroquímico podem estar relacionadas à quantidade excessiva de HS⁻, prejudicando a flotação.

Palavras-chave: Potencial eletroquímico; Sulfeto de sódio; Minerais sulfetados; Flotação.

1 INTRODUCTION

Regulators or modulators of pH are reagents used in the flotation process that, indirectly, have the function of decreasing or increasing the selective adsorption capacity of the collectors and depressants on the mineral surfaces, enabling the mineral separation [1].

Several compounds are used as regulators, such as: salts, acids, alkalis, electrolytes, not-dissociable compounds,

organic and inorganic substances, with large variations in composition and structure.

Fuerstenau [2] points out that in addition to acting as collector adsorption assistant, pH regulators also act to regulate the alkalinity or acidity necessary for the flotation of the desired mineral, even if there are other similar minerals.

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Salum et al. [3] exemplified the multifunctional character of pH regulators to study the role of sodium sulfide on zinc silicate flotation using amine as collector. Such work investigated willemite and hemimorphite activation by sodium sulfide, taking into account its double function: sulfide restorer (as a cleaning agent to remove the oxidation products) and pH regulator. Silvestre et al. [4] observed that additions of Na_2S , as sulfide minerals restorer prior to flotation, raises the efficiency of the process.

Siqueira [5] evaluated, by bench scale tests, the sodium sulfide performance as pH regulator in the flotation of galena and sphalerite. Sodium sulfide at dosages of 200, 300 and 400 g/t provided the highest mass recoveries (71%, 80%, and 70%, respectively) and zinc grades (21.5%, 25%, and 23%, respectively), and lead grades (31%, 36.5%, and 32.5%, respectively) in the bulk (collective) concentrate after cleaner flotation steps.

In processing units of sulfide minerals, Na_2S plays the main role of restoring the surface conditions of the minerals that suffered oxidation at levels considered harmful to flotation, but such a reagent can also act as a depressant for the same minerals depending on the added dosages.

The use of Na_2S may help to maintain the electrochemical potential constant in the system, but this reagent may also remove the ethyl xanthate (EtX) from surface, due to ion exchange reaction as exemplified by Equation 1 [6].



Therefore, much is known about the use of Na_2S as pH regulator, restorer and even as depressant, but its effect on the electrochemical conditions of systems deserves further investigation. Thus, this paper proposed a discussion focused on electrochemical aspects involving the flotation of lead-zinc sulfides (3% to 10%) contained in willemite ore. The ore's electrochemical potential was monitored by evaluation method. The selected responses were the concentrate quality in terms of the content and recovery of zinc, lead, and silver (associated with galena), constituting the elements economically extracted from the ore.

2 METHODOLOGY

2.1 Ore Characterization and Preparation

Raw sample of ore was pulverized and subjected to semi-quantitative analysis by X-ray Diffractometer (XRD), performed on a PANalytical Empyrean® diffractometer using radiation $\text{CuK}\alpha$ and a graphite crystal monochromator.

The chemical analysis for the raw sample carried out by atomic absorption spectrophotometry, Perkin Elmer-EUA, model Analyst 300 to estimate the contents of zinc, lead, silver, and MgO .

The ore preparation for flotation consisted of comminution. More specifically, this step involved grinding that aimed at a product size 85% under $148 \mu\text{m}$ (corresponding to sieve 100# on Tyler® $\sqrt{2}$).

A screening, using the series Tyler sieves, was done as a way to analyze the particle size distribution of flotation feed.

Initially, the ore was forwarded to a sequence of procedures, including crushing in a roller crusher (section output adjusted in 5.4 mm), followed by wet milling in a steel ball mill with parameters summarized in Table 1.

2.2 Desliming Step

The desliming step was conducted in a 15 L glass vessel with addition of water up to the 10 L mark, followed by pH adjustment to 9 or 11 (depending the tests) using NaOH (1% w/v) and HCl (1% v/v) for better efficiency of the dispersion process. Sodium silicate was added (400 g/t) followed by manual agitation. After 10 minutes sedimentation (the sedimentation time was calculated on basis of Stokes' Sedimentation Theory for diameter particles equal to $10 \mu\text{m}$). Finally, the overflow was drained by siphoning action. The underflow was used in the flotation tests. The size distribution of the overflow's particles was determined using the laser granulometer (CILAS®, model 1064).

2.3 Reagents for Flotation

Table 2 lists all reagents used in the flotation tests, informing the reagent function and its dosage or concentration. All reagents were commercial analytical standard donated by Votorantim Metais Zinco S.A.

Table 1. Fixed parameters of grinding systems

Dimension of ball mill	Diameter: 0.203 m Length: 0.274 m	
	Balls	37 mm
	23 mm	50.5%
	18 mm	21.0%
Balls charge	10.23 kg	
Pulp volume	$7.3 \times 10^{-4} \text{ m}^3$	
Specific mass of pulp	1957.53 kg/m ³	
Filling	35%	
Mill velocity	70 rpm	
Grinding time	40 minutes	

Solutions (1% w/v) of the reagents potassium amyl xanthate, potassium amine-dialkyl dithiophosphate, potassium dialkyldithiophosphate, copper sulphate, and sodium sulfide were prepared. The dispersant sodium silicate was dosed at 300 g/L of concentration, and its molecular ratio (SiO₂/Na₂O) was 3.27. Tap water was used in all processes and its pH was adjusted to 9 (initial pH) using the Na₂S (1% w/v) additions.

Diesel oil was used aiming the extensor flotation process of pulp. PAX and MIBC were chosen to form a simple mixture with diesel oil due to the good performance of this collector in industrial levels.

2.4 Bench Scale Flotation Tests

Bulk flotation tests of a polysulfides zinc and lead ore from Vazante's mine, Minas Gerais state, Brazil, constituted the rougher stage and were carried out at laboratory scale, aiming at monitoring the effect of sodium sulfide as pH modulator on the metallurgical recoveries of Pb, Zn, and Ag.

The chemical analyses for the flotation products were carried out by atomic absorption spectrophotometry to estimate the contents of zinc, lead, silver, and MgO. MgO content is related to the presence of dolomite, being useful for recovery calculations.

CDC[®] flotation cell (model GFB-1000 EEPN), equipped with an impeller device with speed was adjusted to 1500 rpm, was used in the tests. Other details were air flow rate controlled by valves and equal to 10 L/minute, 3 L vessel, and automatic froth scraping.

Measurements of pH and Eh (Pt electrode) were conducted using DM22/Digimed[®] equipment.

Flotation was performed at pH values of 9 and 11, controlled by additions of Na₂S. For each test, 1000 g of zinc silicate ore were wet ground in a ball mill. Soon after grinding, the pulp was added to the desliming tank, producing about 900 g of pulp, which was immediately fed

into the flotation cell to avoid surface oxidation. The pulp (% solids approximately equal to 30) with CuSO₄ was conditioned in a CDC flotation cell with impeller speed set at 1500 rpm for 2 minutes. After the first conditioning, the dispersant was added and a second conditioning time of 5 minutes was provided. Finally, frother and collector were added and the pulp was conditioned for 2 minutes. The air valve was opened and the flotation time was set at 3 minutes. The floated and non-floated products were collected, gravity filtered, and oven-dried at 373 K (100°C). The recovery was determined by ratios of mass and zinc, lead, and silver contents.

3 RESULTS AND DISCUSSION

3.1 Chemical Analysis of Raw Sample

Results of chemical analysis using atomic absorption spectrophotometry of the raw sample were obtained in triplicate and are presented in Table 3. The values for each element were obtained from simple average.

3.2 X-ray Diffraction of Raw Sample

The diffractogram on Figure 1 confirmed the presence of willemite, dolomite, sphalerite and galena in addition to the presence of talc, quartz, and hematite. In this set of minerals, the main gangue species were willemite and dolomite. The minerals targeted for concentration were sphalerite and galena.

This analysis is consistent with the geological studies by [7] who confirmed that the zinc silicate ore from the Vazante mine occurs in pockets and consists of willemite (50% to 70%), dolomite (10% to 40%), quartz (10% to 15%), hematite (5% to 20%), barite (> 5%), apatite (> 5%), franklinite (> 5%), zincite (> 5%), magnetite (> 5%) and sphalerite and galena, associated with hematite, quartz and dolomite inclusions.

3.3 Particle Size Analysis

Particle size analysis using a laser analyzer and was performed with overflow desliming (OD) and Tyler sieves was used to flotation feed. And size distribution curves are displayed in Figure 2. For the OD, 95% particle were below 10 μm and an average size of 5 μm. Flotation feed, in turn, showed a 95% particle were below 100 μm.

Table 2. Reagents used

Function	Reagent	Dosage or concentration
Dispersant	Sodium silicate (SS) [SiO ₂ /Na ₂ O = 3.27]	400 g/t
ZnS activator	Copper sulphate (CuSO ₄)	50 g/t
Collectors	Potassium amil xanthate (PAX)	150 g/t
	Potassium dialkyldithiophosphate (PDD)	
	Potassium amine-dialkyldithiophosphate (PAD) PAX + diesel (1:0.15)	
Frother	Methyl Isobutyl Carbinol (MIBC)	50 g/t
pH regulator	Sodium sulfide (Na ₂ S)	1% w/v

Table 3. Results of chemical analysis of raw sample

Raw sample (flotation feed)	(%)			
	Pb	Zn	Ag	MgO
	0.51	8.84	0.031	11.74

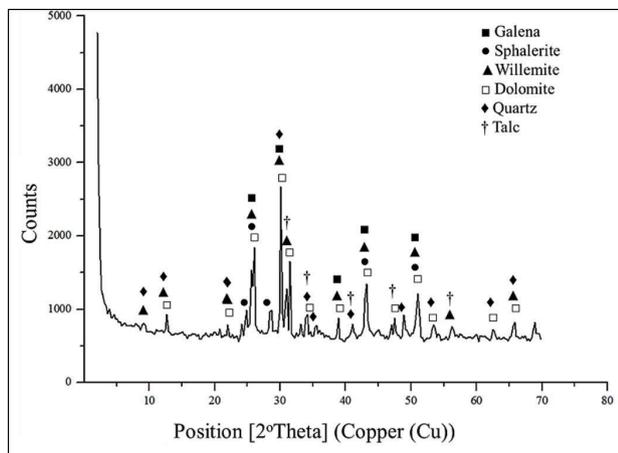


Figure 1. Zinc silicate ore diffractogram.

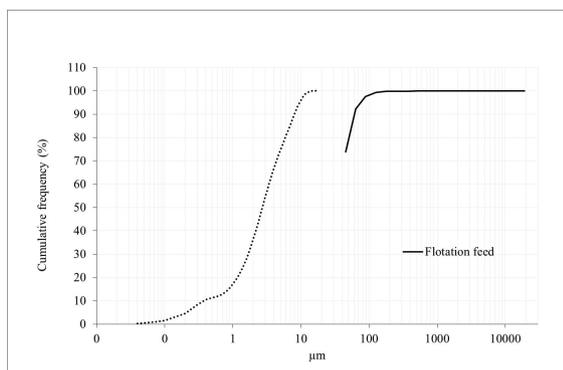


Figure 2. Particle size distribution of overflow desliming and flotation feed screening.

3.4 Flotation Results

From analysis of metallurgical recoveries of Zn, Pb, and Ag (shown in Figures 3-5), it is observed that the pH 9 favored the floatability of sulfides. Only the Zn recovery at pH 11 (52.87%) using PAX as collector exceeded its correspondent at pH 9 (39.93%), but at lower Zn content. While Pb recovery is unchangeable (about 30%) at pH 9 and 11 using PAD.

It has been suggested by Wills [8]; Leja [9], that high pH values promote, for example, the competition between xanthate ions and hydroxyl ions for surface mineral sites, hindering the action of the collector in flotation of the sulfide.

According to flotation models based in electrochemistry, the pH is one of the factors can influence the anodic/cathodic interactions with negative effects on the adsorption mechanisms of collectors [10].

Such interactions between thiol collectors and sulfide minerals depend on the galvanic reactions type mineral-mineral and minerals-grinding media, in which a cathodic response can be represented by Equation 2 (oxygen reduction).

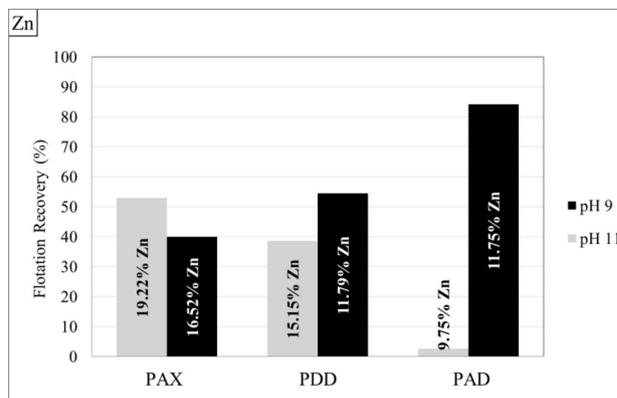


Figure 3. Zinc recovery as a function collector type and pH value. [Collector] = 150 g/t; [SS] = 400 g/t; [CuSO₄] = [MIBC] = 50 g/t. PAX: potassium amyl xanthate; PDD: potassium dialkyldithiophosphate; PAD: potassium amino-dialkyldithiophosphate.

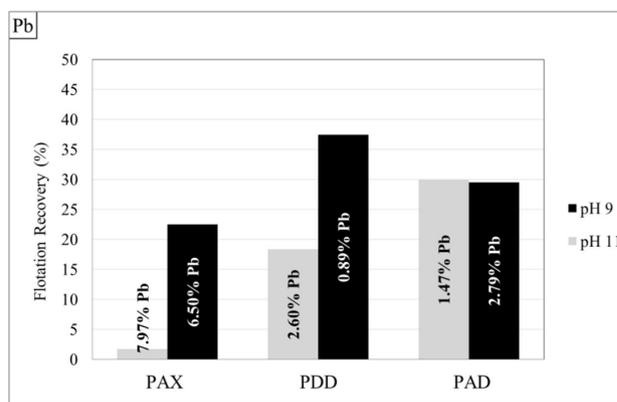


Figure 4. Lead recovery as a function of collector type and pH value. [Collector] = 150 g/t; [SS] = 400 g/t; [CuSO₄] = [MIBC] = 50 g/t. PAX: potassium amyl xanthate; PDD: potassium dialkyldithiophosphate; PAD: potassium amino-dialkyldithiophosphate.

Cathodic reaction:



The increase in pH harms the oxygen reduction resulting in consequences in anodic steps, which is a plausible effect since compressed air is responsible for the aeration of the pulp.

The metallurgical recovery was impaired by a set of factors; highlighted was the interference on the oxygen cathodic reaction, allowing drop in electrochemical potential for flotation of sulfides.

As [11] stated, in flotation systems the recovery and electrochemical potential present similar trends due to pH increase, being the electrochemical potential more affected, as was observed in this work. Göktepe [11], noticed that the floatability of sphalerite with potassium amyl xanthate was higher at pH below and around 9, showing decrease above this value. Galena followed the same trend, with decrease in recovery above pH 6 and change

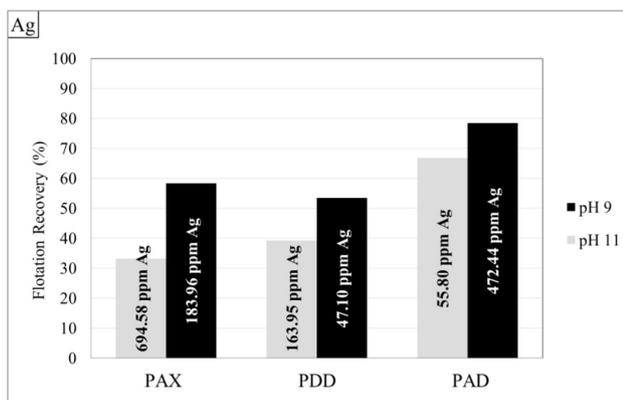


Figure 5. Silver recovery as a function of collector type and pH value. [Collector] = 150 g/t; [SS] = 400 g/t; [CuSO₄] = [MIBC] = 50 g/t. PAX: potassium amyl xanthate; PDD: potassium dialkyldithiophosphate; PAD: potassium amino-dialkyldithiophosphate.

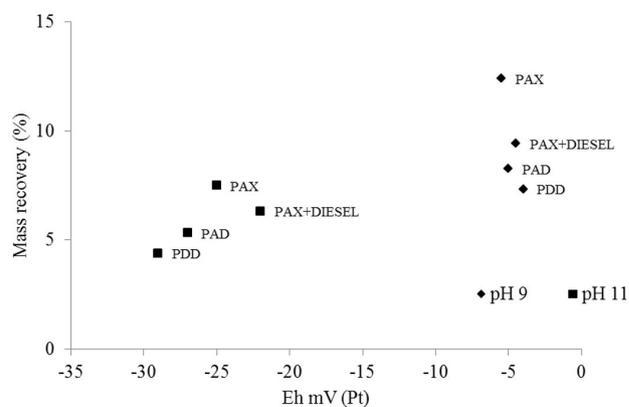


Figure 6. Correlation between the flotation Eh and mass recoveries for pH 9 and 11. PAX: potassium amyl xanthate; PDD: potassium dialkyldithiophosphate; PAD: potassium amino-dialkyldithiophosphate.

in the electrochemical potential of +35 mV to -25 mV as a consequence of pH change from 2 to 11. So, similarly, the recovery of Pb present in the zinc silicate ore was low, registering only 1.74% at pH 11.

It was noted that the bulk flotation of lead-zinc sulfides using potassium amyl xanthate presented the worst results in terms of recovery. Göktepe [11] attributed such decrease to the decomposition of xanthate and the formation of hydrophilic layers of metallic hydroxides on the mineral surface. A fact also observed by Ackerman et al. [12] who investigated the concentration of copper and iron sulfides, using thiol-collectors, and noted a decline in recoveries and content when the pH was raised from 5.0 to 10.5, reinforcing Göktepe's arguments.

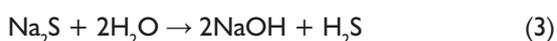
Based on thermodynamic theory Ceylan et al. [13] suggested another explanation in that the reduction of pH can stabilize elemental sulfur, able to enhance the mineral hydrophobization mechanisms. On the other hand, an increase of pH would provide more complex hydrophilic oxidation states (S_x^{2-} , where $2 < x < 8$).

3.5 Electrochemical Potential of Flotation

The electrochemical potential (Eh) corresponding to the end of flotation was registered and correlated to the mass recovery for each test, as shown in Figure 6. Modulation of pH to 11 with Na₂S resulted in decrease of Eh values in all tests, effect probably due to excess of HS⁻ in the pulp.

The ionization of Na₂S, as a function of pH, occurs in three stages, represented by the Equations 3-6 Crozier [14]:

First stage:



Second stage:



Third stage:



Galery [15] stated the predominance of HS⁻ ions in the pH range between 7.5 to 12.0. According to Crozier [13], at pH 11, or lower, the proportion of S²⁻ ions is low in comparison with that of HS⁻.

According to Figure 6, it can be noted that at pH 9 the Eh values were associated with the best recoveries of Zn, Pb, and Ag (i.e., 95.33%, 61.24%, and 79.01%, respectively) and contents of 12.96% Zn, 1.54% Pb and 307.33ppm Ag for each recovery.

The Eh responses whether for pH 9 or 11, focused on the negative region of the electrochemical potentials (Eh < 0) which by itself is unfavorable to the flotation of sulfides.

According to Woods [16], the pH control enhanced mineral oxidation (i.e. competing anodic reaction). Ions which strongly adsorb on the surfaces of minerals will determine their potentials. These ions will determine the electrochemical potential of the electrical double layer and have a pronounced influence on numerous properties. This includes mineral hydrophobicity as well as the ability to adsorb different ions or molecules from the liquid phase. Minerals for which hydrogen and hydroxyl ions are potential determining ions are particularly sensitive to changes in the pulp pH.

In summary, the pH elevation is achieved by H⁺ consumption of the system by sulfur from Na₂S, but can simultaneously decrease the electrochemical potential due to the concentration of residual HS⁻ ions that increase according to Na₂S dosage. Added to this, lower pH values enhance the stability of elemental sulphur, which in turn acts as a hydrophobic agent, assisting the collector.

6 CONCLUSION

The best results were achieved for flotation pH equal to 9, which are linked to the electrochemical conditions of the systems; the pH 9 can interfere less in the oxi-reduction steps, as is common in sulfides flotations.

Sodium sulfide is a restorer the sulfide surface but can acts as a pH regulator too. The sulfide surface can be submitted to oxidation during or prior to flotation and is interesting to use the Na_2S as pH regulator because it can simultaneously it contribute with the sulfide restorer. However, for more alkaline pH conditions, the dosage of Na_2S is deleterious due to the depressant action of this reagent on sulfides.

The use of larger dosages of Na_2S aiming at raising the pH elevation to 11 caused decrease in Eh and consequently reflected negatively on the floatability of sulfides.

Drop in the electrochemical potential and thus in the mineral recovery was due, partially, to excessive HS^- ions in the pulp, rendering the Eh more negative. On the other hand, a lower pH, meaning the use of lower dosages/concentrations of Na_2S , favors the stability of elemental sulfur, hydrophobic species that reinforces the collector action.

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