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Effect of the pulp potential on galena flotation with amyl xanthate as the collector

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Abstract

The flotation mechanism of galena with xanthate as the collector is generally explained based on the mixed potential of the pulp, in which an anodic electron transfer reaction from the collector to the mineral is combined with an O_2 cathodic reduction. Sodium sulphide, often used as a mineral activator, strongly influences the pulp's mixed potential, and depending on the dosage applied, it can become a galena depressor reagent. In this way, the current study assesses galena flotability in the absence of collector, as well as in the presence of the collector potassium amyl xanthate (PAX) and sodium sulphide. The effect of an extremely cathodic potential was also studied through the addition of hydrogen peroxide. In addition, the effect of different stages in the oxidation of the galena surface on the flotability was investigated. Moreover, the zeta potential was measured and contact angle (wettability) tests were carried out. The contact angle measurements were taken for a distilled water, PAX solution and for a mixture of PAX and sodium sulphide solution on the oxidized and non-oxidized surface of galena. All the results showed that galena could be floated in all the PAX concentrations tested. It was observed that a moderate oxidation in the galena surface may contribute to an improvement of its flotation with PAX. However, extremely anodic and cathodic potentials cause flotability close to zero. The zeta potential results showed that sodium sulphide affected the interaction between PAX and galena. The measurements of the contact angle corroborated the results obtained in the microflotation tests.

Keywords: galena; sodium sulphide; contact angle; wettability.

1. Introduction

According to Grano *et al.* (1990) & Woods (2003), without a clear understanding of electrochemistry, the flotation process of the sulphide minerals cannot be fully understood. Given the importance of mastering such a process, by means of the various electrochemical techniques, a considerable number of researchers have investigated the interaction among the collectors and the sulphide minerals (Ranta *et al.* 1981; Ho & Conway 1978; Page & Hazell 1989; Chernyshova 2002; Fredriksson & Holmgren 2008). According to Buswell *et al.* (2002), the main factor affecting the electrochemical process during the flotation of these minerals is the redox potential existing between the mineral and the solution. The authors claim that the redox potential controls the formation of hydrophilic and hydrophobic species on the mineral's surface. Therefore, the regulation of the pulp potential (Eh) may modify the redox properties of the system, hence rendering the flotation process more efficient.

Electrochemical investigations proposed by Woods (1984) and Woods & Richardson (1986), demonstrated that a mixed potential model may be utilized in the explanation of the electrochemical nature of the galena-xanthate interaction. This model indicates that this interaction involves simultaneous electrochemical reactions that include the electron anodic transfer process from the collector to the mineral, and also, a cathodic reduction involving oxygen. As in Guy & Trahar (1984), the main hydrophobic entity formed on the surface of the galena accounting for the induced flotation by the collector amyl xanthate is lead dixanthate (PbX_2). Equations 1, 2 and 3 present the formation of lead dixanthate, where X^- stands for the xanthate ion:

$$PbS + 2X^- + 4H_2O \rightarrow PbX_2 + SO_4^{-2} + 8H^+ + 8e^- \qquad (1)$$

$$2PbS + 4X^- + 3H_2O \rightarrow 2PbX_2 + S_2O_3^{-2} + 6H^+ + 8e^- \qquad (2)$$

$$PbS+2X^- \rightarrow PbX_2 + S + 2e^- \qquad (3)$$

Although lead dixanthate is the main hydrophobic product formed on galena's surface, the dixanthogen (X_2), Equation 4, and the chemisorbed xanthate (X_{ads}), Equation 5, are also responsible for the mineral surface hydrophobization process (Laajalehto *et al.*, 1993; Nowak, 1993; Buckley & Woods,1994).

$$2X^- \rightarrow X_2 + 2e^- \qquad (4)$$

$$X^- \rightarrow X_{ads} + e^- \qquad (5)$$

Finkelstein (2007) demonstrated that the flotation capacity of galena, with the use of xanthate, rises as the O_2 content increases. According to this author, a rise in oxygen concentration affects the pulp potential, resulting in an increase in the xanthate oxidation ratio on the surface of the galena. Chen *et al.* (2014), argue that, given the reducer character of galena, the formation of dixanthogen on the mineral's surface does not occur in the absence of O_2. Furthermore, it was demonstrated that the xanthate adsorption energy onto galena reduces from - 82.71 kJ/mol to 102.00 kJ/mol in the presence of O_2. Ahmed (1978) suggests that in the absence of O_2, the xanthate hydrophobic group may be attached to the surface of the sulphide minerals by the van der Waals forces, whereas the polar group is exposed to the solution, so that the hydrophilicity of the surface is kept. According to Page & Hazell (1989), the oxidation resulting from the galena comminution process is influential enough to cause the formation of oxidation products on the mineral's surface. The authors argue that the xanthate treatment on the surface of galena results in an ionic exchange between the species formed on the oxidized surface of the mineral and the xanthate ions, thus forming lead dixanthate.

Moreover, the application of sodium sulphide before the addition of the collector, is used with a view to improve the flotation of zinc oxide minerals (Salum 1982; Bustamante & Shergold 1983). Galena is commonly associated with zinc oxide minerals and is often explored together; however, lead is usually extracted as a byproduct of zinc mining (Hitzman *et al*., 2003; Monteiro *et al*., 1999). One of the circuits used by the industry in the recovery of these minerals consists of previous sulphidation of the ore, followed by the flotation of the lead minerals The refuse of this phase is sent to the following stage, dedicated to the recovery of the zinc minerals (Nexa Resources 2019).

However, in the case of galena, electrochemical studies into potential reducers, emerging from the addition of sodium sulphide, lead dixanthate is unstable when compared to lead sulphide (Sato 1960). Still according to Leppinen & Mielczarski (1986), the addition of sodium sulphide after the galena has been treated with amyl xanthate leads to the removal of the xanthate product from the surface of galena; this occurs by means of an ionic exchange reaction, as depicted by Eq. 6. This mechanism was also proposed by Fuerstenau (1982), in the depression of lead sulphide.

$$PbX_2 + S^{2-} \rightarrow PbS+ 2X^- \qquad (6)$$

The investigation carried out by Herrera-Urbina *et al.* (1998), shows that the galena flotation ceases when the sodium sulphide reaches a determined concentration. The author argues that a fall in the pulp potential coincides with a reduction in the galena flotation, thus demonstrating a close relation existing between the pulp potential and the galena flotation when the collector amyl xanthate is used.

Therefore, considering that lead is

widely used in lead-acid batteries, bullets and shot, weights, solder, pewter, and fusible alloys, and galena being the most important primary source of this metal, the understanding of the factors that affect the flotability of this mineral is of utmost importance. In this context, the current study analyzed the behaviour of galena, having, or not, the surface oxidized during floatability tests in the presence of different sodium sulphide concentrations at pH 9.5.

2. Materials and methods

2.1 Materials

The pure galena sample utilized in the current study was collected in Brazil. The reagent potassium amyl xanthate (PAX) was used as a collector and sodium sulphide as the sulphidisation agent. A 3 % hydrogen peroxide (30 vol) solution was employed as the oxidation agent. To adjust the pH, solutions of 1 % of nitric acid and potassium hydroxide were prepared. All the trials were carried out with distilled water at pH 9.5.

2.2 Experimental procedures

2.2.1 Microflotation

In the microflotation tests, 100 g of the galena sample were comminuted in a porcelain mortar until it reached the particle size between 212 and 75 µm. Immediately after comminution, a portion of the sample was sent for microflotation tests, in order to prevent oxidation of the mineral's surface. The remaining material was exposed to the ambient, thus promoting oxidation of the galena surface for periods of 24, 120, 240 and 480 h. The microflotation trials were conducted in a Hallimond tube, with the use of nitrogen as the flotation gas in a flow rate of 60 mL/min. These trials were carried out in phases. In the first phase, the flotability of non-oxidized galena was analyzed in the absence and presence of the collector PAX. The collector concentrations used were 10^{-5}, 10^{-4}, 10^{-3} e 10^{-2} mol/L. After establishing the best PAX concentration, in the second phase, the influence of an extremely anodic potential of the suspension in the mineral's flotability was tested. In this regard, before the start of the microflotation experiment, a solution of 3 % of hydrogen peroxide (30 vol), was added to the mineral suspension. In the third phase, the analysis of the effect of different periods of oxidation of the galena surface on the flotability was performed (24, 120, 240 and 480 h). Finally, in the fourth stage, the effect of different concentrations of sodium sulphide on the galena flotability was tested. The sodium sulphide concentrations evaluated were 10^{-5}, 10^{-4}, 10^{-3} and 10^{-2} mol/L. The time of conditioning for each reagent was 5 min and the flotation period was 2 min. The pulp potential was recorded continuously in all the tests, using a platinum electrode by a Hanna Instruments apparatus, model HI3230B. All the trials were conducted in duplicate, and the margin of error considered was 2 %.

2.2.2 Zeta potential measurements

The zeta potential measurements were made in the Zeta Meter 4.0 apparatus. In this direction, a galena suspension was prepared with potassium chloride KCl at a concentration of 10^{-3} mol/L as an indifferent electrolyte. The zeta potential of the galena was determined without the addition of collectors and in the presence of the PAX and a mixture of 50 % of the PAX solution plus 50 % of sodium sulphide solution. The averages of at least three repeated tests were adopted as the final results reported in this study and the margin of error considered was 5 mV.

2.2.3 Contact angle

Contact angle measurements were carried out with the liquids: distilled water, PAX solution, and a mixture of 50 % of PAX solution and 50 % of sodium sulphide solution on the surface of both oxidized and non-oxidized galena, in order to obtain information about the wettability of these surfaces. All the liquids were prepared at a temperature of 23.5 °C at pH 9.5. To perform the measurements, the mineral was cut in the dimensions 3 x 2 x 0.5 cm; subsequently, the surface of the samples were polished with diamond paste. After polishing, the samples were rinsed several times with deionised water. In the tests of the non-oxidized galena surface, the samples were dried in nitrogen and placed in a deaerator for 60 min. In the case of the oxidized surfaces, the samples were immersed in a solution of 3 % of hydrogen peroxide (30 vol) for 60 min. Each measurement was repeatedly conducted three times and the average value was considered as the reported result. The experimental error in the measurement of angles is 2 %, according to laboratory statistics. The trials were carried out in a goniometer developed and calibrated for this purpose. This apparatus is equipped with a digital magnifying lens with a 2.0 megapixel camera, whereby the images were obtained. Using these images, the contact angles measurements were taken. The tool used was the software QuantDim, developed by Surface Engineering Laboratory and Related Techniques of REDEMAT- UFOP, for this purpose.

3 Results and discussion

3.1 Microflotation

Figure 1a presents the results of the flotability of the non-oxidized galena in the absence of the collector and under different PAX concentrations. The high recovery shown in the collectorless test indicates that galena presents natural hydrophobicity. Kang & Chen (2011) studied the effect of pH on the colletorless flotation of galena and showed that the recovery of this mineral was low in a strongly acidic solution (pH 2) and in a strongly alkaline solution (pH 11); however, it was only satisfactory in other pH values (over 75 %). According to Sun *et al.* (1994) in the colletorless flotation of the galena process, the equilibrium relationship between hydrophobicity and hydrophilicity can be described as the ratio of elemental sulphur concentration to hydroxyl concentration ([S^0]/[OH^-]). At a particular pH value, the greater the [S^0], the higher the hydrophobicity, and the better the flotability. In addition, the collectorless microflotation test presented a potential value of 35 mV (Figure 1b). Ralston (1991) suggested that the collectorless flotation of sulfide minerals can only occur in moderately oxidizing environments, which can be controlled by the pulp potential, but it cannot be achieved under reducing conditions. Kartio *et al.* (1996) investigated galena oxidation at pH 4.6 by synchrotron X-ray photoelectron spectroscopy (SR-XPS) and found that galena oxidizes at high potential forming new species such as metal polysulfides and lead-deficient sulfides. According to the authors, at 250 mV, the formation of metal polysulfide increased and when the potential increases, the polysulfides can be further oxidized to elemental sulfur. Elemental sulfur (S^0), lead polysulfide (PbSn, n > 1) and lead-deficient sulfide (Pb1-XS, X < 1) are oxidation products that causes hydrophobicity on the surface of sulfides, which contribute to an increase in the rate of collectorless flotation (Hampton *et al.*, 2011, Aghazadeh *et al.*, 2015, Mineralurgii, 2002)

As seen, the flotability of the mineral was successful in all PAX concentrations analyzed, presenting an average flotation equal to 95 %. The results obtained meet the concept of strong chemisorption of xanthate onto the galena, suggesting that the flotability of the mineral is induced even in very low concentrations of PAX (Buckley & Woods 1994). Figure 1b shows that an increase in the concentration of the collector in the values of 10^{-5}, 10^{-4}, 10^{-3} and 10^{-2} mol/L, leads to a reduction of the pulp Eh, -94.3, -107, -144 and -183 mV, respectively. However, taking into consideration that the flotation of the mineral was close to 100 % in all the potassium amyl xanthate concentrations added, it can be inferred that in such a case, there is not a direct correlation between the suspension Eh and the galena flotability. These results corroborate the findings by Herrera-Urbina *et al.* (1998).

According to the authors, the values of the potential, measured according to this system, correspond to the oxidation of xanthate and the reduction of oxygen in the pulp, as described by Woods (1984) and Woods & Richardson (1986).

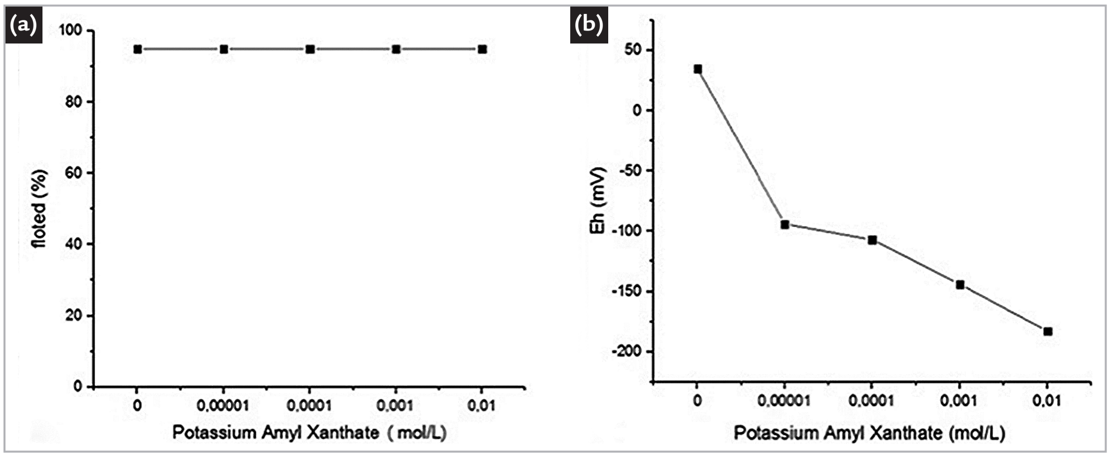

Figure 1 - (a) Floted (%) non-oxidized surface galena recovery, at pH 9.5, in the absence of the collector and under different PAX concentrations, and (b) Eh of the system, in the absence of the collector and under different PAX concentrations, under the same conditions.

Figure 2 presents the flotability of galena subjected to an extremely anodic potential, with the use of a hydrogen peroxide solution, and the flotability of the oxidized galena samples in periods of 24, 120, 240 and 480 h, in function of the system redox potential (Eh), with the use of PAX in the concentration of 10^{-4} mol/L. Thus, it was observed that the flotability of galena in the presence of hydrogen peroxide fell sharply, presenting a flotation value of only 0.5 %. Moreover, the Eh value presented was extremely high - equal to 384 mV. The same tendency was observed by Guy & Trahar (1984). The results obtained by these authors showed a fall in the galena flotability - to zero - in values above 350 mV, with the application of amyl xanthate as the collector. According to the authors, highly anodic charges lead to the decomposition of the lead dixanthate (PbX_2), Eq 7 and 8, thus hampering the galena surface hidrophobization process, and consequently affecting the flotation.

$$PbX_2 + 2H_2O \rightarrow HPbO_2^- + X_2 + 3H^+ + 2e^- \qquad (7)$$

$$PbX_2 + 2H_2O \rightarrow Pb(OH)_2 + X_2 + 2H^+ + 2e^- \qquad (8)$$

With regard to the samples that were exposed to the ambience in different oxidation periods, the Eh values obtained were -77, -138, -111 and -95 mV, for the periods of 24, 120, 240 and 480 h, respectively. As noticed, the Eh values recorded for the oxidized samples did not present significant difference; besides, these values were very close to the ones displayed by the non-oxidized samples (-107 mV), when submitted to the same amyl xanthate concentration (10^{-4} mol/L). However, the oxidized samples displayed an average floatability equal to 98.75, presenting a slight improvement, near 4%, in relation to the flotability average found in the non-oxidized samples (Fig 3a). Also observed was the fact that the oxidized samples did not present any difference in flotability with regard to the oxidation time they were exposed to. Greenler (1962) showed that the galena samples having a higher ratio of oxidation in the ions sulphide adsorb a higher amount of xanthate than the less oxidized samples, suggesting that the interaction of xanthate with the oxidized galena surface is enhanced. Therefore, the control of the galena surface oxidation process may render the selective flotation process of this mineral even more efficient.

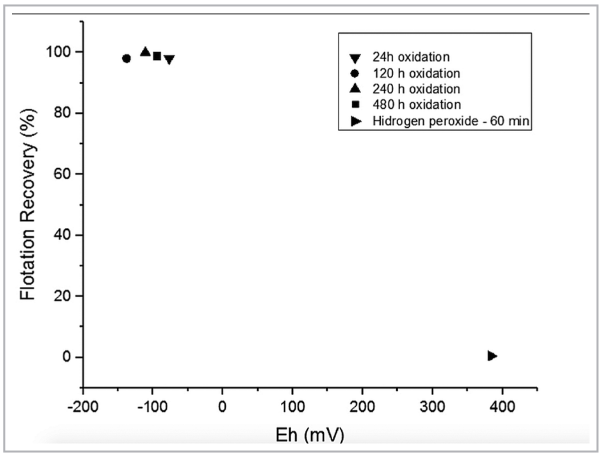

Figure 2 - Floted (%) of oxidized surface galena, at pH 9.5, in different ambience exposure periods (time) and with extremely anodic potential promoted by hydrogen peroxide, in the presence of PAX (10^{-4} mol/L), in function of the system Eh.

The flotability of galena in the presence of different concentrations of sodium sulphide and amyl xanthate in the concentration of 10^{-4} mol/L, at pH 9.5, is depicted in Figure 3a. As noted, a galena floatability of 98 % was achieved for additions of sodium sulphide in concentrations of 10^{-5} and 10^{-4} mol/L. However, in concentrations equal to 10^{-3} and 10^{-2} mol/L, the flotation of the mineral diminishes dramatically, down to 17 and 2.5 %, respectively. The fall in the galena flotation occurs alongside a rise in the sodium sulphide concentration, and consequently, with a decrease in the pulp's redox potential, as presented in Figure 3b. A fall in flotability when the concentration of the sodium sulphide added is greater than 10^{-4} mol/L, may be directly related with an acute cathodic change in the suspension potential for values below the ones necessary for the catalysis of xanthate into dixanthogen onto the galena, as reported by Chen *et al.* (2014). Herrera-Urbina *et al.* (1998) observed the same tendency and claimed that under smaller sodium sulphide doses, the hydrosulphide ions (HS^-) react with the aqueous lead (Pb^{2+}) dissolved from the mineral, therefore, not affecting the pulp potential. However, once all the lead has precipitated as PbS, the residual sulphide returns to the solution, inducing a sharp fall in the redox potential, thus inhibiting the xanthate chemisorption onto the mineral. According to Page & Hazell (1989), the formation of lead dixanthate (PbX_2) occurs in an ionic form, only on the oxidized PbS surfaces. XPS studies carried out by the authors shows that the treatment of galena with Na_2S, previous to the addition of potassium amyl xanthate, results in the removal of the products of oxidation, such as PbO, PbS_2O_3 and $PbSO_4$, formed on the surface of the mineral during the comminution process, thus strongly affecting the xanthate chemisorption process and consequently the galena flotation process.

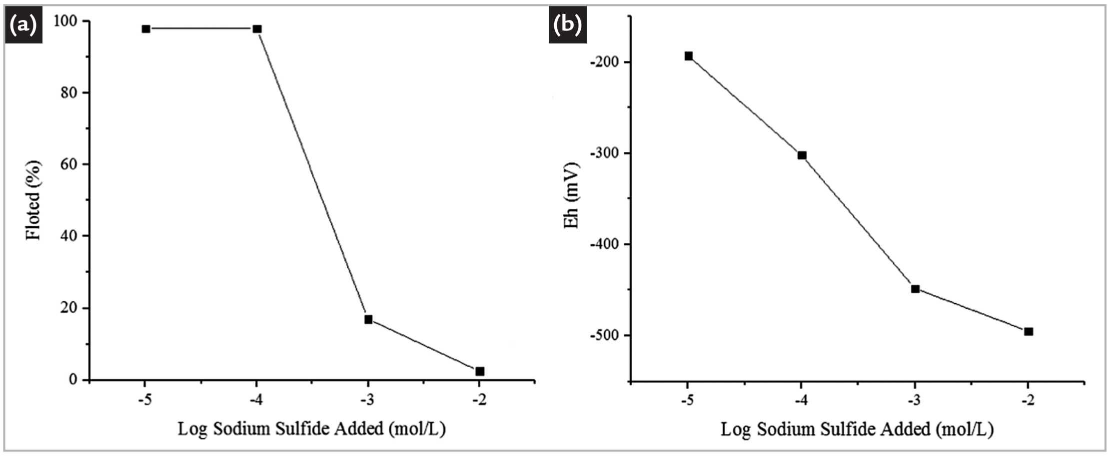

Figure 3 - (a) Floted (%) of non-oxidized surface galena at pH 9.5, in the presence of the collector potassium amyl xanthate (10^{-4} mol/L), in function of different concentrations of added sodium sulphide and (b) system Eh in function of different concentrations of added sodium sulphide – under the same conditions.

3.2 Zeta potential measurements

In order to understand the chemical interaction between flotation reagents and mineral, the zeta potentials of galena before and after conditioning with PAX solution in the concentration of 10^{-4} mol/L and a mixture of 50 % of the PAX solution plus 50 % of sodium sulphide solution in concentrations of 10^{-4} and 10^{-2} mol/L were measured, and the results are illustrated in Figure 4. Clearly, without any reagent, the galena isoelectric point was 2.7, which was in line with previous studies (Healy & Moignard 1976). After the addition of PAX, the significant shifts towards the negative direction in the zeta potential were observed: near pH 9.5, the zeta potential of galena decreased from - 40 mV to - 60 mV, indicating that the adsorption of an anion has occurred on the surfaces. When a mixture of 50 % of the PAX solution plus 50 % of sodium sulphide solution were added, the zeta potential of galena near pH 9.5 were the same as that without any reagent. This result indicated that sodium sulphide affected the intense interaction between PAX and galena, which agreed with the microflotation results.

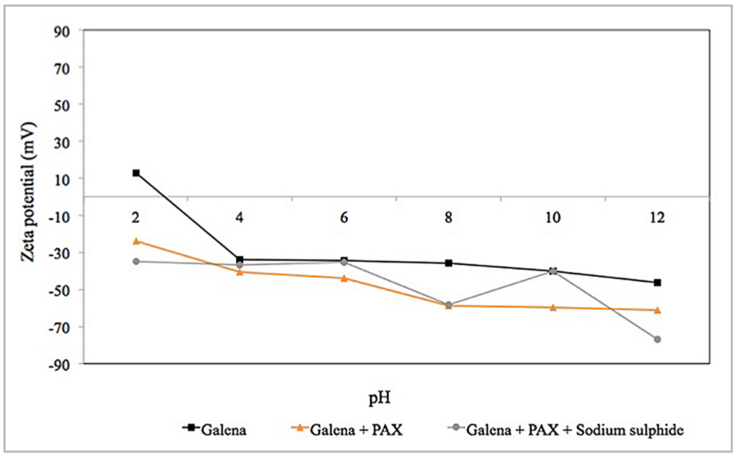

Figure 4 - Zeta potentials of galena treated with PAX (10^{-4} mol/L) and a mixture of 50 % of the PAX solution plus 50 % of sodium sulphide solution (10^{-4} and 10^{-2} mol/L) as a function of pH.

3.3 Contact angle

The contact angle is considered a direct reflex of the mineral surface hydrophobicity, having a strong correlation with the flotability of the minerals (Chen *et al*. 2017; Zhu 2020). Figure 5 presents the contact angle values obtained on the galena surface, for oxidized and non-oxidized samples. The liquids applied were distilled water, PAX solution in the concentration of 10^{-4} mol/L, and a mixture of 50 % of the PAX solution plus 50 % of sodium sulphide solution in concentrations of 10^{-4} and 10^{-2} mol/L, respectively.

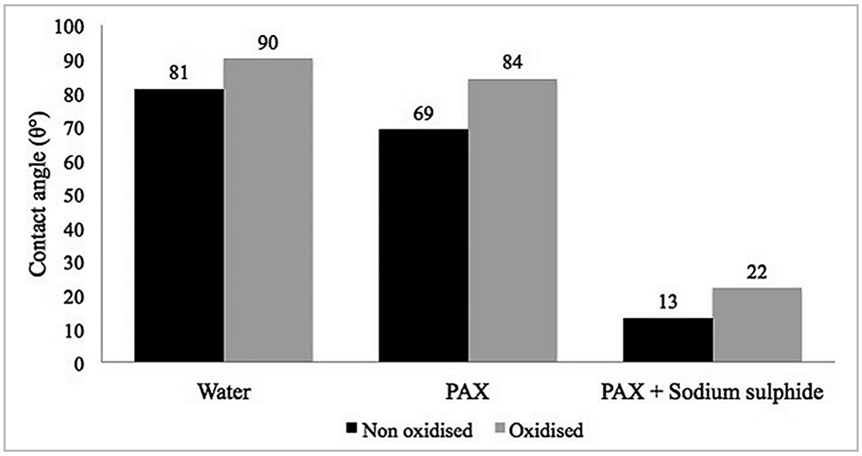

Figure 5 - Contact angles of the oxidized and non-oxidized galena surfaces, measured in the presence of distilled water, amyl xanthate solution, and amyl xanthate + sodium sulphide solution, at pH 9.5.

The contact angles presented in Figures 6a and 6b, were 81° and 90°, respectively. The high recovery observed indicates that galena presents natural hydrophobicity, corroborating the result obtained in the microflotation trial. The greater hydrophobicity of the oxidized galena surface when compared to the non-oxidized surface, may be related to the fact that the oxidation process may have cleaned the mineral's surface of natural impurities, thus making it more hydrophobic. According to Hu (1987), the natural galena may contain Ag, Cu, Zn, Fe, Sb, Bi, Mn and other impurities. Lan *et al.* (2016) showed that the impurities like Zn, Sb, Mn and Cu, could inhibit the adsorption of xanthate onto the galena.

Both oxidized and non-oxidized samples, as shown in Figures 7a and 7b, when submitted to a PAX solution in the concentration 10^{-4} mol/L, presented contact angles equal to 69° and 84°, respectively. The results demonstrate that the oxidized galena surface presented a greater contact angle when compared to the non-oxidized surface. According to Page & Hazell (1989), oxidation by dissolved oxygen in aqueous solution alone is insufficient to provide the degree of surface oxidation necessary for the chemisorption reaction. However, chemical oxidation with hydrogen peroxide or crushing/grinding pretreatments, do generate enough oxide and sulphate/thiosulphate-like groups on the surface for chemisorption of xanthate to occur via ion-exchange with these species.

The samples presented in Fig 8a and 8b, non-oxidized and oxidized submitted to a mixture of 50 % of the solution KAX plus 50 % of the sodium sulphide solution, presented contact angle values equal to 13° and 22°, respectively. As seen, the addition of sodium sulphide at the concentration of 10^{-2} mol/L, caused an expressive reduction in the contact angle. These results corroborate the ones obtained in the microflotation trials, where the sodium sulphide in the concentration above 10^{-4} mol/L, impaired the galena flotation expressively.

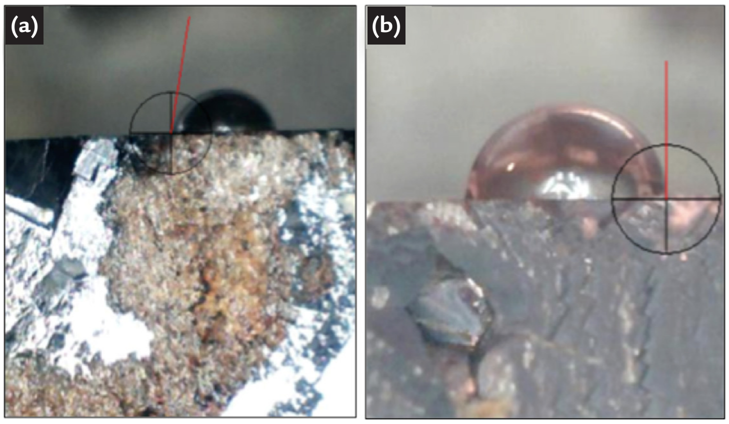

Figure 6 - Images of the measurements of the contact angle on galena for distilled water. (a) natural galena surface θ = 81°; (b) oxidized galena surface θ = 90°. Magnified 4 x.

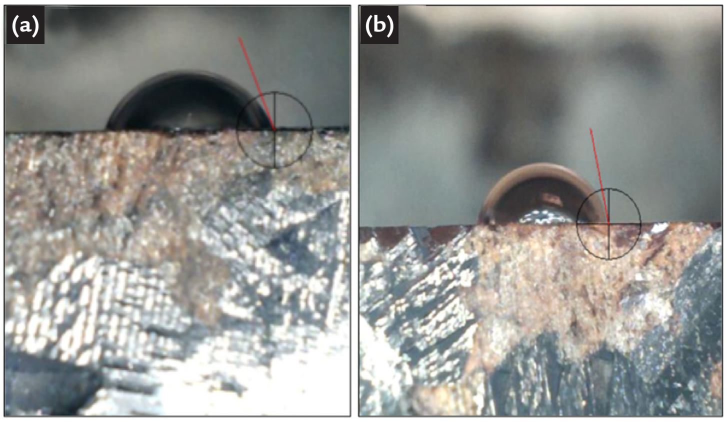

Figure 7 - Images of the measurements of the contact angles on galena for the amyl xanthate solution (10^{-4} mol/L) treatment. (a) natural galena surface θ = 69°; (b) oxidized galena surface θ = 84°. Magnified 4 x.

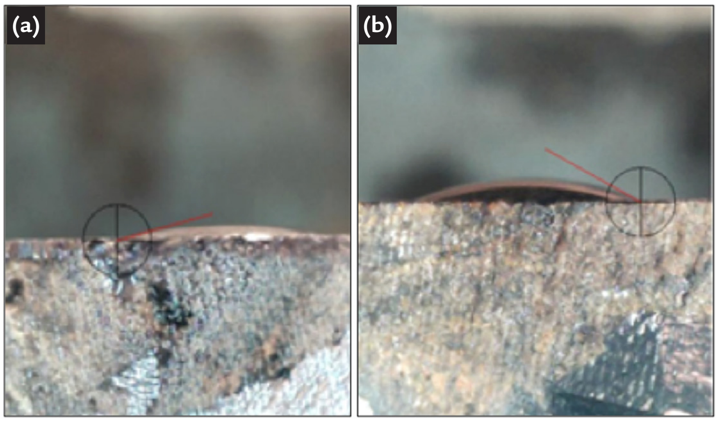

Figure 8 - Images of the measurement of the contact angles on galena for the amyl xanthate (10^{-4} mol/L) + sodium sulphide (10^{-2} mol/L) treatment. (a) surface of natural galena θ = 13°; (b) oxidized galena surface θ = 22°. Magnification 4 x.

4. Conclusions

The microflotation test conducted in the absence of the collector showed that galena presents natural hydrophobicity. The recovery of galena was successful under all concentrations of the collector potassium amyl xanthate tested. A rise in the collector concentration results in a reduction of the pulp Eh values. However, in this case, the galena flotation was practically 100%. Moreover, it was evident that a severe oxidation of the galena surface resulted in a sharp rise in the Eh, reducing the flotability of the mineral to values close to nil. On the other hand, it was noticed that a moderate oxidation of the galena surface may contribute to an increase in flotation. With regard to the addition of sodium sulphide, a sharp fall in the galena flotation was observed in concentrations higher than 10^{-4} mol/L, coinciding with a decrease in the pulp's potential. The measurement values of the contact angle agree closely with results obtained in the microflotation trials. Apart from that, the high values of the contact angles presented by the galena samples for distilled water show that, under the conditions investigated, this mineral presents natural hydrophobicity.

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