

Hydrophobic aggregation of galena fine particles**Agregação hidrofóbica de partículas finas de galena**

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ABSTRACT

The evolution of mining activities has driven the implementation of new concepts for processing low-grade ores with liberation of small-size particles. Several alternative techniques have been developed, among which hydrophobic aggregation should be emphasized. In this process, selective hydrophobization is induced by collectors that adsorb onto the desired minerals, forming aggregates that capable of adhering to air bubbles and can be recovered via flotation. Despite its great potential, this process still has limited application in the mineral industry because of its great complexity. This research aimed to study the applicability of hydrophobic aggregation to assist the flotation of sulfide ores of zinc and lead with particle sizes below 16 μm . Fundamental studies were performed with samples of galena and sphalerite minerals using amyl xanthate and propyl xanthate as collectors. For each reagent, the influence of pH and the stirring speed was analyzed. The experimental results demonstrated that hydrophobic aggregation was closely correlated with particle hydrophobicity. The aggregation did not decrease with increasing the particle surface charges due to collector adsorption, which is considered by extended DLVO theory. Analysis of the results suggested that the hydrophobic aggregation is a promising technique for recovering fine particles of zinc and lead sulfide.

Keywords: hydrophobic aggregation, shear flocculation, galena

RESUMO

A evolução das atividades de mineração impulsionou a implementação de novos conceitos para o processamento de minérios de baixo teor com liberação de partículas de tamanho pequeno. Várias técnicas alternativas foram desenvolvidas, dentre as quais a agregação hidrofóbica deve ser enfatizada. Nesse processo, a hidrofobização seletiva é induzida por coletores que absorvem os minerais desejados, formando agregados capazes de aderir às bolhas de ar e que podem ser recuperados por flutuação. Apesar de seu grande potencial, esse processo ainda tem aplicação limitada na indústria mineral devido à sua grande complexidade. Esta pesquisa teve como objetivo estudar a aplicabilidade da agregação hidrofóbica para auxiliar a flotação de minérios de sulfeto de zinco e chumbo com tamanhos de partícula abaixo de 16 μm . Estudos fundamentais foram realizados com amostras de minerais de galena e esfalerita usando amil xantato e propil xantato como coletores. Para cada reagente, a influência do pH e a velocidade de agitação foram analisadas. Os resultados experimentais demonstraram que a agregação hidrofóbica estava intimamente correlacionada com a hidrofobicidade das partículas. A agregação não diminuiu com o aumento das cargas na superfície das partículas devido à adsorção do coletor, o que é considerado pela teoria DLVO estendida. A análise dos resultados sugeriu que a agregação hidrofóbica é uma técnica promissora para recuperar partículas finas de zinco e sulfeto de chumbo.

Palavras-chave: agregação hidrofóbica, floculação de cisalhamento, galena

1 INTRODUCTION

The applicability of flotation as a concentration process is restricted to a narrow size range out of which the effectiveness of the method substantially decreases (Gaudin *et al.*, 1931). The size range in which flotation can be applied depends on the mineral: for galena, it is 6–70 μm , and for sphalerite the range is 8–90 μm (Trahar and Warren, 1976). Processing of really fine particles causes problems in the flotation stage, such as high reagent consumption, low selectivity, foam stability, and entrainment, which can affect the grade and recovery in the concentrate (Subrahmanyam and Forssberg, 1990). In this context, recovery of galena (PbS) from fine sulfide ores is a challenge.

Many processes have been developed or enhanced to improve the efficiency of the flotation of fine particles. One of these processes is the hydrophobic aggregation of fine particles, followed by conventional flotation of these aggregates. This article discusses shear flocculation, in which aggregates are obtained through adsorption of selective collectors into desired minerals by applying a shear field of sufficient magnitude (Song *et al.*, 2001).

The classical DLVO theory and extended DLVO theory (X-DLVO) describe the forces of interaction between colloidal particles. According to classical theory, the electrical double layer is responsible for repulsion, while van der Waals forces are responsible for attraction. When the stability of a colloidal suspension is not adequately described by the classical DLVO theory, the forces included in the X-DLVO are applicable (Xu and Yoon, 1989) e.g., in hydrophobic aggregation by shear flocculation.

In addition to the electrical double layer and van der Waals forces, the extended DLVO theory considers hydrophobic forces, hydration forces, steric forces and magnetic forces. The last two do not have great influence in the system described in herein, unlike the first two. Steric forces are related to repulsion between the adsorbed polymer layers and magnetic forces are present in systems that have magnetic field action.

Hydrophobic interactions play an important role in hydrophobic aggregation because of the hydrocarbon chain associations of collectors adsorbed on the particles. The magnitude of the hydrophobic forces contributes to the overcome of the repulsion forces providing aggregation of mineral fines (Forbes, 2011). In addition to hydrophobic forces, hydration forces also favor hydrophobic aggregation. Hydration forces are a consequence of the configurational rearrangement of water molecules in the vicinity of hydrophobic surfaces, which induces them to a state of aggregation. Hydration forces are called hydrophobic hydration by some researchers (Israelachvili and Pashley, 1984).

According to (Song *et al.*, 2000), several authors have investigated the hydrophobic aggregation of minerals, such as scheelite, wolframite, apatite, rhodochrosite, hematite, and quartz. However, despite a great number of investigations regarding the hydrophobic aggregation of fine particles, few studies have considered sulfide minerals.

This article presents the selective hydrophobic aggregation of galena by shear flocculation, as a function of suspension stirring speed and pH, aiming at the subsequent concentration of galena in fine lead and zinc ores via flotation.

2 MATERIALS AND METHODS

2.1 MATERIALS

A sample consisting of the single mineral galena was obtained from the Morro Agudo mine - Votorantim Metais. Sphalerite sample was provided by the Laboratory of Mineralogy at the University of Ouro Preto. The samples were separately crushed in an agate mortar. Their size distributions were measured by a CILAS – 1064 laser diffraction particle size analyzer and were found to have volumetric diameters d_{90} of 16.6 μm and 16.1 μm for galena and sphalerite, respectively.

2.2 HYDROPHOBIC AGGREGATION TESTS

The purpose of this study is to find selective conditions to separate fine galena from fine sphalerite by depressing the zinc mineral and creating aggregates of the lead mineral. Therefore, hydrophobic aggregation tests were divided into two groups. The first one, using depressants for

sphalerite, aimed to prevent the formation of sphalerite aggregates during the hydrophobic flocculation of galena. Previous information shows that depressants evaluated do not have effect for galena. The second group of tests was conducted with galena using collectors to correlate flocculation with parameters, such as pH and suspension stirring.

Hydrophobic aggregation tests were carried out in a 400 mL beaker with an inner diameter of 8,3 cm using a stirrer shaft with one paddle from Scientific Equipment Fisatom Ltda model 710. Mineral suspensions of 1g of mineral and 100 mL of water were first adjusted for pH using hydrochloric acid and sodium hydroxide solution, and then strongly conditioned for 10 min in the presence of a collector (amyl xanthate or propyl xanthate). Furthermore, 10 mL of suspension was gathered with a pipette for turbidity and absorbance measurements; in all tests, the pipette was placed at a fixed height of 2 cm from the base of the beaker. For tests performed with sphalerite, prior to the addition of the collector, 10 mL of depressant solution (either zinc sulfate, depropol HM, zinc sulfate + depropol HM, or dextrin + depropol HM) were conditioned with the mineral suspension for 6 min.

2.3 INFLUENCE OF STIRRING SPEED ON AGGREGATION

The effect of stirring speed on aggregation was analyzed with values of 300, 500, 700, 900, or 1100 rpm. Galena fine particles were rendered hydrophobic by amyl xanthate (10^{-4} mol/L), at pH 9 and 10 min of stirring time. Turbidity measurements were performed in a portable turbidity meter model 966 from Orbeco manufacturer - Hellige and absorbance measurements were carried out in a UV-visible spectrophotometer UV SP 2000 _ brand BEL Photonics.

2.4 INFLUENCE OF PH ON AGGREGATION

To analyze the effect of pH on aggregation, pH values of 3, 5, 7, or 9 were tested. Galena fine particles were rendered hydrophobic by amyl or propyl xanthate (10^{-4} mol/L), at a stirring speed of 500 rpm and 10 min of stirring time.

2.5 MICROFLOTATION

Microflotation of mineral aggregates was performed in a modified Hallimond flotation tube (0.415 L) with nitrogen as the bubble source. Diluted solutions of hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used for pH adjustment.

For each test, the suspension of mineral aggregates was transferred to the Hallimond tube. After the addition of MIBCOL (10 mg/L), the system was conditioned for 90 s. Next, using nitrogen gas at 70 mL/min, flotation was carried out for 120 s. Floated and nonfloated products were dried and weighed. The floatability was determined using Equation (1).

$$Recovery(\%) = \frac{mass_{floated}}{(mass_{floated} + mass_{non\ floated})} \times 100 \quad (1)$$

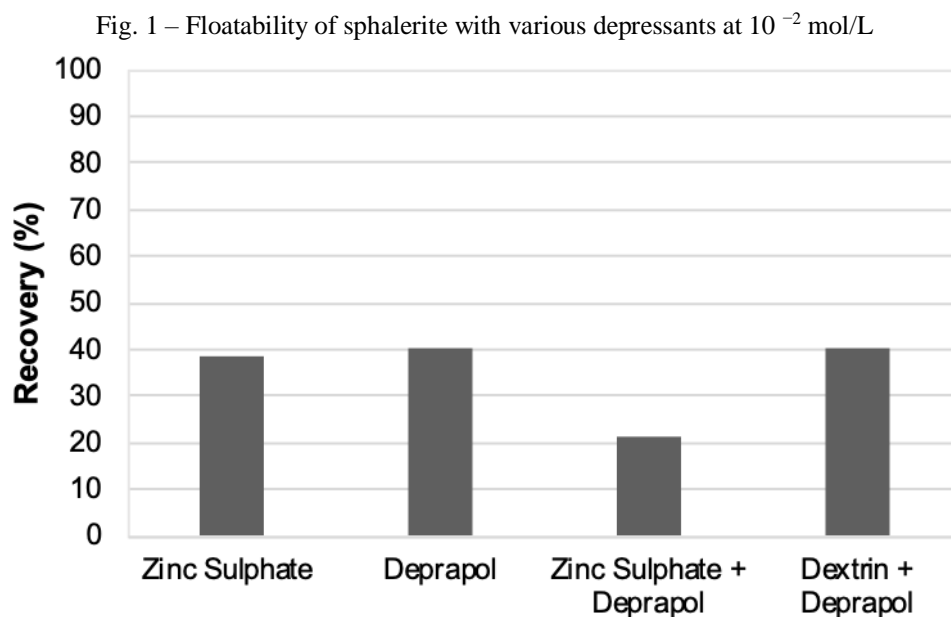
2.6 ZETA POTENTIAL MEASUREMENTS

Zeta potential determinations were obtained using a Zeta Meter 4.0 apparatus. The operation is based on the electrophoretic light scattering technique. Values of the zeta potential of galena were reported as a function of pH, in both the absence and presence of either amyl or propyl xanthates.

3 RESULTS AND DISCUSSION

3.1 TESTS WITH SPHALERITE

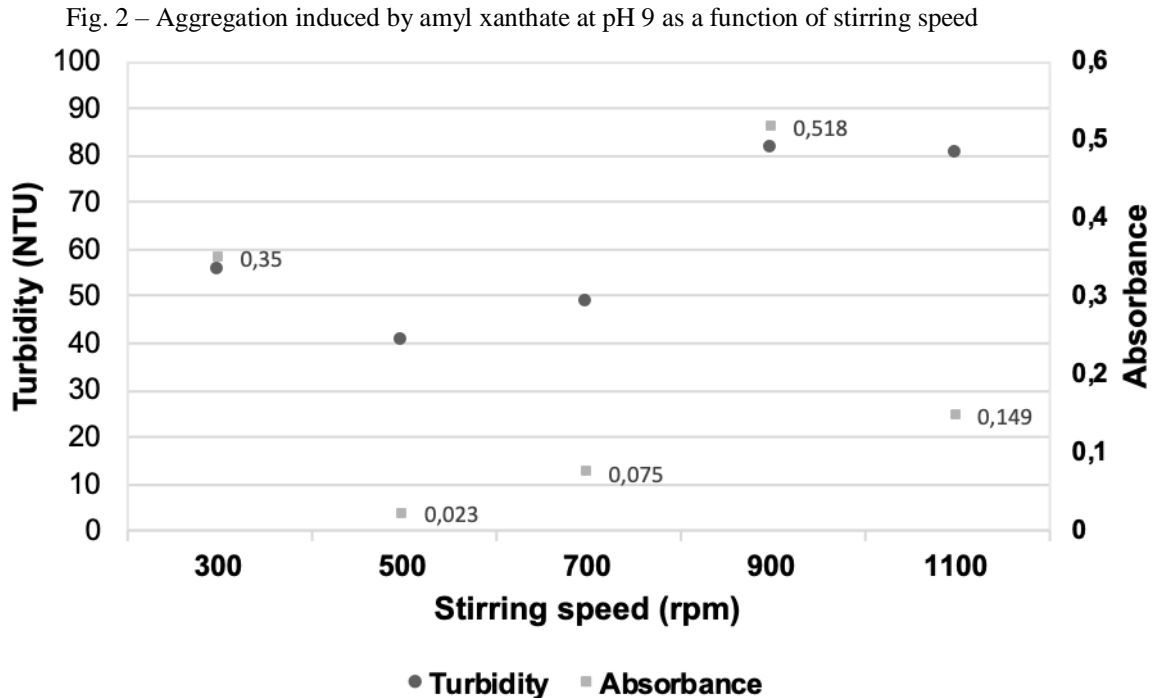
These tests were carried out to verify the most effective reagent for depressing sphalerite. Analyzing Fig. 1, one may observe that lowest floatability (21.2%) was found with a combination of reagents: zinc sulfate and deprapol HM.



3.2 EFFECT OF STIRRING SPEED

Fig. 2 shows the aggregation of galena induced by amyl xanthate at pH 9 as a function of stirring speed. The maximum aggregation was observed at 500 rpm (suspension with lower values of turbidity and absorbance). In such a system, hydrophobic particles are also charged and repel one another. Therefore, particles require enough kinetic energy to approach sufficiently close enough to allow the attractive forces to take over repulsive forces (Warren, 1975).

The decline of aggregation at high values of stirring speed indicates the rupture of hydrophobic aggregates because of the strong shear and strain forces resulting from the severe agitation of the suspension.

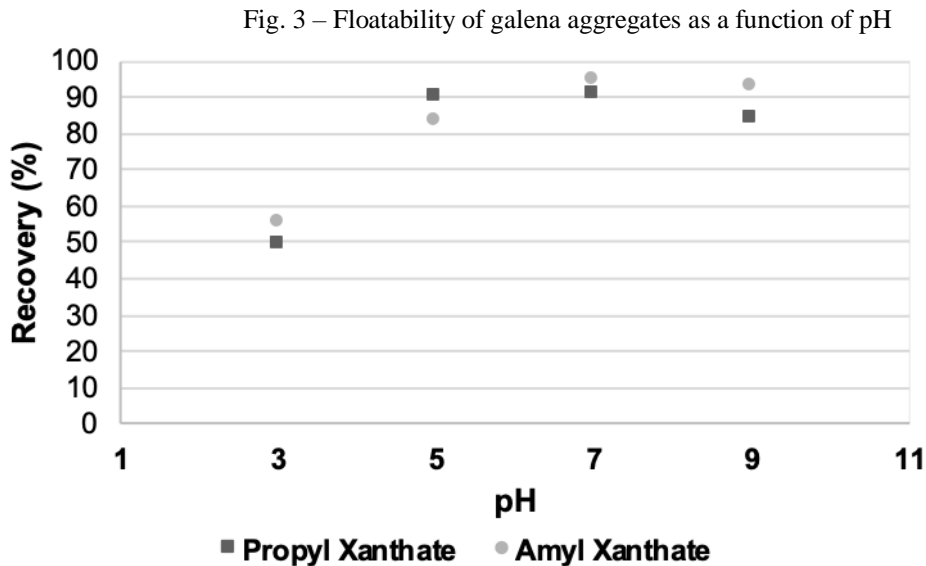


After studying the hydrophobic aggregation of several minerals, (Warren, 1975) concluded that in a laboratory, stirring speed over 500 rpm is required for aggregation. In a similar study, it was observed that the range of stirring speeds necessary for hydrophobic aggregation varies from 800 to 3000 rpm (Subrahmanyam and Forssberg, 1990). After studying the hydrophobic aggregation of galena with amyl xanthate (PAX), 5×10^{-4} mol/L, pH 6, (Song *et al.*, 2000) concluded that the largest aggregate diameter was obtained using a stirring speed of 550 rpm for a sample with particle sizes of less than 2 μm and 700 rpm for samples with particle sizes between 2 and 5 μm . The optimum value of stirring speed for achieving the maximum degree of aggregation varies from system to system and depends on variables, such as the cell geometry, particle hydrophobicity, and surface charge. Most published studies refer to the stirring speed (rpm) instead of shear rate (s^{-1}). However, stirring speed values for different systems can only be directly compared if the geometry of the tank and stirrer are identical (Warren, 1982).

3.3 INFLUENCE OF PH ON FLOATABILITY

The flotation recovery of the aggregates of galena as a function of pH is shown in Fig. 3. The floatability sharply increased with increasing pH and the lowest value of floatability at pH 5 can be

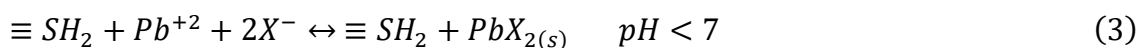
explained by the instability of xanthate in acidic medium, in which the reagent is hydrolyzed, after being converted into xanthic acid (ROCS_2H). Afterwards, this acid is decomposed into alcohol and carbon disulfide (CS_2), as shown in Equation (2).



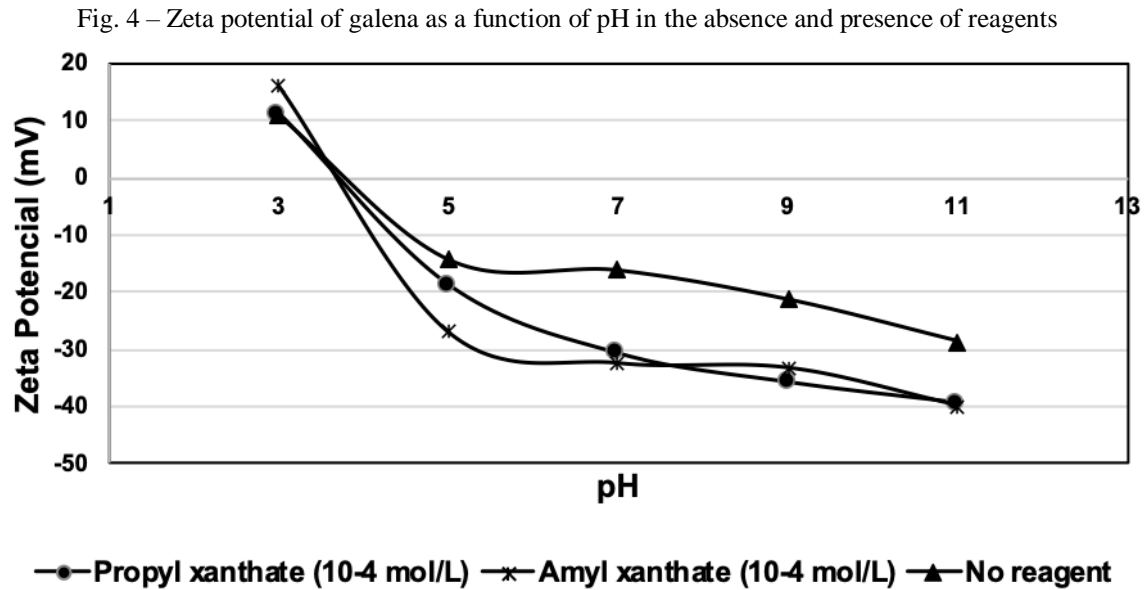
3.4 DETERMINATION OF ZETA POTENTIAL

Zeta potential is a way to measure repulsive interactions between particles aiding to evaluate aggregation behavior (Subrahmanyam *et al.*, 1990). Fig. 4 presents the zeta potential of galena as a function of pH in aqueous solution of sodium chloride ($\text{NaCl} - 10^{-3} \text{ mol/L}$) and in the presence of amyl xanthate and propyl xanthate, both at 10^{-4} mol/L .

The analysis of Fig. 4 demonstrates that for both reagents, the zeta potential became more negative with increasing pH. The xanthate reactions on the surface of galena depend on the pH of the system, as shown in Equations (3) and (4). In the acidic pH range lead xanthate is precipitated, while in the alkaline region, chemisorption of the polar group of xanthate occurs on the surface sites of galena, resulting in a more negative zeta potential (Subrahmanyam *et al.*, 1990).



Considering the classical DLVO theory and the graph of Fig. 4, the maximum dispersion is expected to occur in the basic pH range. However, Fig. 3 shows that maximum aggregation occurred at basic pH (leading to maximum floatability), which is contrary to the classical DLVO theory. This fact can be justified by the extended DLVO theory, which includes the hydrophobic forces and hydrophobic hydration forces as attractive forces that overcome the repulsion of the electric double layer.



Similar results were achieved by (Warren, 1975) in systems of quartz particles (<30 μm). The tests were conducted by conditioning the particles in the absence and presence of dodecylamine and sodium oleate. The authors observed a correlation between the state of aggregation and zeta potential in systems without surfactants where a significant aggregation was observed at zeta potential values near zero. Conversely, when proper surfactants were added, it was not possible to correlate the aggregation of the system with the zeta potential. The aggregation did not decrease with increasing the particle surface charges due to collector adsorption, whereas a correlation between particle hydrophobicity (measured by floatability) and the aggregation of the system was observed. This means that a strong attractive force arises from the hydrophobic surfaces and becomes the governing factor in the particle-particle interaction instead of the double layer electrostatic repulsion or the van der Waals attraction.

The isoelectric point (IEP) of galena was determined in the pH range of 3-4. This value is consistent with results achieved by (Healy and Moignard, 1976) who found IEP values for galena in the pH range of 2.4-4. Wide variations in the electrokinetic behavior of minerals are due to the

heterogeneity of the mineral surface, e.g., the effect of oxidation, capacity for ion adsorption, and differences in preparation and pretreatment of samples (Subrahmanyam *et al.*, 1990).

4 CONCLUSIONS

It can be concluded that hydrophobic aggregation of galena by shear flocculation is possible using amilxanthate and propilxanthate. Additionally, suitable conditions to prevent the formation of sphalerite aggregates during the hydrophobic flocculation of galena were investigated. The combination of deprapol HM + zinc sulfate showed the best results.

The stirring speed influenced the formation of the aggregates. The maximum aggregation was observed with a stirring speed of 500 rpm. Above this critical speed, the hydrophobic aggregates break up as a result of the stirring action.

The pH has an influence on the charge distribution of the particles. In the presence of both collectors (amyl xanthate and propyl xanthate), the zeta potential of galena became more negative with increasing pH. However, increasing the surface charge did not decrease the aggregation, but rather enhanced it. These results suggest that aggregation is a consequence of collector adsorption on the surface of galena, which increases the hydrophobic attraction to overcome the repulsive forces of electrical double layer, which is considered by X-DLVO theory

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REFERENCES

- FORBES, E. Shear, selective and temperature responsive flocculation: A comparison of fine particle flotation techniques. **International Journal of Mineral Processing**, v. 99, p. 1-10, 2011.
- HEALY, T. W.; MOIGNARD, M. S. A Review of electrokinetic studies of metal sulphides. In: Fuerstenau, M.C. **Flotation: A. M. Gaudin Memorial Volume**. New York: American Institute of Mining, Metallurgical, and petroleum Engineers, Inc, 1976. 637 p.
- ISRAELACHVILI, J. N.; PASHLEY, R. M. Measurement of the hydrophobic interaction between two hydrophobic surfaces in aqueous electrolyte solutions. **Journal of Colloid and Interface Science**, v. 98, p. 500-514, 1984.

GAUDIN, A. M., GROH, J. O., HENDERSON, H. B. Effect of particle size on flotation. **AIME, Tech. Publ.** v. 414, p. 3-23, 1931.

SONG, S.; VALDIVIESO, A. L.; BAHENA, J. L. R; PEREZ, H. I. B.; TRASS, O. Hydrophobic flocculation of galena fines in aqueous suspensions. **Journal of Colloid and Interface Science**, v. 227, p. 272-281, 2000.

SONG, S.; VALDIVIESO, A. L.; BAHENA, J. L. R; PEREZ, H. I. B. Hydrophobic flocculation of sphalerite fines in aqueous suspensions induced by ethyl and amyl xanthates. **Colloids and Surfaces A: Physicochemical and Engineering Aspects**, v. 181, p. 159–169, 2001.

SUBRAHMANYAM, T. V.; SUN, Z.; FORSSBERG, K. S. E.; FORLING, W. Variables in the shear flocculation of galena. *In*: GRAY, P. M. J; BOWVER, G. J; CASTLE, J. F; VAUGHAN, D. J. **Sulphide deposits-their origin and processing**. Dordrecht: Springer, 1990 p. 223-231.

SUBRAHMANYAM, T.V.; FORSSBERG, K. S. E. Fine particles processing: shear flocculation and carrier flotation – a review. **International Journal Mineral Processing**, v. 30, p. 265-288. 1990.

TRAHAR, W. J.; WARREN, L. J. The flotability of very fine particles --A review **International Journal of Mineral Processing**, v. 3, p. 103-131, 1976.

WARREN, L. J. Shear flocculation of ultrafine scheelite in sodium oleate solutions. **Journal Colloid Interface Science**, v. 50, p. 307–318, 1975.

WARREN, L. J. Flocculation of stirred suspensions of cassiterite and tourmaline. **Colloids Surfaces**, v. 5, p. 301–319, 1982.

WARREN, L. J. Shear flocculation. *Developments in Mineral Processing*. **Colloidal Chemistry in Mineral Processing**. Elsevier Science Publishers, New York, USA, v.12, p. 309-329, 1992.

XU, Z.; YOON, R. H. The Role of Hydrophobic Interactions in Coagulation. **Journal of Colloid and Interface Science**, v. 132, p. 532-541, 1989.