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Tannins: the organic depressants alternative in selective flotation of sulfides

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ABSTRACT

The use of quebracho extract as a pyrite depressing agent to improve Cu/Fe ratio in copper minerals flotation was studied. The depressing effect in the case of pure pyrite, pure chalcopyrite and a sample of disseminated copper ore was tested considering different pH values and modifiers, and different levels of tannin addition. Results show that quebracho extract can be considered a cleaner option in these processes.

1. Introduction

In terms of world production, copper is the second base metal in importance with current world production levels above 18 Mton (million of metric tons- US Geological Survey, 2014). Main producers are Chile (5.7 Mton), China (1.6 Mton), Peru (1.3 Mton) and US (1.2 Mton), and estimated reserves are located mainly in Chile (190 Mton), Australia (87 Mton) and Peru (70 Mton). The global economic importance is huge (only in the US was estimated in $9 billion in 2013), so companies and institutions increase their efforts steadily to incorporate in the whole production chain the sustainability standards, which can lead as much as possible to the integration of the ecological, ethical, economic, and technological dimensions.

To understand the environmental implications of copper production, it is neccesary to point that copper content in ore deposits (mainly as sulfides) are barely greater than 1%, so figures of volume of mined rock (open pit and underground), power consumption and water use are huge. This fact affects the environmental impact and social perception of copper mining activity, both at great and small scale.

Currently, about 80 percent of global copper production is extracted from sulfide sources. Development of froth flotation techniques, particularly in the synthesis of highly selective collectors, has been a key point in the possibility of processing large amounts of low metal content ores as is the case of disseminated Cu ores, in processing plants up to 150,000 metric ton per day (Singer et al., 2005). In almost all cases, attaining high levels of selectivity in pyrite separation becomes a priority (Bulatovic and Wyslouzil, 1998).

To carry out these flotation processes, a variety of chemical reagents are employed to modify the physicochemical properties in the pulp and/or on the mineral surface, in the most selective way possible (Bulatovic and Wyslouzil, 1998). The environmental impact of these processes is directly related to the use and toxicity of the reagents (Gunson et al., 2012; Nedved and Jansz, 2006).

Recently, some works have studied the impact of flotation reagents on water quality (Liu et al., 2013a, 2013b) concluding that more research is needed in the area associated with solutions to problems in the biotic domain and that costs of environmental and human health issues associated with flotation reagents most be solved.

The focus of this paper is on the study of organic depressant reagents which are cleaner than the conventional ones. The aim of using depressants is to avoid specific minerals in a specific part of the process becoming hydrophobic (Castro, 1981). Being pyrite (iron sulphide) the main gangue mineral associated with copper sulphides, it is of the main interest to study conditions to obtain selective depression of pyrite. In the case of Cu–Mo flotation plants, inorganic depressant reagents are commonly used, such as cyanide, Na_2S, NaSH or some sulphites. The main drawbacks in using inorganic depressants are reagent toxicity and high consumption levels,

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so the need to find alternative reagents has been repeatedly expressed (Laskowski et al., 2007a,b; Subramanian and Nyamekye, 1993a,b; Mackenzie, 1986a,b).

In the case of Na_2S, the depression effect is reached at a very high reagent concentration (Bulatovic and Wyslouzil, 1998), with collector/depressant concentration ratio of 10 and even higher (Bulatovic, 2007). In the case of NaSH, consumption rates are even higher because of oxidation decomposition, so the injection of CO_2 in flotation cells is obligatory and maintaining reagent levels in pulp is a difficult task (Buckley et al., 1988). Finally, it is well known that cyanide is a strong sulphide depressant, but in the case of Cu–Mo flotation, consumption rates reach 10 kg/t.

The use of organic depressant reagents as an alternative has been suggested in previous work; Lopez-Valdivieso et al. (2004) proposed the use of polysaccharides as clean sulphide depressants, because of their biodegradability and very low pollution potential. They also suggested that quebracho absorption on the mineral surface can be influenced by the presence of certain ions (Ca^{2+}, Fe^{3+}, Al^{3+}, etc.) which could form insoluble compounds with quebracho extract.

In this paper, the use of quebracho extract as a sulphide depressant was studied. This extract, which is tannin (a complex mixture of natural polyphenols), is obtained from the quebracho tree (*Schinopsis balansae*). This tree grows mainly in northern Argentina and some areas of Paraguay (Lincoln, 2006). Tannin is a non-toxic, biodegradable reagent, approved for use as a flocculant in water purification plants in several countries and also as a dispersant in drilling muds, due to its surfactant properties on particles in a water suspension (Watkins and Whyne, 1957).

References to the use of quebracho extract in froth flotation can be found recently in the depression of calcite, dolomite and other gangue minerals. Inorganic depressants work in alkaline conditions. An advantage of tannins is that the depressing function is active in both acidic (in some cases the effect is even stronger below pH 4.5) or alkaline conditions (Sarquís et al., 2011). Inskra et al. (1980) focused on the depressant effect of different tannins for pure pyrite flotation. They observed that all tannins studied depressed pyrite more than the controls at pH $<$ 10 and one particular tannin showed a strong depression maximum at pH 7. More recently, Liu et al. (2012) focused on the use of tannins as a depressant in a mix system separating chalcopyrite from pyrite via froth flotation.

The contribution of the experiments presented here is the evaluation of tannin as a selective depressant in sulphides differential flotation, particularly for pyrite depression, defining the conditions leading to the optimal selectivity and efficiency in the flotation process.

2. Experimental

Laboratory flotation tests on samples of pure pyrite and pure chalcopyrite were performed in a Hallimond tube device to study the depressant effect of quebracho extract. In the case of samples of disseminate ores from Argentina, Chile and Peru, flotation tests were performed in a Denver lab flotation cell.

2.1. Tests carried out on pure pyrite sample

A program of laboratory tests was designed to study the influence of basic flotation variables, as tannin concentration and pH. The concentration of Cu^{+2} ion was aldo studied, because this cation is always present in sulphide flotation pulps and is known to form insoluble compounds with tannin, reducing its availability in the pulp to act as a depressant (Mackenzie, 1986a,b).

In the case of tannin concentration, a pH value of 8 was selected for the test. The pH modifier selected was sodium carbonate. As a collector, ethyl xanthate was used with a constant concentration of 60 mg/l. The flotation tests in this study were carried out in a 300 cm^3 Hallimond tube (Parekh and Miller, 1999). A 2 g sample of material with size of 45–150 μm was used for each test. After a 5 min conditioning period with collector, and pH adjusting, flotation was carried out for 4 min. After the flotation tests, the concentrate and tailing were carefully filtered, dried, and weighed. The experimental error was determined using the experimental repeatability; therefore, the experiments were repeated three times and the error was estimated in the order of 2.5%.

The effect of pH in the range pH 4–10 on pyrite recovery was studied using the following modifiers: HCl (solution 1% v/v) (acid range); lime powder (assay >99%) and NaOH (assay >97%) (alkaline range). Tannin concentration was set at 0.25 g/l and collector consumption was the same as in the previous series of tests, 0.60 mg/l.

Finally, in the case of pure pyrite the influence of Ca^{2+} ions on the depressing effect of quebracho extract was also studied. Some flotation tests were prepared using NaOH to adjust the pH conditions, without Ca^{2+} or tannin addition. Another series of tests was prepared using CaO to adjust pH conditions, without tannin. Finally, tests with CaO and 30 g/l of quebracho extract were carried out.

2.2. Tests on pure chalcopyrite sample

A series of flotation tests were carried out on pure chalcopyrite. Flotation procedure in the Hallimond tube was similar as described above, tests were made with NaOH as pH regulator, with and without tannin addition (0.3 g/l).

2.3. Tests on a disseminated copper ore

Due to lack of mineral homogeneity, the differences in flotation behaviour of minerals are usually revealed at different flotation stages at industrial scale. Flotation tests with real run-of-mine samples cannot be carried out in the Hallimond tube, since representative sample size is larger and a device with greater capacity is required. In this case, flotation tests were performed in a Denver laboratory machine. Tests were conducted on 1 kg ore samples in a Denver lab flotation cell, using HCl and lime as pH modifiers, in the range 5.5–10.5, to determine the effect of pH, tannin concentration and number of cleaning stages. Experimental error both in recovery and Cu grade was proven to be less than 5%.

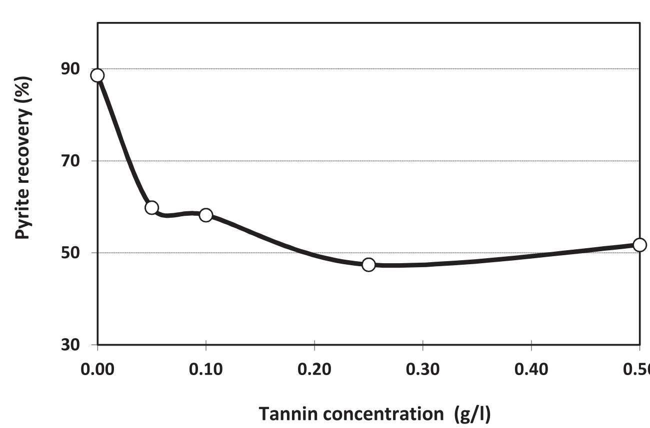

Fig. 1. Effect of tannin concentration on pure pyrite flotation.

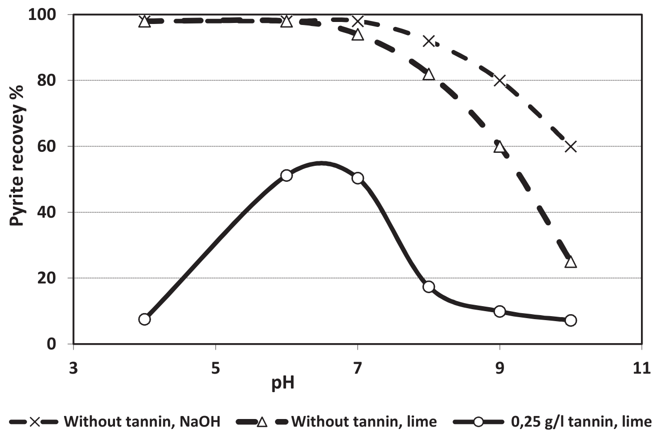

Fig. 2. Effect of pH on depressing action of tannin, along with curves recovery-pH using different modifiers (CaO, NaOH).

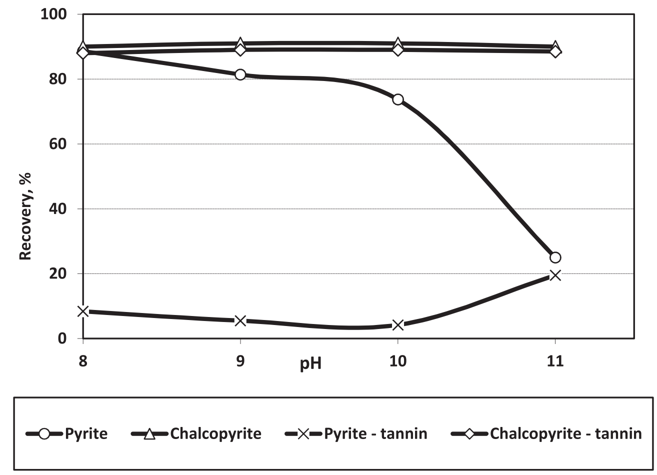

Fig. 4. Comparison between pyrite and chalcopyrite, with and without tannin.

3. Results and discussion

3.1. Tests carried out on pure pyrite sample

Results obtained with tannin concentration variation between 0.0 and 0.5 g/l are plotted in Fig. 1. A steep decrease in pyrite recovery with tannin addition can be observed, reaching a minimum at 0.25 g/l and showing that higher concentration does not improve the depressing effect.

Results with pure pyrite cannot be directly extrapolated to the industrial flotation of Cu ores, since tests were made with distilled water and pyrite content in industrial flotation ranges between 2% and 25%. At industrial scale, as mentioned above, the presence of Cu and Fe ions with tannin results in the formation of insoluble compounds, reducing tannin absorption on the pyrite surface. As a consequence of this, in each case flotation conditions and reagent concentration to best pyrite depression at industrial scale must be determined.

The effect of pH in the range pH 4–10 on pyrite recovery was studied, and results are plotted in Fig. 2, as well as pH-recovery curves without depressant, in the case of CaO and NaOH as modifiers. It can be seen that without tannin, the depressing effect with increasing pH starts at pH 7, when the presence of OH^- ions compete with the tannin to be absorbed on the pyrite surface. This effect is more visible when using CaO, because of the additional hydrophilicity produced when Ca^{2+} ions are absorbed on the pyrite surface. In the case of quebracho extract addition, the depressing effect is improved throughout the pH range, showing the strongest effect in both alkaline and acid range.

Results in Fig. 2 seems different to those reported by Inskra et al. (1980), and this can be explained by surface oxidation of pyrite: fresh pyrite presents a behaviour similar to that reported by Inskra, while some surface oxidation of pyrite results in a behaviour similar to that depicted in Fig. 2.

Finally, the influence of Ca^{2+} ions on the depressing effect of quebracho extract was also studied. In Fig. 3, the obtained results are plotted. In all cases, 30 mg/l of $CuSO_4$ were added, which is the reference level found in process water at Bajo de la Alumbrera Mine (Argentina). It seems clear that the presence of Ca^{2+} ions improves the tannin depressing effect.

3.2. Tests on pure chalcopyrite sample

Initial research focused on differential behaviour between pyrite and chalcopyrite. The only previous report found about the depressing effect of tannin in the case of chalcopyrite is the work of Liu et al. (2012), using lignosulfate calcium; Inskra et al. (1980) reported tannin use only on chalcocite and Liu et al. (2000)

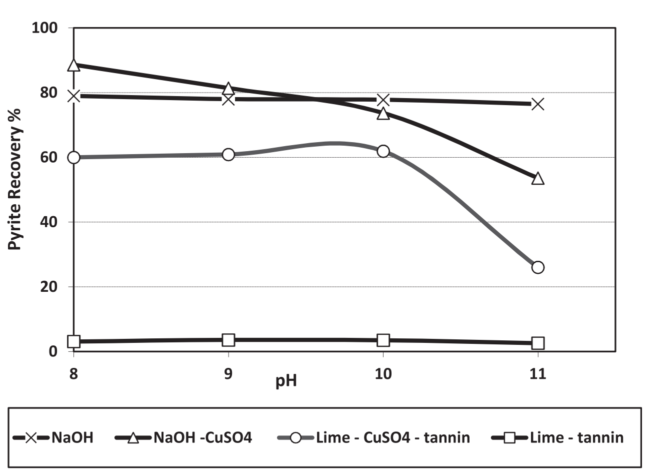

Fig. 3. Effect of Ca^{2+} concentration on depression action of tannin, using: a) NaOH; b) NaOH and $CuSO_4$; c) Lime, $CuSO_4$ and tannin; d) Lime and tannin.

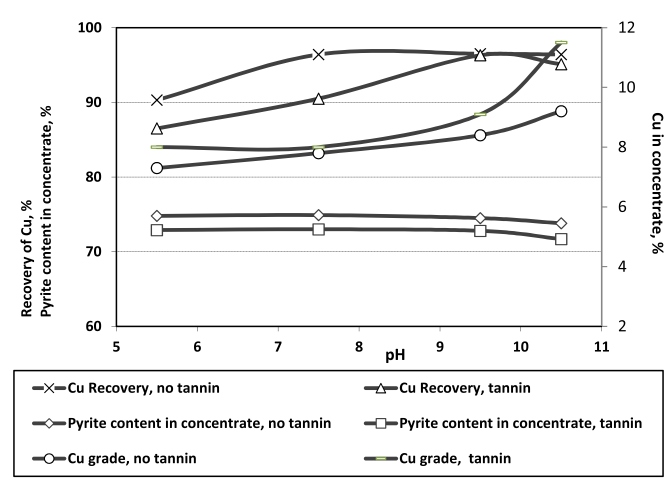

Fig. 5. Effect of tannin on disseminate copper ore; tests at different pH, with and without tannin.

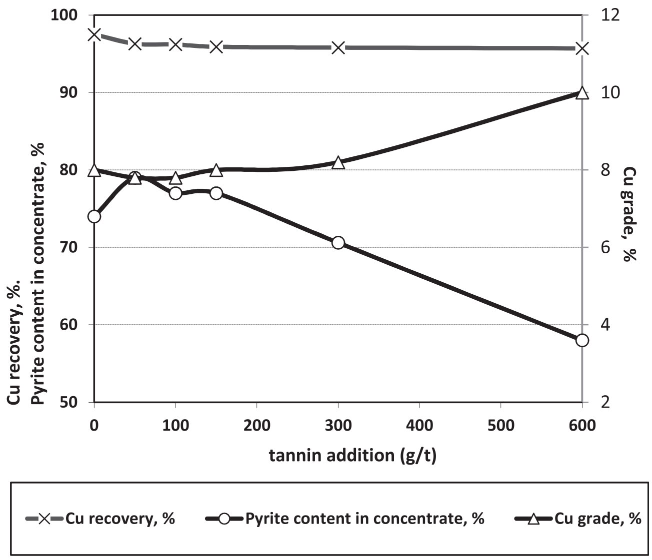

Fig. 6. Effect of tannin addition on a disseminated copper ore flotation.

reported on chalcopyrite depression using dextrin. In all cases a strong influence of pH in the acid range was evident.

Results of flotation tests carried out on pure chalcopyrite are compared in Fig. 4 with those corresponding to pyrite in the same conditions; it can be easily concluded that the selectivity of tannin action is marked in the pH range studied, especially below pH 10.

3.3. Tests on a disseminated copper ore

In the first series of tests, the tannin addition was set at 300 g/t. Plots of Cu recovery and grade in concentrate, with and without tannin addition, and also of pyrite content values, obtained via microscopy analysis are presented in Fig. 5. In the case of Cu recovery, the depressing effect of tannin is clear in the range 5.5–9, whereas in the range 9–11 it seems to show little influence (of note, the usual pH value in copper industrial flotation is within the range 9.5–11). On the contrary, in the case of Cu content in concentrate, pH above 9 yields higher grade concentrates when using tannin. Finally, in the case of pyrite content in concentrate, the effect of tannin reduces the pyrite recovery in concentrate throughout the pH range considered.

In a second series of tests, pH was set constant at 10 using lime, and tannin addition was tested from 0 to 600 g/t. With pulp conditioned al pH 10 we can expect high pyrite depression with high Cu content and recovery in concentrate (as seen Fig. 5).

Results are presented in Fig. 6. As can be observed, tannin addition entails a slight loss in Cu recovery (around 1 point), whereas in the case of Cu grade the improvement is noticeable above 300 g/t of tannin addition, reaching 12% Cu in concentrate at 600 g/t of tannin. This improvement of Cu grade is directly related with the pyrite depression, and the plot of pyrite recovery in concentrate decreases steadily from 150 g/t to 600 g/t of tannin addition.

Additional tests on Cu ores from Argentina, Peru and Chile (Sarquís et al., 2011) indicated that the depressing effect of tannins on pyrite increases the Cu/Fe ratio in concentrates between 8 and 40%, at different operating conditions and for different ores.

4. Conclusions

The quebracho extract (tannin) is a good depressing agent of pure pyrite, this depressing action being influenced by tannin addition and pH. In the case of pure chalcopyrite, the depressing action is moderate.

The depressing effect on pyrite, in the case of disseminated copper ores is enhanced in the alkaline range. At pH above 9.5 the Cu grade in concentrates increases due to the reduction of pyrite content.

Additional tests indicate that the depressing effect of tannins on pyrite increases the Cu/Fe ratio in concentrates between 8 and 40%, at different operating conditions and for different ores.

The quebracho extract can be considered a cleaner alternative to conventional depressing reagents in sulphide flotation.

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