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Effect of Magnesium on the Hydrophobicity of Sphalerite

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Abstract: The use of untreated recycled water has negative effects in the flotation of zinc sulfide ores due to the presence of dissolved species, such as magnesium and calcium. Although it has been found that magnesium is a more potent depressant than calcium, it has not been investigated in this role or for the effect of adding sodium carbonate. The results of an investigation to evaluate the effect of magnesium on the hydrophobicity of Cu-activated sphalerite conditioned with Sodium Isopropyl Xanthate (SIPX) are presented. Zeta potential of natural and Cu-activated sphalerite as a function of the conditioning pH and Cu(II) concentration, respectively, was first evaluated. Later, the effect of pH and presence of magnesium on the contact angle of Cu-activated sphalerite conditioned with SIPX was studied; it was also evaluated the effect of sodium carbonate to counteract the effect of magnesium. Cu-activation enhances the zeta potential of sphalerite up to a concentration of 5 mg/L. Contact angle tests, thermodynamic simulation, and surface analysis showed that magnesium hydroxide precipitates on the sphalerite surface at pH 9.6, decreasing its hydrophobicity. Addition of sodium carbonate as alkalinizing agent precipitates the magnesium in the form of a species that remained dispersed in the bulk solution, favoring the contact angle of Cu-activated sphalerite and, consequently, its hydrophobicity. It is concluded that the use of sodium carbonate as alkalinizing agent favors the precipitation of magnesium as hydromagnesite ($Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O$) instead of hydroxide allowing the recovery of sphalerite.

Keywords: sphalerite; hydrophobicity; water chemistry; contact angle; magnesium



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1. Introduction

The management of water resources has become an important issue in sulfide concentrators due to the increasing requirements to use high proportions of recycle water from tailings dams, thickener overflows, dewatering, and filter products. Further, the extraction and transportation of fresh water are usually expensive. As a result, the mineral processing industries have adopted water recycling as a common practice in most of the countries, even in those where water scarcity does not represent a current problem. Accordingly, recent studies have focused on the treatment and effects of using recycled water to concentrate sulfide ores [1–5].

Recycled water may contain chemical species that contribute to the already complex chemistry of the flotation process. The ions found in the recycled water interact with the mineral surface causing inadvertent activation of undesirable minerals or depression of valuable ones, affecting the recovery and selectivity of mineral concentration [2,6]. The species commonly present in such water are colloidal material (e.g., silicates, clays, metal hydroxides, gypsum, etc.), base metal ions, hydroxo-complexes, sulfate, sulfite, thiosalts, chloride, magnesium, calcium, sodium, and potassium; as well as traces of organic-based substances as frothers, collectors, and depressants [7].

The role of calcium and magnesium in the flotation of sphalerite have been already studied since both are nearly always present. Calcium has received more attention and although important advances have been made, there are still phenomena to elucidate.

Levay et al. [2] evaluated the role of several water chemistry parameters (e.g., chemical composition, pH, dissolved oxygen, redox potential, and microbiological factors) on the flotation performance of an industrial operation. The authors associate the presence of calcium, magnesium, and iron salts with the precipitation of compounds that adversely affects the recovery of valuable sulfides. The researchers delved into the nature of the calcium precipitates, but did not investigate the magnesium ones.

El-Ammouri et al. [8] conducted a study making use of settling and turbidity techniques to determine the effect of magnesium (50 mg/L) and pH on the aggregation behavior of sphalerite and chalcopyrite samples as well as industrial slurries. According to the authors, adsorption of magnesium hydroxo-complex (i.e., MgOH^+) and magnesium hydroxide (i.e., $\text{Mg}(\text{OH})_2$) at pH above 9 causes aggregation of the particles by an electrostatic bridging mechanism and when the particles become fully covered by abstracted magnesium hydroxide (between pH 10 and 11) repulsive forces appear between them and aggregation diminishes.

Lascelles et al. [9] studied the effect of magnesium (50 mg/L) on the flotation behavior of Cu-activated sphalerite in the range of pH from 8 to 13 and compared it with the effect of calcium (500 mg/L). The authors found that the flotation of Cu-activated sphalerite with ethyl xanthate was depressed by magnesium at pH above 10. Since copper adsorption and xanthate uptake were not substantially affected by the presence of magnesium, depression was attributed to the adsorption of magnesium species, particularly the precipitated hydroxide; this phenomenon was confirmed by XPS. The authors concluded that magnesium is a more potent depressant than calcium since the later did not show a significant contribution to depression at pH below 12.

This work was aimed to study the effect of magnesium on the hydrophobicity of Cu-activated sphalerite conditioned with Sodium Isopropyl Xanthate (SIPX). Although some studies have been carried out to determine the pH range in which magnesium affect the floatability of Cu-activated sphalerite, it is necessary to delve into the contact angle behavior and thermodynamics of the responsible magnesium species. The effect of adding sodium carbonate as alkalizing agent has not been evaluated and neither has the mechanism by which it counteracts the negative effect of magnesium. For this purpose, the zeta potential of natural sphalerite as a function of the conditioning pH and Cu-activated sphalerite at pH 9 as a function of Cu(II) concentration was first evaluated; at this stage, sphalerite surface analysis by Scanning Electron Microscopy and Energy-Dispersive Spectrometry (SEM-EDS) to evaluate the adsorption of $\text{Cu}(\text{OH})_2$ was carried out. Later, the effect of pH and presence of magnesium on the contact angle of Cu-activated sphalerite further conditioned with SIPX was studied; it was also evaluated the effect of adding sodium carbonate (Na_2CO_3) to counteract the effect of magnesium. Contact angle results were complemented with thermodynamic simulation of the $\text{Mg}-\text{H}_2\text{O}$ and $\text{Mg}-\text{CO}_3-\text{H}_2\text{O}$ systems and characterization by Schottky Field Emission ultra-high-resolution Scanning Electron Microscopy Energy Dispersive X-ray Spectrometry (Schottky FE-SEM-EDXS) to identify the nature of the formed precipitates and evaluate their texture.

2. Materials and Methods

2.1. Materials and Reagents

Sphalerite specimens used are high-pure samples collected from the mining district of Bismark mine (Ascensión, Chihuahua, Mexico). Elemental analysis (wt.%) of the specimens obtained by Atomic Absorption Spectroscopy (AAS, PerkinElmer AAnalyst 200) and Inductively Coupled Plasma (ICP, Perkin Elmer Optima 8300) are as follows: 59.07% Zn, 29.09% S, 0.03% Cu, 5.71% Fe, 0.012% Pb, and 6% insoluble species. X-ray diffraction (Philips X-Pert) analysis revealed that the only major mineral species present in the sample is sphalerite.

The presence of magnesium and its concentration range was noted after a sampling campaign to determine the process water quality of four lead-zinc sulfide ores flotation

plants. Chemical species were determined by AAS and ICP and the results were useful to determine the magnesium concentration to evaluate its effect on sphalerite hydrophobicity.

Magnesium was added as magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$) while copper used to activate sphalerite was copper sulphate (CuSO_4), both reagent grade. Purified sodium isopropyl xanthate (SIPX) was used as collector. In all the experiments deionized and deoxygenated water of a constant ionic strength of 10^{-2} mol/L NaNO_3 (reagent grade) were used. The pH was regulated by adding 0.01 mol/L solutions of sodium hydroxide (NaOH) and hydrochloric acid (HCl), as required. Sodium carbonate (Na_2CO_3) added as alternative alkalizing agent was also reagent grade.

To properly study the effect of magnesium on the hydrophobicity of sphalerite the contribution of factors such as particle size, mineral composition, and water chemistry were kept constant.

2.2. Zeta Potential

Zeta potential measurements were carried out using a Pen Kem zeta potential analyzer (Lazer Zee Meter 501), which allows the direct reading of the zeta potential calculated from the electrophoretic mobility of the particles in suspension and the Smoluchowski equation. The zeta potential of natural and Cu-activated sphalerite was measured from a suspension of 1 g/L of ground mineral (ionic strength of 10^{-3} mol/L NaNO_3) as a function of pH and Cu(II) concentration, respectively. The suspensions were conditioned for 15 min under nitrogen bubbling in a stoppered Erlenmeyer flask under constant magnetic stirring. To minimize mineral oxidation and atmospheric oxygen absorption, sphalerite was ground prior to each measurement and the flask was equipped with a vent which allows nitrogen exhaust. The pH of the suspension was regulated by adding 0.1 mol/L NaOH or HCl, as required.

The measurements were carried out in triplicate so that the average zeta potential obtained and the error bars defining the 95% confidence interval of a student's t-distribution is reposted.

2.3. Contact Angle

The captive bubble technique is the most used method to measure the contact angle of minerals concentrated by froth flotation. It has some advantages, for example, it requires few square millimeters of mineral surface and a small volume of liquid [10]. This technique has been described in detail in previously published research [11,12]. In general, the technique consists in grinding the sample using deionized and deoxygenated water. Followed by conditioning the polished sample under the chemical environment of interest. Subsequently, the sample surface, which is immersed in the aqueous solution, is contacted with an air bubble of about 1 mm diameter. The resulting contact angle is measured with the help of image analysis software. Three chemical environments were evaluated, which are described below.

1. The sphalerite sample was activated with 50 mg/L of Cu(II) at pH 5.4 for 15 min. The sample was then decanted and further conditioned during 5 min with 10^{-4} mol/L SIPX at the pH of interest (i.e., from 5 to 11) and the contact angle was measured in the latter solution.
2. After copper activation as in previous experiment, the sample was conditioned during 5 min in the presence of both SIPX and magnesium (50 mg/L) at the pH of interest (8 to 11.5). Then, the contact angle was measured.
3. After copper activation as in previous cases, the sample was conditioned during 5 min in the presence of SIPX, magnesium, and sodium carbonate (2 g/L). The pH was adjusted at 10.5 and 11 because in previous tests high mineral depression was observed at these values. Then, the contact angle was recorded and measured in a 10^{-3} mol/L NaNO_3 solution of the same pH values (i.e., 10.5 and 11) to avoid the optical interference caused by the precipitates.

The generic term Cu(II) is used to refer to both the cation Cu^{2+} , which is the predominant copper species at pH below 6, and to the solid $\text{Cu}(\text{OH})_2$, which predominates at pH above 6.

The experiments were carried out in triplicate so that the mean of the measured contact angle error bars defining the 99% confidence interval of a student's t-distribution are reported.

2.4. Thermodynamic Simulation, Surface Analysis, and Characterization

The thermodynamic analysis of the Mg-H₂O and Mg-CO₃-H₂O systems was performed making use of HSC Chemistry v.6 software. In the case of Mg-CO₃-H₂O, the computation conducted consisted in adding an accumulation amount of sodium carbonate from 0 to 2 g to 1 L of water of pH 7 containing 50 mg of magnesium (added as $\text{Mg}(\text{NO}_3)_2$) at 25 °C and 1 atm. The conditions used in the thermodynamic simulation are similar to those encountered in industrial operations, in the sense that not enough time is allowed for the aqueous system to reach equilibrium with the atmospheric CO₂ (0.035% by volume). This fact was simulated by considering a relatively small volume of atmosphere per liter solution (e.g., 22.4 L). The amount of sodium carbonate added in the contact angle measurements and the thermodynamic simulation is similar to that used in the industrial concentrators.

Characterization techniques were employed to complement the experimental results and thermodynamic simulation. In the case of the evaluation of the zeta potential of Cu-activated sphalerite, the mineral surface was analyzed by Scanning Electron Microscopy coupled with Energy-Dispersive Spectrometry (Philips XL30-ESEM) to evaluate the adsorption of $\text{Cu}(\text{OH})_2$. The contact angle measurements were also complemented by surface analysis of the Cu-activated sphalerite (SIPX + Mg and SIPX + Mg + Na₂CO₃) by Schottky Field Emission ultra-high-resolution Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectrometry microanalysis system (JEOL JSM-7800F Prime) to evaluate the texture of the precipitates and chemical composition.

Sample preparation of surface characterization was performed under similar conditions to those used in the experimental tests (i.e., zeta potential and contact angle). First, a sphalerite crystal was activated with Cu(II) and, second, it was conditioned with SIPX/Mg/Na₂CO₃ depending the case. The samples were removed from the aqueous solution and left to dry at room temperature in a dissector with the purpose of evaporating the water present on the mineral surface; then a gold coating was applied to the surface by sputtering. The samples were characterized by SEM-EDS and FE ultra-high-resolution SEM-EDXS.

3. Results and Discussion

3.1. Process Water Chemical Characterization

To carry out this investigation the process water of four lead-zinc sulfide ores concentrators was chemically characterized to determine the proper magnesium concentration, the results are shown in Table 1.

Table 1. Main metals and sulphate ions concentrations present in the process water of four lead-zinc sulfide ores flotation plants.

Plant	Fe (mg/L)	Pb (mg/L)	Zn (mg/L)	Cu (mg/L)	Ca (mg/L)	Mg (mg/L)	SO ₄ (mg/L)
1	0.54	2.15	112	0.35	587	471	4127
2	0.36	0.44	0.158	–	566	124.7	1809
3	0.003	0.014	0.398	0.573	665	11.2	1910
4	1.59	0.07	1.03	0.011	270	37.2	–

It is generally accepted that the chemical species listed in the Table 1 have an adverse impact on the mineral recovery and selectivity. As can be seen, magnesium concentration varies from 11 to 471 mg/L but, since very high concentrations would make very difficult

the experimentation, 50 mg/L was chosen as a proper value. This value is in accordance with previous research [8,9]. It is also observed the presence of chemical species as iron, lead, zinc, copper, calcium, and sulfate; these species are derived from the mineral species contained in the ore like copper sulfides (e.g., chalcopyrite and bornite), pyrite, and non-sulfide gangue.

The process water reported in Table 1 is used in the grinding and flotation circuits, and it is made up of different sources as thickeners overflow, tailings dam, and fresh water. Several potentially detrimental chemical species were detected. However, only magnesium was considered to elucidate its effect on the hydrophobicity of sphalerite.

3.2. Zeta Potential of Sphalerite

The isoelectric point of sphalerite (i.e., IEP) depends on the pH of the preconditioning stage, degree of oxidation of the mineral surface, and iron content [13–17]; IEP values between 2 and 7 are common. Zeta potentials of natural sphalerite as a function of the conditioning pH and Cu-activated sphalerite at pH 9 as a function of Cu(II) concentration were evaluated. It can be observed in Figure 1 that sphalerite develops negative charge along the pH range from 5 to 10. The potential determining ions in absence of oxidation products are those of water, that is hydrogen and hydroxyl ions. It appears that proton adsorption onto sulfur sites is favored in acid solutions, giving rise to a slightly positively charged surface. Under neutral or alkaline conditions, adsorption of hydroxyl ions onto the zinc sites is favored, resulting in a negatively charged surface.

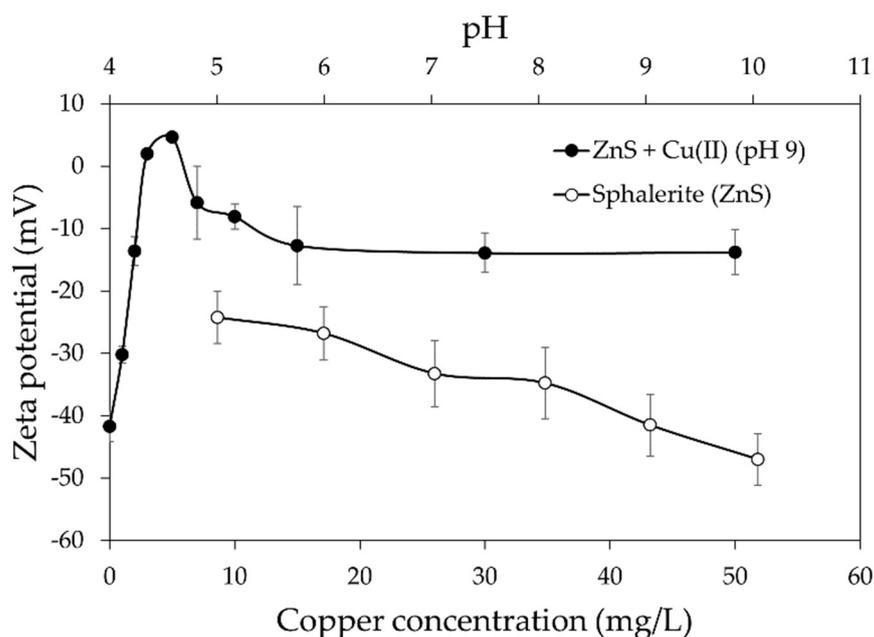


Figure 1. Zeta potential of sphalerite as a function of conditioning pH and Cu-activated sphalerite at pH 9 as a function of Cu(II) concentration (constant ionic strength of 10^{-3} mol/L NaNO_3).

It can also be observed in Figure 1 the effect of Cu(II) concentration on the zeta potential of sphalerite at pH 9. Zeta potential increases as the Cu(II) concentration is varied from 0 to 5 mg/L. This behavior is due to the adsorption of copper hydroxide species onto the sphalerite surface and the exchange of Zn^{2+} of the crystal lattice by Cu^{2+} . Then, cupric ions react with the nearby sulfides oxidizing them, leading to the formation of a new surface consisting of cuprous sulfide (Cu_2S) and polysulfides (e.g., Sn^{2-} , or cuprous disulfide (Cu_2S_2)), allowing the formation of copper xanthate and a greater zeta potential. This replacement mechanism also gives rise to the precipitation of Zn^{2+} from the sphalerite lattice as zinc hydroxide, which slowly dissolves and disperses exposing the hydrophobic surface previously formed [16,18].

At concentrations above 5 mg/L Cu(II) the electric charge of sphalerite decreases from positive to negative values (see Figure 1). When Cu(II) concentration is varied from 5 to 15 mg/L, the zeta potential drops from 4.6 to -12.8 mV to later remain practically constant at around -13.8 mV from 15 to 50 mg/L Cu(II). This behavior describes the detrimental effect of adding Cu(II) in excess and it is attributed to the precipitation and accumulation of copper hydroxide onto the sphalerite surface.

The formation of copper xanthate on the surface of sphalerite enhances its hydrophobicity, but this mechanism only occurs until 5 mg/L Cu(II). In Figure 2 can be seen the copper hydroxide adsorption/precipitation on the sphalerite surface when the mineral is conditioned at pH 9 and 50 mg/L Cu(II). The copper hydroxide does not cover the entire surface, but it begins to accumulate. The patches labeled as “1” corresponds to copper hydroxide and the zones labeled as “2” are uncovered sphalerite where no copper content was detected.

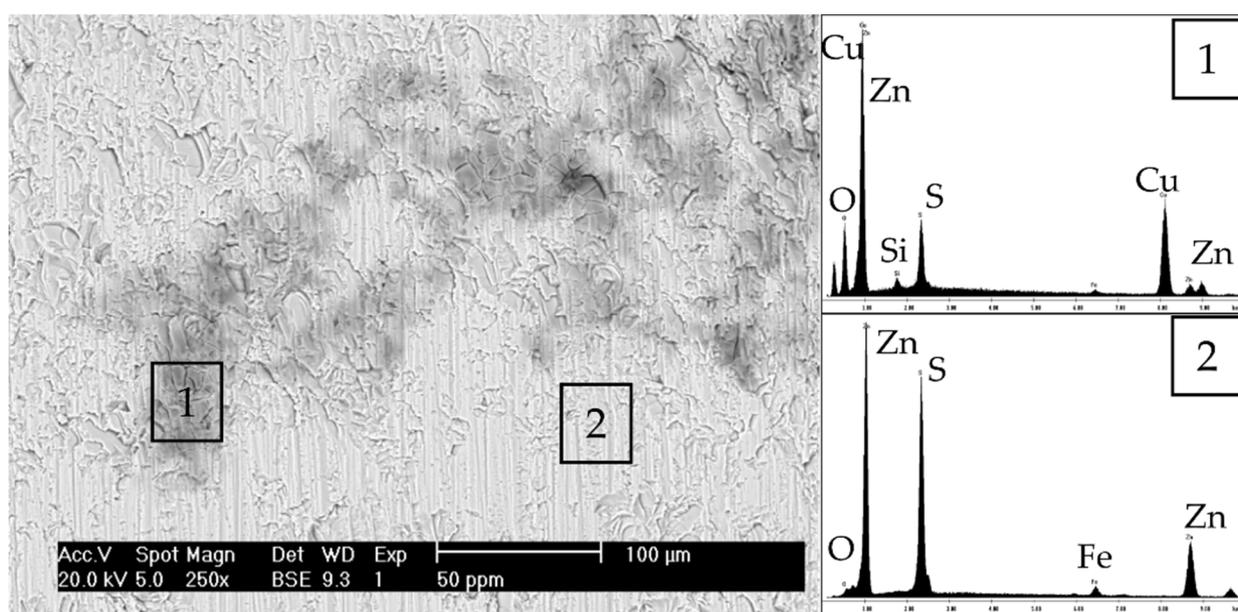


Figure 2. SEM micrograph and microprobe analysis showing $\text{Cu}(\text{OH})_2$ adsorption/precipitation onto the sphalerite surface conditioned at pH 9 with 50 mg/L of Cu(II).

It can be seen in Figure 3 that as the concentration of Cu(II) increases from 50 to 200 mg/L, the extent of copper hydroxide patches on the sphalerite surface become bigger and eventually would cover practically the whole surface. This would result in lower recoveries since copper hydroxide is a hydrophilic species. Copper hydroxide adsorption/precipitation on the sphalerite surface can be observed as patches (labeled as “1”); they practically cover the whole sphalerite surface. The zones labeled as “2” are uncovered sphalerite where no copper content was detected. The copper hydroxide patches are dark, and their morphology is flaky.

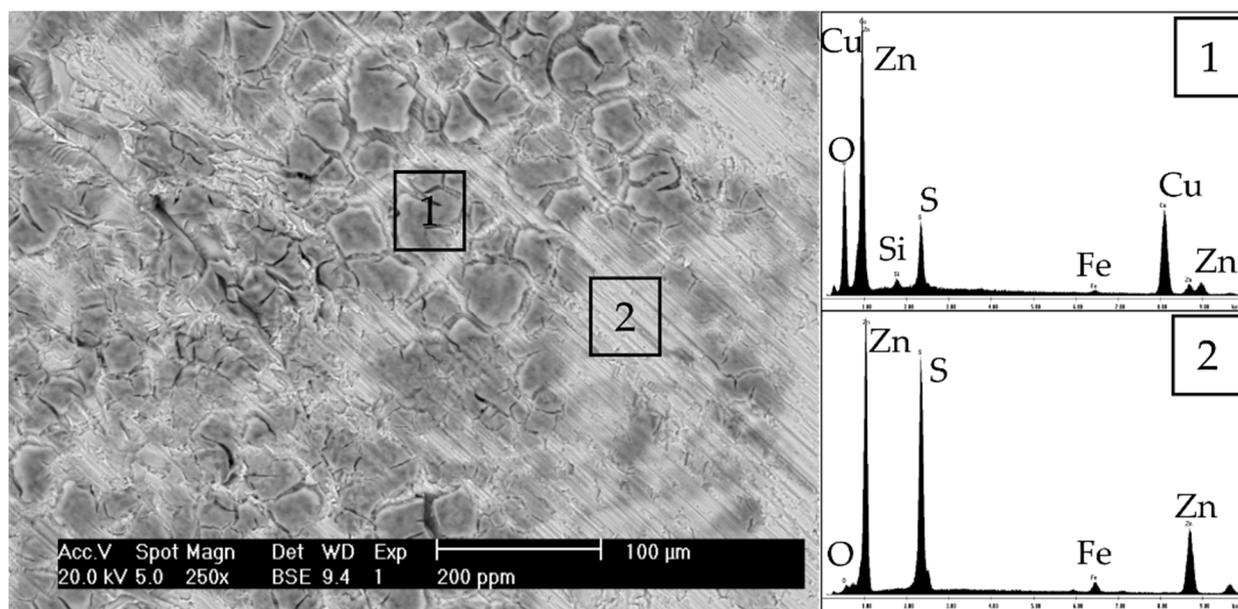


Figure 3. SEM micrograph and microprobe analysis showing $\text{Cu}(\text{OH})_2$ adsorption/precipitation onto the sphalerite surface conditioned at pH 9 with 200 mg/L of Cu(II).

3.3. Effect of Magnesium on the Contact Angle of Cu-Activated Sphalerite

It has been suggested that adsorption of magnesium species (e.g., MgOH^+ and $\text{Mg}(\text{OH})_2$) onto the sphalerite will be favored by a negatively charged mineral surface, which is precisely the case for pH values from 8 to 10. Mirnezami et al. [19] have shown that MgOH^+ adsorbs onto sphalerite at pH below 10, while at more alkaline conditions, precipitation and coagulation of $\text{Mg}(\text{OH})_2$ also occurs. Thus, decreasing the number of available sites for xanthate adsorption [9]. Magnesium hydroxide ($\text{Mg}(\text{OH})_2$) is slightly positively charged at pH from 9.5 to 10, values at which precipitation begins [20]. This will enhance the electrostatic interaction with the negatively charged sphalerite. Copper attraction will result in less adsorption of magnesium hydroxide complexes onto the activated sphalerite as its surface charge would be less negative.

Figure 4 shows the effect of pH on the contact angle of Cu-activated sphalerite conditioned with SIPX (dashed line), Cu-activated sphalerite conditioned with SIPX in presence of magnesium, and Cu-activated sphalerite conditioned with SIPX in presence of magnesium and sodium carbonate.

It can be observed in Figure 4 (dashed line) that the contact angle of Cu-activated sphalerite in absence of magnesium and sodium carbonate increases as the pH of the SIPX conditioning stage is varied from 5 to 9, reaching a maximum of 62° . From to pH 9 to 11 this tendency is reversed to end at approximately 48° . This is because at more alkaline solutions, the $\text{Cu}(\text{OH})_2$ patches originated during copper activation (see Figures 2 and 3) slightly hinders the hydrophobicity caused by xanthate adsorption.

Magnesium has a negative effect on the contact angle of Cu-activated sphalerite conditioned with SIPX as a function of pH, as can be seen in Figure 4. At pH from 8 to 9 the effect on the contact angle is not significant, compared with the behavior of Cu-activated sphalerite in absence of magnesium. At these conditions, the interaction between the mineral surface and MgOH^+ is negligible since the mineral charge is almost zero and the concentration of MgOH^+ is about 10^{-5} mol/L, as revealed by the Mg- H_2O distribution diagram of Figure 5a. Otherwise, at pH above 9 the contact angle drop sharply from 55° to 20° as a consequence of the adsorption and precipitation of $\text{Mg}(\text{OH})_2$ onto the sphalerite surface. This is supported by the distribution diagram of Figure 5a where is clearly shown that $\text{Mg}(\text{OH})_2$ predominates at pH 10 but begins to precipitate at 9.6.

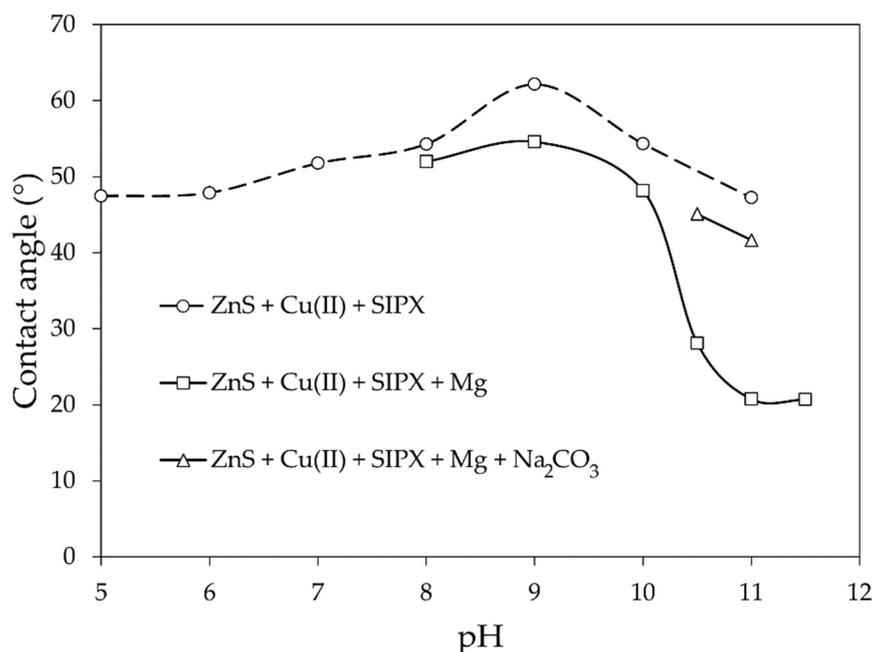


Figure 4. Effect of pH and magnesium (50 mg/L), on the contact angle of Cu-activated (50 mg/L, 15 min) sphalerite further conditioned with SIPX (10^{-4} mol/L, 5 min) at 25 °C. It is also shown the effect of sodium carbonate, added during xanthate conditioning (2 g/L), to counteract the detrimental effect of magnesium.

Sodium carbonate has been used in industrial operations to reduce the concentration of calcium in flotation water since it dissolves gypsum precipitated and heterocoagulated onto the galena and sphalerite particles; it also avoids further gypsum precipitation [21,22]. Calcium and magnesium have chemical similarities, which suggest that magnesium may also precipitate in the form carbonate as calcium does, hence the use of soda ash as alkalinizing agent was tested.

It can be seen in Figure 4 that the use of sodium carbonate has a positive effect on the contact angle of Cu-activated sphalerite conditioned with SIPX in presence of 50 mg/L Mg. For pH values of 10.5 and 11 the contact angles are 45° and 42°, respectively. Thus, the depressing effect of magnesium hydroxide is avoided by employing soda ash as alkalinizing agent since, according with Figure 5b, magnesium precipitates as hydromagnesite ($Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O$) rather than hydroxide. It can be seen in the distribution diagram of the Mg-CO₃-H₂O system of Figure 5b that at pH 9.4 hydromagnesite starts to precipitate and it will keep precipitating while increasing the pH. Apparently, the basic carbonate does not substantially affect sphalerite hydrophobicity since it remains dispersed in the bulk solution as calcium carbonate does in the case of calcium removal from the solution by soda ash addition [22].

Sodium carbonate can be employed in the sphalerite flotation circuit as an operational strategy to avoid the detrimental effect of magnesium on the hydrophobicity of sphalerite. Other option will be to maintain a flotation pH below 10 to avoid precipitation of magnesium hydroxide.

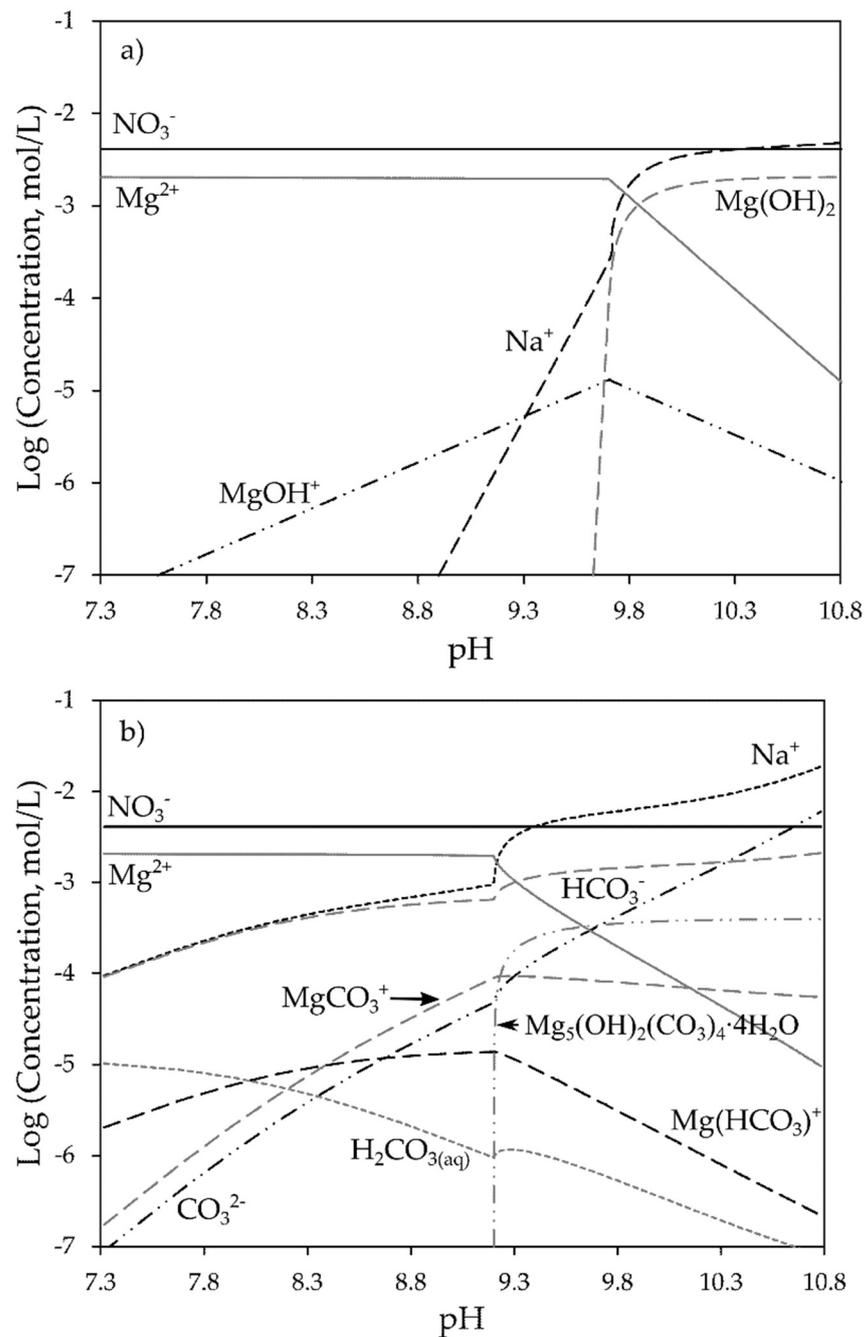


Figure 5. Species distribution diagrams of the (a) Mg-H₂O and (b) Mg-CO₃-H₂O systems for 50 mg/L of Mg at 25 °C. The latter diagram stands for the cumulative addition of 2 g/L of Na₂CO₃ to 1 L of solution. Hydromagnesite starts to precipitate when 0.05 g/L of soda ash has been added.

To complement and support the findings made by experimental techniques and thermodynamic simulation, the surface of a Cu-activated sphalerite conditioned with SIPX in presence of: (1) 50 mg/L of Mg and (2) 50 mg/L + 2 g/L Na₂CO₃ was characterized by Schottky field emission SME-EDSX. The results can be seen in Figures 6 and 7.

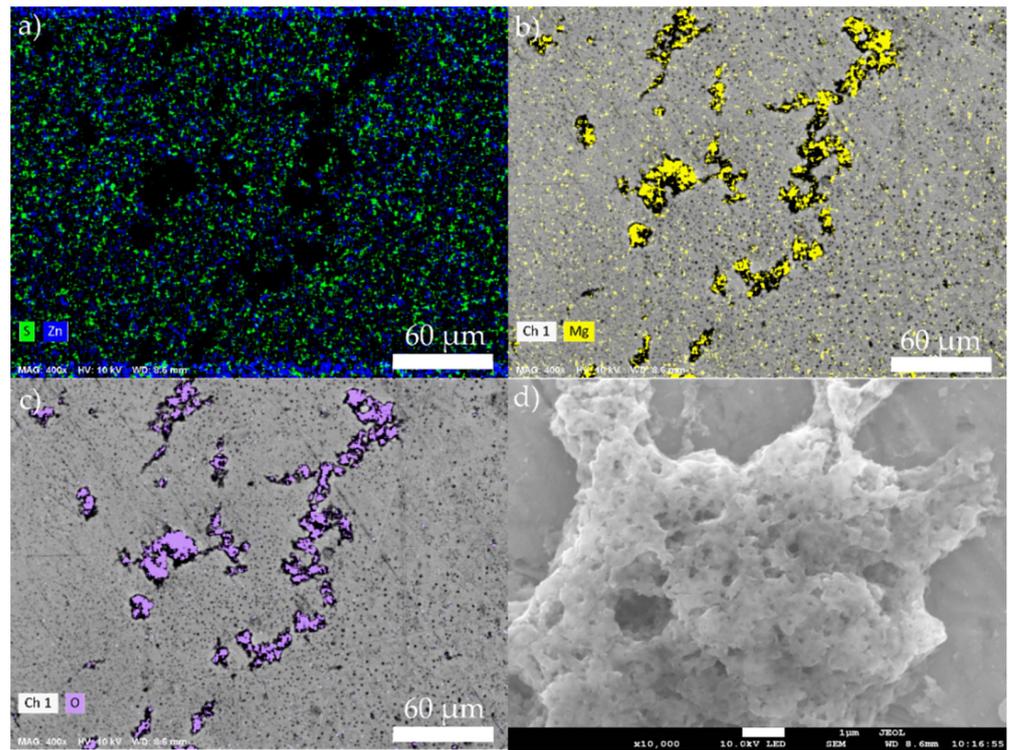


Figure 6. Mapping of location elements for the surface of Cu-activated sphalerite conditioned with SIPX in presence of Mg and morphology of the precipitated Mg(OH)₂: (a) S and Zn, (b) Mg, (c) O, (d) morphology.

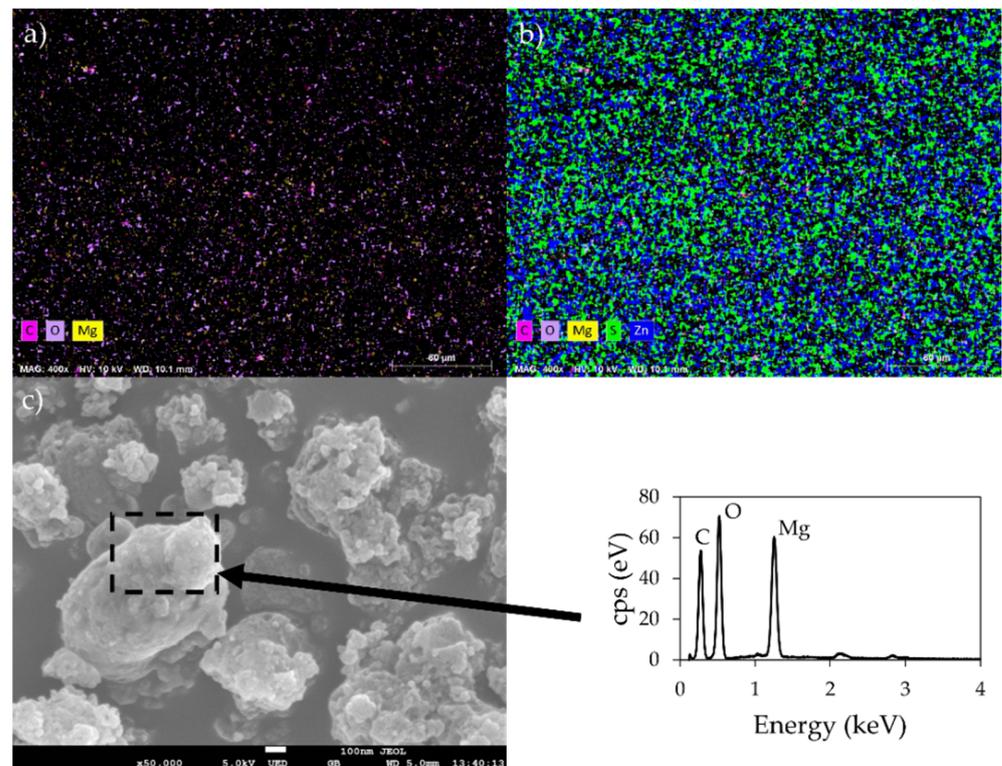


Figure 7. Mapping of location elements for the surface of Cu-activated sphalerite conditioned with SIPX in presence of Mg + Na₂CO₃ and the morphology and composition of the dispersed Mg species: (a) C, O, and Mg, (b) C, O, Mg, S, and Zn, and (c) morphology and EDSX microprobe analysis.

The elemental X-ray maps and high-resolution SEM micrograph in Figure 6 clearly shows the magnesium hydroxide precipitated on the surface of Cu-activated sphalerite conditioned with SIPX. The elemental mapping of Figure 6a shows that the elements that composes the surface are those of sphalerite but, as represented in dark areas, magnesium hydroxide precipitates. The elemental mapping of Figure 5b,c shows that the species precipitated is composed of magnesium and oxygen, supporting the results presented in Figures 4 and 5a. High-resolution SEM micrograph of Figure 6d shows the morphology of the magnesium hydroxide which could cover the entire sphalerite surface affecting the recovery of sphalerite.

The elemental X-ray maps in Figure 7a,b clearly shows that the presence of sodium carbonate avoids the precipitation of magnesium hydroxide on the surface of Cu-activated sphalerite conditioned with SIPX. The elemental composition of the surface corresponds to that of sphalerite although it was conditioned in the presence of 50 mg/L of magnesium. Magnesium hydroxide precipitation/adsorption onto the mineral surface was not detected. These findings support the results of the contact angle experiments and thermodynamic simulation. The addition of sodium carbonate as alkalinizing agent enhances the hydrophobicity of sphalerite in presence of magnesium by preventing or dissolving the precipitated magnesium hydroxide. In the high-resolution SEM micrograph of Figure 7c can be seen the morphology of the dispersed precipitated magnesium compound, which avoids the detrimental effect on the hydrophobicity of sphalerite. According to a EDX microprobe analysis, the magnesium species corresponds to hydromagnesite ($Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O$) as indicated by the thermodynamic simulation presented in Figure 5b. The microprobe analysis was carried out in the area indicated in the dotted box of Figure 7c; magnesium, oxygen, and carbon were detected.

4. Conclusions

The experimental and thermodynamic study, in conjunction with surface characterization, to elucidate the effect of magnesium on the hydrophobicity of sphalerite has shown the following:

1. Cu-activation of sphalerite enhance its zeta potential up to a concentration of 5 mg/L; at concentrations greater than 5 mg/L, copper hydroxide will adsorb/precipitate onto the sphalerite surface decreasing its zeta potential because $Cu(OH)_2$ is hydrophilic in nature.
2. Magnesium has a detrimental effect on the contact angle of Cu-activated sphalerite conditioned with SIPX beginning at pH of approximately 10 due to the precipitation of magnesium hydroxide onto its surface. The precipitation of this species starts at pH 9.6 and rapidly becomes a predominant species as pH increases. If the process pH is not rigorously controlled to keep it below 10, it will cover the whole sphalerite surface diminishing its recovery.
3. The use of sodium carbonate as alkalinizing agent avoids the sodium hydroxide precipitation onto the surface of Cu-activated sphalerite conditioned with SIPX. When sodium carbonate is present, hydromagnesite ($Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O$) begins to precipitate at pH 9.3 and it will keep precipitating at greater pH values, allowing the recovery of sphalerite.

In summary, magnesium has a negative effect on the contact angle of sphalerite, and it could be considered more detrimental than calcium since magnesium hydroxide begins to precipitate at pH 9.6. An operational strategy must be considered since magnesium species are common in the process water, increasingly with a higher proportion of recycled water. A pH lower than 10 must be keep avoiding the precipitation of magnesium hydroxide or sodium carbonate must be added aiming to precipitate the magnesium as hydromagnesite ($Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O$) instead of hydroxide.

Author Contributions: Conceptualization, methodology, writing—original draft preparation, visualization, and formal analysis, supervision, G.I.D.-P.; writing—original draft preparation, investigation, and writing—review and editing, A.A.G.-I.; data curation, visualization, M.G.-G.; methodology, data curation, D.A.C. All authors have read and agreed to the published version of the manuscript.

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