

Communication

Effects of Potassium Propyl Xanthate Collector and Sodium Sulfite Depressant on the Floatability of Chalcopyrite in Seawater and KCl Solutions

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Abstract: This study demonstrates the effects of a potassium propyl xanthate (PPX) collector and sodium sulfite (Na₂SO₃) depressant on pure chalcopyrite in synthetic seawater (SSW) and potassium chloride (KCl) solutions. SSW solutions with 35 g/L of salt and 0.01-M KCl were used for microflotation and zeta potential tests. Particles sized between 200# and 100# (75–150 μ m) were used, and the pH was between 8.0 and 8.5. The surface of the mineral and its interaction with the collector were characterized using Raman spectrometry. The zeta potential of the chalcopyrite was measured in KCl solution at a pH range of 3–12 using the collector and depressant at a monodispersed particle size of 635# (20 μ m). The results indicate that the floatability of chalcopyrite is not affected by the presence of PPX collectors in SSW solutions. SSW provides better recoveries than KCl solutions with values of 91.42% and 88.15%, respectively. The Na₂SO₃ depressant does not hinder the mineral floatability throughout the entire concentration range used; however, special care must be taken when adjusting the pH range to avoid increasing the zeta potential.

Keywords: flotation; chalcopyrite; PPX; Na₂SO₃; KCl; seawater

1. Introduction

The use of desalinated or raw seawater has become a necessary alternative in many operations in Chile and other parts of the world [1]. The scarcity of water has generated the need to manage this resource more efficiently [2], optimize its recycling [3], seek alternatives of using waste brines [4], and operate with seawater with and without desalination [5,6]. In fact, several mining companies already use or plan to use seawater in their concentrator plants [1,2,7,8]. However, less than half of these mining companies use seawater without desalinating it due to the complications arising from its low-quality. On the one hand, the use of desalinated seawater can have adverse effects, such as high energy consumption in water supply systems and the generation of brines that can alter marine ecosystems [2]. On the other hand, the use of raw seawater can adversely affect the flotation of sulfides such as molybdenite (MoS₂) and increase lime consumption due to the buffering effect of seawater at high pH values [9–12]. However, the use of raw seawater reduces frother consumption by inhibiting the coalescence of bubbles [13,14], even at low salinity concentrations [15]. In practice, the reactants that have gained prominence include thionocarbamates and xanthates as collectors and sodium cyanide, sodium bisulfite, zinc sulfate as dispersants [16–22]. One of them is potassium propyl



xanthate (PPX), a short-chain collector of the xanthate family [23]. Several sulfur-oxy species, including sulfur dioxide (SO₂), bisulfite (HSO₃⁻), metabisulfite (S₂O₅²⁻) and sulfite (SO₃²⁻), have been employed in flotation as pyrite depressants [17,24]. These sulfur-oxy species function mainly through SO₃²⁻ [25]. The reducing agents sulfide/sulfite ions are more reducing than the xanthate ion/dixanthogen couple. Since dixanthogen is the main species responsible for pyrite flotation, the sulfide/sulfite ions couple acts as pyrite depressants by preventing the oxidation of xanthate. The application of sodium sulfite (Na₂SO₃) is versatile. It is used for its reducing effect in several industries, such as food, photography, paper, water treatment and mineral processing [26–29]. Individual applications have been studied in flotation studies of Galena with PPX [30], and depressant action for chalcopyrite in the flotation of molybdenite from copper–molibdene ores [29]. However, the joint application of these materials under saline conditions such as seawater has not been analyzed in depth. This study investigated the effects of PPX and sodium sulfite on the flotation of pure chalcopyrite in synthetic seawater (SSW) and potassium chloride (KCl) solutions. The objective is to evaluate the effect of sodium sulfite and PPX on the flotation of chalcopyrite in these types of solutions and their possible application as an alternative for copper sulfide minerals in seawater.

2. Materials and Methods

Pure chalcopyrite from Durango, Mexico, acquired through Ward Science, was used in all tests. An agate mortar was used to reduce the particle size, and then the particles were classified by 635#–100# (20–150 µm) sieves. The mineral was characterized by analysis with a Hitachi SU 5000 model scanning electron microscope (Hitachi, Tokyo, Japan) and Bruker advance d8 model X-ray diffractor (Bruker, Billerica, MA, USA). Particles sized between 200# and 100# (75–150 µm) were used for the microflotation tests at pH between 8.0 and 8.5 since this is the pH typical of seawater. The SSW was prepared using 1.81 g of CaCl₂·2H₂O; 10.31 g MgCl₂·6H₂O; 0.88 g KCl; 23.79 g NaCl; 0.0043 g Na₂HPO₄·7H₂O and 4.13 g Na_2SO_4 in a liter of solution. The solution obtained has a chemical composition close to the seawater with a salinity of 35 [31]. The mineral surface and its interaction with the collector were qualitatively characterized using Raman spectrometry. The zeta potential measurements were performed in a KCl solution at a pH range of 3–12 in the presence of collector particles sized 635# (20 µm). The zeta potential in SSW solutions were not measured because the high presence of cations affects the results. All samples were stored under a nitrogen-neutral atmosphere to prevent mineral oxidation and ensure the reproducibility of the tests. High purity samples of PPX and sodium sulfite (>99%) were provided by Industrias Químicas de México. PPX and Na₂SO₃ solutions were prepared daily with deionized water of resistivity 18.2 M Ω cm⁻¹. See Table 1 for a summary of the information.

Parameter	Property	Dose	Units
Mineral	Chalcopyrite	1	g
	Granulometry	75–150	μm
Solution	KCl	0.01	mol/L
	SSW	0.54	mol/L
	Volume	150	mL
Collector type	РРХ	0-0.01	mol/L
Depressant	Na_2SO_3	0-0.01	mol/L
Cell type	Hallimond tube	150	mL
pH	HCl/NaOH	8.0-8.5	
Air type	Nitrogen	20	mL/min
Agitation	Magnetic	700	rpm
Flotation	Time	1	minutes

2.1. Microflotation in Saline Solutions

The microflotation assays were performed in a 150-mL Hallimond tube [32]. The KCl or SSW solution was adjusted to a pH between 8.0 and 8.5. Once one gram of the mineral was added, the pH was adjusted again. Once the collector and pulp were added, the solution was stirred at 900 rpm for 20 min as suggested by Fullston [33]. When a collector and depressant were used in the test, first, the collector was added over 5 min, and then, the depressor was added over an additional 15 min. All samples were decanted for 2 min to preserve the suspension. Then, the pulp was transferred to a microflotation cell and stirred at 700 rpm. Aeration was performed at a nitrogen flow rate of 20 mL/min, and flotation was performed for 1 min. All tests were performed in duplicate, and their averages were reported with an average deviation of 3.8%. The recovery of the float material (*R*) was calculated from:

$$R = \frac{m_1}{m_1 + m_2} \times 100$$
 (1)

where m_1 and m_2 are masses of the floating and non-floating fractions, respectively.

2.2. Electrokinetics of Chalcopyrite

The chalcopyrite potential was measured by electrokinetic studies in a Riddick Zeta model D instrument and an electrophoretic cell No. S-2479. Five-hundred milligrams of mineral was used in 50 mL of 0.01 mol/L KCl solution in a pH range of 3–12 in the presence of the collector and the depressor studied. The tests were carried out with 0.01-mol/L KCl solutions and in the presence of PPX and Na₂SO₃ at different doses. See Table 2 for a summary of the information. The order of aggregation and conditioning of the reagents was the same as those applied in the microflotation tests. An average of 10 readings was used to measure the mobility of the chalcopyrite, which presented a standard deviation of 0.19 mV. The zeta potential was measured using the Smoluchowski Equation [34].

Parameter	Property	Doses	Units
Mineral	Chalcopyrite	500	mg
	Granulometry	20	μm
Solution	KCl	0.01	mol/L
		50	mL
Collector type	РРХ	0-0.01	mol/L
Depressant	Na_2SO_3	0-0.01	mol/L
Cell type	Riddick Zeta D model	150	mL
pH	HCl/NaOH	03-dic	
Agitation	Magnetic	800	rpm
Energy	Voltage	100	mV
Conditioning	Time	15	min

Table 2. Experimental conditions of the zeta potential measurement.

3. Results and Discussions

3.1. Mineralogical Characterization of Chalcopyrite by SEM and Raman

The Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis indicated that the mass fractions of elements in chalcopyrite were 31.39% Cu, 34.40% Fe and 31.02% S and the mole ratio of Cu to Fe to S was 1:1.25:1.96, which is close to the stoichiometry of chalcopyrite. Impurities includes 1.25% Si, 0.82% Ca and 1.11% Mg. Figure 1 displays the SEM and XRD analysis— a standard XRD analysis of chalcopyrite [35,36].



Figure 1. SEM and XRD analysis of chalcopyrite. The meaning of different colors of the SEM photograph: white—oxygen, blue—silicon, red—sulfur, green—calcium, navy blue—iron, light blue—copper, magenta—magnesium.

The results of the spectrometry (Raman) test are shown in Figure 2. The frequency bands below 500 cm⁻¹ are typical of sulfides creating metal–sulfur bonds, and these results are repeated for the rest of the particles analyzed [37–39].



Figure 2. Pure chalcopyrite Raman spectrum with a wavelength of 663 nm, power of 5 mW, opening of $25 \,\mu\text{m}$, resolution of 2.6–4.4 cm⁻¹, and a target number of 20.

3.2. Effects of Salinity on Chalcopyrite Flotation Using PPX

The floatability of chalcopyrite in KCl and SSW solutions with an equivalent ionic strength is shown in Figure 3 as a function of the PPX collector at pH between 8.0 and 8.5. Mineral recoveries over 80% are observed from doses of 1×10^{-5} mol/L of PPX in SSW. The chalcopyrite shows reduced floatability in the KCl solutions over the entire range of doses studied with respect to SSW. In their study and analysis of natural sulfide floatability, Fuerstanou [40] found that recovery rates without collectors or frothing agents are similar (>90%) for chalcopyrite samples of different origins. For this sample,

the flotation without the collector for both types of solutions have recoveries of 7% and 30% for KCl and SSW, respectively. In the presence of PPX, SSW enhances the oxidation of chalcopyrite, reducing the energy barrier in the double layer, facilitating the adhesion of the collector as it was observed when the effects of chloride ions on the surface of chalcopyrite and pyrite in seawater were studied [41,42]. The oxidation reduction potential (ORP) values reported in Figure 3B show the reduction in potential as the dose of PPX increases. The ORP values, according to the type of solution, do not indicate significant differences. Fuerstenau [40], in his study on the floatability of chalcopyrite from different origins, found that recovery without collectors or foaming agents is similar (>90%). This study was carried out with freshwater, so the lower recovery can be attributed to the reduction in dissolved oxygen [42].



Figure 3. Floatability (**A**) and oxidation reduction potential (ORP) (mV vs. Ag/AgCl) (**B**) measurements of chalcopyrite in potassium chloride (KCl) and synthetic seawater (SSW) as a function of potassium propyl xanthate concentration at pH 8.0–8.5.

3.3. Effect of Sodium Sulfite Concentration on Flotation without the Chalcopyrite Collector in Saline Solutions

Figure 4 shows the recoveries of the mineral at doses between 0 and 0.01 mol/L Na₂SO₃. The recovery of the chalcopyrite without the collector at different doses of Na₂SO₃ was slightly higher than the natural floatability achieved, as indicated above. Na₂SO₃ does not have a depressing effect on the mineral since the surface of the chalcopyrite was not oxidized and exhibited behavior similar to that reported by [29,43], using the same mineral size and in the presence of sodium sulfite. For doses of 1×10^{-4} mol/L, in both solutions, a decrease in the floatability of the mineral was observed. The ORPs reported in Figure 4B help to clarify the behavior of the mineral at different doses of depressant. This shows that spontaneous changes are generated in the reducing capacity of Na₂SO₃, which has repercussions in reducing floatability by lowering the redox potential as reported by Castro in his study when comparing ORP in distilled water and seawater [44]. The speciation of sulfite and bisulfite in seawater was studied in the literature [45]. In pure water at 4.5 < pH < 10, the sulfite and bisulfite ions are in equilibrium. In seawater, the intermolecular interactions with dissolved ions affect the speciation equilibrium. In studies of sodium and potassium chloride aqueous solutions with a concentration of chloride similar to seawater, solvation shells around the bisulfite and the sulfite were observed. Nevertheless, the sulfur species were not influenced by an exchange of the monovalent cation. However, if magnesium or calcium ions are present in concentrations similar to seawater, a significant decrease in the concentration of sulfite was observed, but no influence on bisulfite was observed. This behavior is primarily attributed to a stronger interaction between the divalent cations with sulfite than with bisulfite. This interaction of the sulfite and bisulfite ions with the monovalent and divalent ions can explain the behavior in chalcopyrite recovery and ORP values of in Figure 4.



Figure 4. (**A**) Floatability and (**B**) ORP (mV vs. Ag/AgCl) measurements of chalcopyrite in KCl and SSW as a function of sodium sulfite concentration at pH 8.0–8.5.

The results of the spectrometry test (Raman) are shown in Figure 2. Frequency bands below 500 cm^{-1} are typical for sulfides when creating metal–sulfur bonds, and these results are repeated for the rest of the particles analyzed [37,38].

4. Discussion

4.1. Chalcopyrite Floatability in the Presence of PPX and Na₂SO₃ in Saline Solutions

Figure 5 shows the floatability of chalcopyrite at a dose of 0.01 mol/L PPX as a function Na₂SO₃ concentration. At this collector dose, the effects of the depressant are negligible throughout the concentration range studied. Both salinity solutions give similar values for recovery rates. This can be attributed to the pH and type of aeration used. It is known that xanthate decomposes at pH 6.5 and when oxygen is dissolved [19]. However, the doses studied show that the xanthate and sulfite interactions are not at a level that hinders the floatability of the chalcopyrite, inhibiting the surface oxidation of the mineral [46]. Again, the effect of the interaction between the monovalent and divalent cations with sulfite, as opposed to bisulfite, was observed.



Figure 5. Floatability (**A**) and ORP (mV vs. Ag/AgCl) (**B**) measurements of chalcopyrite in KCl and SSW with 0.001 mol/L of potassium propyl xanthate (PPX) as a function of sodium sulfite concentration at pH 8.0–8.5.

When the floatability of the mineral is evaluated at different concentrations of PPX and at constant doses of sodium sulfite, the effects of the water type are observed, as shown in Figure 6. The difference

in recovery in the range of concentrations studied converges only at one point at 0.01 mol/L PPX. The spectrometry performed on the sample with a concentration of 0.005 mol/L Na₂SO₃ shows that the sulfite does not affect the surface of the chalcopyrite, showing the same frequency bands as the mineral without sodium sulfite. This coincides with what was reported by Fullston [33], who classified chalcopyrite as the most stable mineral at different pH and oxidation conditions compared to other sulfides in the following order:



chalcocite < tennantite < enargite < bornite < covellite < chalcopyrite.

Figure 6. Floatability (**A**) and ORP (mV vs. Ag/AgCl) (**B**) measurements of chalcopyrite in KCl and SSW with 0.005 mol/L of sodium sulfite as a function of PPX concentration at pH 8.0–8.5.

In KCl, higher doses of the PPX collector are required to achieve results the same as those with SSW because of the types of ions that make up the solutions. In the case of KCl, the presence of K⁺ ions, a type of chaotropic ion (also known as structure-breakers for their higher ionic radius), induces the breaking of the structures formed by water molecules [47]. Regarding the effect of sodium sulfite, Figure 7 shows the spectrometry of the sodium sulfite attack on chalcopyrite in a KCl solution [46]. The resulting frequency bands were equal to those of the untreated sample, that is, below 500 cm⁻¹, without any frequency peaks indicating an altered mineral surface. Typical sodium sulfite vibrational Raman frequencies' spectra were not observed [48]. This makes sense based on the difference in the flotation of the mineral in SSW and KCl.



Figure 7. Raman spectrum of chalcopyrite with 0.005 M of Na₂SO₃.

4.2. Effects of Potassium Propyl Xanthate and Sodium Sulfite on Chalcopyrite Zeta Potential Using KCl

The results obtained for the zeta potential measurements, shown in Figures 8 and 9, are consistent with the recoveries obtained in the floatability of the mineral. These curves replicate the results obtained by Fullston and Li [33,42]. The effects of the collector and depressant on the negativity of the mineral potential are generated by increasing their concentration. This increase makes the surface of the mineral more electrostatically repulsive. For the dose of 0.001 mol/L PPX and 0.005 mol/L sodium sulfite, the zeta potentials obtained throughout the entire pH range show subtle variation in their values with respect to the concentrations studied. This indicates that KCl does not significantly affect the zeta potential of the mineral in the case of the collector. Concerning the depressant, the zeta potential behavior varies as a function of the pH in the doses used in the microflotation tests.



Figure 8. Zeta potential of chalcopyrite as a function of pH in the absence and presence of various initial PPX concentrations in KCl solution.



Figure 9. Zeta potential of chalcopyrite as a function of pH in the absence and presence of various initial Na₂SO₃ concentrations in KCl solution.

5. Conclusions

The results indicate that the mineral floatability of chalcopyrite is affected by the presence of Na₂SO₃ in the SSW and KCl solutions in the absence of a collector. These results are confirmed with studies of zeta potential and Raman spectra. The zeta potential varies depending on the concentrations of the reagents, becoming more electronegative at higher doses throughout the pH range. In the presence of a collector, the improvements are more notable in SSW solutions than in KCl solutions,

with values of 91.42% and 88.15%, respectively, which is attributed to the different types of ions present in both solutions. Na₂SO₃ does not hinder the floatability of the mineral in the presence of the collector or in the entire concentration range used. However, the interaction of the sulfite and bisulfite ions with the monovalent and bivalent ions affects the behavior in chalcopyrite recovery. However, studies with mixtures of more minerals should be continued to determine their potential application in saline media applying design of experiment.

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References

- 1. Cisternas, L.A.; Gálvez, E.D. The use of seawater in mining. *Miner. Process. Extr. Metall. Rev.* 2017, 39, 1–16. [CrossRef]
- 2. Herrera-León, S.; Lucay, F.A.; Cisternas, L.A.; Kraslawski, A. Applying a multi-objective optimization approach in designing water supply systems for mining industries. The case of Chile. *J. Clean. Prod.* **2019**, 210, 994–1004. [CrossRef]
- 3. Gálvez, E.D.; Cruz, R.; Robles, P.A.; Cisternas, L.A. Optimization of dewatering systems for mineral processing. *Miner. Eng.* **2014**, *63*, 110–117. [CrossRef]
- 4. Ordóñez, J.I.; Moreno, L.; González, J.F.; Cisternas, L.A. Use of discharged brine from reverse osmosis plant in heap leaching: Opportunity for caliche mining industry. *Hydrometallurgy* **2015**, 155, 61–68. [CrossRef]
- 5. Ordóñez, J.I.; Moreno, L.; Gálvez, E.D.; Cisternas, L.A. Seawater leaching of caliche mineral in column experiments. *Hydrometallurgy* **2013**, *139*, 79–87. [CrossRef]
- 6. Hernández, P.; Taboada, M.; Herreros, O.; Graber, T.; Ghorbani, Y. Leaching of chalcopyrite in acidified nitrate using seawater-based media. *Minerals* **2018**, *8*, 238. [CrossRef]
- 7. Araya, N.; Cisternas, L.A.; Lucay, F.; Gálvez, E.D. Design of desalinated water distribution networks including energy recovery devices. *Comput. Aided Chem. Eng.* **2017**, *40*, 925–930.
- Wessman, H.; Salmi, O.; Kohl, J.; Kinnunen, P.; Saarivuori, E.; Mroueh, U.M. Water and society: Mutual challenges for eco-efficient and socially acceptable mining in Finland. *J. Clean. Prod.* 2014, *84*, 289–298. [CrossRef]
- Lucay, F.; Cisternas, L.A.; Gálvez, E.; Lopez-Valdivieso, A. Study of the natural floatability of molybdenite fines in saline solutions and effect of gypsum precipitation. *Miner. Metall. Process.* 2015, 32, 203–208. [CrossRef]
- Jeldres, R.I.; Arancibia-Bravo, M.P.; Reyes, A.; Aguirre, C.E.; Cortes, L.; Cisternas, L.A. The impact of seawater with calcium and magnesium removal for the flotation of copper-molybdenum sulphide ores. *Miner. Eng.* 2017, 109, 10–13. [CrossRef]
- 11. Ramos, O.; Castro, S.; Laskowski, J.S. Copper-molybdenum ores flotation in sea water: Floatability and frothability. *Miner. Eng.* **2013**, *53*, 108–112. [CrossRef]
- 12. Jeldres, R.I.; Calisaya, D.; Cisternas, L.A. An improved flotation test method and pyrite depression by an organic reagent during flotation in seawater. *J. S. Afr. Inst. Min. Metall.* **2017**, *117*, 499–504. [CrossRef]
- 13. Quinn, J.J.; Sovechles, J.M.; Finch, J.A.; Waters, K.E. Critical coalescence concentration of inorganic salt solutions. *Miner. Eng.* **2014**, *58*, 1–6. [CrossRef]
- 14. Quinn, J.J.; Kracht, W.; Gomez, C.O.; Gagnon, C.; Finch, J.A. Comparing the effect of salts and frother (MIBC) on gas dispersion and froth properties. *Miner. Eng.* **2007**, *20*, 1296–1302. [CrossRef]

- Arancibia-Bravo, M.P.; Lucay, F.A.; López, J.; Cisternas, L.A. Modeling the effect of air flow, impeller speed, frother dosages, and salt concentrations on the bubbles size using response surface methodology. *Miner. Eng.* 2019, 132, 142–148. [CrossRef]
- Maree, W.; Kloppers, L.; Hangone, G.; Oyekola, O. The effects of mixtures of potassium amyl xanthate (PAX) and isopropyl ethyl thionocarbamate (IPETC) collectors on grade and recovery in the froth flotation of a nickel sulfide ore. *S. Afr. J. Chem. Eng.* 2017, 24, 116–121. [CrossRef]
- 17. Mu, Y.; Peng, Y.; Lauten, R.A. The depression of pyrite in selective flotation by different reagent systems— A Literature review. *Miner. Eng.* **2016**, *96–97*, 143–156. [CrossRef]
- 18. Houot, R.; Duhamet, D. Floatability of chalcopyrite in the presence of dialkyl-thionocarbamate and sodium sulfite. *Int. J. Miner. Process.* **1993**, *37*, 273–282. [CrossRef]
- 19. Grano, S.R.; Prestidge, C.A.; Ralston, J. Solution interaction of ethyl xanthate and sulphite and its effect on galena flotation and xanthate adsorption. *Int. J. Miner. Process.* **2002**, *52*, 161–186. [CrossRef]
- 20. Janetski, N.D.; Woodburn, S.I.; Woods, R. An electrochemical investigation of pyrite flotation and depression. *Int. J. Miner. Process.* **1977**, *4*, 227–239. [CrossRef]
- 21. Mustafa, S.; Hamid, A.; Naeem, A. Xanthate adsorption studies on chalcopyrite ore. *Int. J. Miner. Process.* **2004**, 74, 317–325. [CrossRef]
- 22. Shen, W.Z.; Fornasiero, D.; Ralston, J. Flotation of sphalerite and pyrite in the presence of sodium sulfite. *Int. J. Miner. Process.* **2001**, *63*, 17–28. [CrossRef]
- 23. Rani, A.; Gupta, C.S. Synthesis and characterization of various xanthates and their effects on germination and early seedling growth in wheat (*Triticum aestivum* L.). *Asian J. Chem.* **2013**, 25, 6995–6996. [CrossRef]
- Chandra, A.P.; Gerson, A.R. A review of the fundamental studies of the copper activation mechanisms for selective flotation of the sulfide minerals, sphalerite and pyrite. *Adv. Colloid Interface Sci.* 2009, 145, 97–110. [CrossRef]
- 25. Dávila-Pulido, G.I.; Uribe-Salas, A.; Espinosa-Gómez, R. Comparison of the depressant action of sulfite and metabisulfite for Cu-activated sphalerite. *Int. J. Miner. Process.* **2011**, *101*, 71–74. [CrossRef]
- 26. Doi, S. One-Step Microwave-Assisted Aqueous Synthesis of Silver-Based Nanoparticles Functionalized by Glutathione. *MRS Online Proc. Libr. Arch.* **2014**, *1*, 163–168.
- 27. Lucas, M.S. Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation. *Dyes Pigment.* **2006**, *71*, 236–244. [CrossRef]
- 28. Pan, J.; Jiang, J.; Xu, R. Chemosphere Removal of Cr(VI) from aqueous solutions by Na₂SO₃/FeSO₄ combined with peanut straw biochar. *Chemosphere* **2014**, *101*, 71–76. [CrossRef]
- 29. Miki, H.; Hirajima, T.; Muta, Y.; Suyantara, G.P.W.; Sasaki, K. Effect of sodium sulfite on floatability of chalcopyrite and molybdenite. *Minerals* **2018**, *8*, 172. [CrossRef]
- Klimpel, R.R. Selection of Chemical Reagents for Flotation. In *Mineral Processing Plant Design*, 2nd ed.; Mular, A., Bhappu, R., Eds.; AIME: New York, NY, USA, 1980; pp. 907–934.
- 31. Millero, F.J.; Feistel, R.; Wright, D.G.; McDougall, T.J. The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale. *Deep. Res. Part I Oceanogr. Res. Pap.* **2008**, *55*, 50–72. [CrossRef]
- Farrokhrouz, M.; Haghi, H. The Application of Hallimond Tube for Floatability Study of Pure Galena. In Proceedings of the 13th Conference on Environment and Mineral Processing, Ostrava, Czech Republic, 4–5 June 2009; Volume 1, pp. 89–96.
- 33. Fullston, D.; Fornasiero, D.; Ralston, J. Zeta potential study of the oxidation of copper sulfide minerals. *Colloids Surfaces A Physicochem. Eng. Asp.* **1999**, *146*, 113–121. [CrossRef]
- 34. Adamson, A.; Gast, A. *Physical Chemistry of Surfaces*; Adamson, G., Ed.; Wiley: Hoboken, NJ, USA, 1997; p. 190.
- Process, I.J.M.; Bafghi, M.S.; Emami, A.H.; Khaki, J.V.; Zakeri, A. Development of a mathematical expression for the variation of amorphization phenomenon during intensive milling of minerals. *Int. J. Miner. Process.* 2009, 93, 149–154.
- 36. Pan, G.; Zhang, G.; Shi, Q.; Chen, W. The effect of sodium alginate on chlorite and serpentine in chalcopyrite flotation. *Minerals* **2019**, *9*, 196. [CrossRef]
- 37. Andreev, G.N.; Barzev, A. Raman spectroscopic study of some chalcopyrite-xanthate flotation products. *J. Mol. Struct.* **2003**, *661–662*, 325–332. [CrossRef]

- Jehlička, J.; Vítek, P.; Edwards, H.G.M.; Heagraves, M.; Čapoun, T. Application of portable Raman instruments for fast and non-destructive detection of minerals on outcrops. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 2009, 73, 410–419. [CrossRef]
- 39. Vazquez-Sanchez, E.E.; Cabrera-Robledo, A.; Tong, X.; Lopez-Valdivieso, A. Raman spectroscopy characterization of some Cu, Fe and Zn sulfides and their relevant surface chemical species for flotation. *Physicochem. Probl. Miner. Process.* **2020**, *56*, 483–492. [CrossRef]
- 40. Fuerstenau, M.C. On the natural floatability of sulfides. Int. J. 1981, 8, 79–84. [CrossRef]
- 41. Mu, Y.; Peng, Y. The effect of saline water on copper activation of pyrite in chalcopyrite flotation. *Miner. Eng.* **2019**, *131*, 336–341. [CrossRef]
- 42. Li, Y.; Li, W.; Xiao, Q.; He, N.; Ren, Z.; Lartey, C.; Gerson, A. The influence of common monovalent and divalent chlorides on chalcopyrite flotation. *Minerals* **2017**, *7*, 111. [CrossRef]
- 43. Kal'nyi, D.B.; Kokovkin, V.V.; Mironov, I.V. Sodium sulfite: A promising reagent in the electrochemical oxidation of metallic silver. *Russ. J. Gen. Chem.* **2011**, *81*, 793–798. [CrossRef]
- 44. Castro, S. Physico-chemical factors in flotation of Cu-Mo-Fe ores with seawater: A critical review. *Physicochem. Probl. Miner. Process.* **2018**, *54*, 1223–1236.
- 45. Birkmann, J.; Pasel, C.; Luckas, M.; Bathen, D. Development of a measuring method for the determination of bisulfite and sulfite in seawater. *Chem. Ing. Tech.* **2019**, *91*, 1563–1574. [CrossRef]
- 46. Chander, S.; Khan, A. Effect of sulfur dioxide on flotation of chalcopyrite. *Int. J. Miner. Process.* **2000**, *58*, 45–55. [CrossRef]
- 47. Hancer, M.; Celik, M.S.; Miller, J.D. The significance of interfacial water structure in soluble salt flotation systems. *J. Colloid Interface Sci.* 2001, 235, 150–161. [CrossRef]
- 48. Damian Risberg, E.; Eriksson, L.; Mink, J.; Pettersson, L.G.M.; Skripkin, M.Y.; Sandström, M. Sulfur X-ray absorption and vibrational spectroscopic study of sulfur dioxide, sulfite, and sulfonate solutions and of the substituted sulfonate ions X 3 CSO 3-(X = H, Cl, F). *Inorg. Chem.* **2007**, *46*, 8332–8348. [CrossRef] [PubMed]

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