EVALUATING COLLECTOR BEHAVIOUR IN COARSE PARTICLE FLOTATION OF COPPER ORES

Daniel Nyarko[1], Massimiliano Zanin[1,2], George Abaka-Wood[1,3], William Skinner[1,3], Richmond Asamoah[1,3]

1. Future Industries Institute, University of South Australia, Mawson Lakes, SA 5095, Australia.
2. MZ Minerals Pty Ltd, Adelaide SA 5082.
3. ARC Centre of Excellence for Enabling Eco-Efficient Beneficiation of Minerals, University of South Australia, Mawson Lakes, SA 5095, Australia

Abstract

Most studies on collectors for copper ores have predominantly focused on conventional flotation systems (mechanical cells) and typical particle size ranges (<150 um particles), leaving a gap in understanding how different collector types perform under the unique hydrodynamic and mineralogical constraints of coarse particle flotation. This study evaluates the performance of four collector types: xanthates (PAX), dithiophosphates (C4450), thionocarbamates (C6523), and mercaptans (C1203) in coarse particle flotation of a copper ore in HydroFloat™. Focus was both on copper recovery and selectivity versus pyrite. Comparative flotation tests were conducted in both mechanically agitated cells and the HydroFloat™ at varying reagent dosages. Preliminary results demonstrate that, while pH significantly affects the selective flotation of chalcopyrite from pyrite, mineralogical limitations (poor liberation) associated with coarse particles affect selectivity. Additionally, collector concentration above baseline levels did not significantly influence flotation performance, except for PAX, which exhibited a gradual increase in recovery with increasing dosage. In HydroFloat™, PAX produced the highest copper recovery and grade. Ongoing work is focused on studying the influence of collectors on bubble-particle attachment and adsorption efficiency.

Keywords: Coarse particles, flotation, collectors, selectivity, HydroFloat

1 Introduction

Collectors are the primary agents used for enhancing hydrophobicity of particles during flotation by selectively adsorbing on the surface of the valuable mineral and modifying its interfacial properties (Wills and Finch, 2016). Collector molecules typically consist of a hydrophilic group that chemically or electrostatically binds to active sites on the mineral surface, and a non-polar aliphatic tail that extends into the aqueous phase, providing hydrophobic character. This adsorption increases the contact angle at the particle interface, promoting bubble–particle attachment and improving flotation efficiency (Castellón et al., 2022; Fuerstenau, 2007; McFadzean et al., 2015). In the flotation of coarse particles, typically larger than 150 µm, the main challenge lies in maintaining stable attachment forces between bubbles and particles, as well as reducing the probability of particle detachment (Awatey et al., 2014; Dankwah et al., 2021; Dankwah et al., 2022; Jameson, 2010; Kohmuench et al., 2018). These limitations necessitate diligent management of both hydrodynamics and collector chemistry to sustain effective flotation performance.

In sulphide flotation, anionic thiol-based collectors such as xanthates, dithiophosphates, thionocarbamates, and mercaptans are commonly employed (Castellón et al., 2022; Wills and Finch, 2016). The adsorption of collectors on sulphide minerals and the resulting flotation behaviour are strongly influenced by both pH and pulp redox potential (Eh). In complex mineral systems selectivity is dependent on the reagent dosage and pH as there exists an optimal pH range for floating each sulphide mineral within a mixed mineral system (Forson et al., 2023; Muzenda et al., 2011; Zanin et al., 2019). The pH controls the reaction between the ionic collectors and the surface charges of the mineral. Flotation of sulphides is carried out in alkaline conditions as most sulphide collectors tend to be unstable at lower pH ranges. High pH also tends to depress the sulphide minerals: pyrite being a noble mineral depresses first at pH 10 whiles chalcopyrite depresses at pH 12, creating a practical window for selective flotation between these minerals (Forson et al., 2021; Lee and Peng, 2024). Additionally, the Eh affects the oxidation of the mineral surfaces and the complexation with collectors by modifying surface charge and the availability of adsorption sites for collectors (Ralston, 1991). High Eh conditions can oxidize collectors or the mineral surface, reducing adsorption efficiency, whereas low Eh helps maintain collector stability and effective surface coverage (Dzinza, 2018; Göktepe, 2002).

The degree of hydrophobicity imparted to a mineral particle depends largely on the amount and chain length of the collector adsorbed on its surface, which is controlled by collector dosage (Brill et al., 2023; Santana et al., 2008). Studies have demonstrated that in coarser feeds, finer fractions float readily at low collector dosages, whereas coarser sizes require careful optimisation (Hassanzadeh and Karakaş, 2017). Other studies have likewise demonstrated that while small amounts of collector are needed to float fine and intermediate particles, a much higher degree of surface coverage is required for effective flotation of coarse particles when liberated (Crawford and Ralston, 1988; Shannon and Trahar, 1986; Vianna et al., 2003). Because collector molecules adsorb primarily onto exposed sulphide surfaces, the degree of surface liberation directly controls the extent of adsorption. In coarse particle flotation, the exposure of valuable minerals is often extremely limited, leaving few adsorption sites. Under these conditions, increasing collector dosage may enhance hydrophobicity on the limited exposed surfaces but also increases adsorption onto gangue minerals and the likelihood of multilayer or reverse adsorption, where polar hydrophilic groups are exposed to the pulp and active sites are masked (Castellón et al., 2022; Özün and Ergen, 2019). Together these effects reduce selectivity and can alter interfacial properties. Hence effective coarse particle flotation requires collectors which impart high hydrophobicity at minimum dosage.

As increasing collector dosage alone does not always compensate for limited surface exposure, the intrinsic molecular properties of collectors become critical in coarse particle flotation. The molecular structure including polar group chemistry, hydrophobic tail volume (or length) of collectors is central to their performance, especially for coarse particles. Studies have shown that longer alkyl chains on collector molecules enhance hydrophobicity by increasing the contact angle at the mineral surface, thus improving bubble-particle attachment collectors (Fosu et al., 2015; Taguta et al., 2017; Wark and Wark, 2002; Wills and Finch, 2016). Both the chemistry of the polar group and the size of the non-polar tail influence not only the strength of adsorption but also froth stability and selectivity. Collectors with bulky non-polar groups may improve attachment but can also increase gangue entrainment if the polar head is weakly binding (CAO et al., 2014; Özün and Ergen, 2019). This highlights that the balance between polar head and non-polar tail governs adsorption efficiency, hydrophobicity, and selectivity, which are all critical in coarse particle flotation.

While the effect of molecular chain length on xanthate collectors in coarse particle flotation has been explored in the literature, comparative studies of different collector groups and their impact on key coarse particle flotation parameters such as copper recovery, bubble–particle attachment and stability remain limited. This study seeks to explore the performance of different collector types, including xanthates, dithiophosphates (DTP), thionocarbamates (TC), and mercaptans, with a particular focus on coarse particle recovery and selectivity versus pyrite in HydroFloat™, also aiming at understanding how the different molecular structure influences adsorption. Future studies will also look into more fundamental aspects such as surface hydrophobicity of particles conditioned with collector and attachment efficiency in subsequent flotation.

2 Materials and methods

2.1 Sample preparation

Chalcopyrite and pyrite model minerals were used in this study. Approximately 500 g of each mineral was ground in a ring mill to achieve 80% passing 250 μm. To reduce the presence of ultrafine particles, the ground material was subjected to dry sieving to remove a portion of the −38 μm fraction. The samples were then split into 50 g portions and stored in airtight containers to minimise oxidation prior to flotation testing.

A porphyry copper-gold ore obtained from a mine in Australia, containing 0.4% Cu, was crushed using a laboratory jaw crusher, followed by a roll crusher to achieve 100% passing 2 mm. The crushed material was then split into 8 kg charges to serve as feed for a pilot-scale laboratory rod mill. Grind calibration was conducted using an 8 kg charge at a pulp density of 67% w/w solids, targeting a P_{80} of 250 μm. The resulting wet-milled product was used as feed for subsequent HydroFloat™ flotation experiments. The major copper-bearing minerals were chalcopyrite and bornite, with a combined abundance of approximately 1.3%. Pyrite and silicates being the major gangue minerals were present at abundances of 1.8% and 89%, respectively.

2.2 Flotation reagents

Flotation reagents (collectors and frother) used in this test were sourced from InterChem (Victoria, Australia). Their specific molecular weights are shown in Table 1. For the comparison, reagents were added in flotation at the same molar concentration (mmol/t), as discussed further below.

Table 1 Flotation collectors tested and their respective molecular weights (MW).

Class	Collector	MW, g/mol
Xanthate	Potassium Amyl Xanthate (PAX)	202
DTP	Intercol C4450	144
TC	Intercol C6523	142

Mercaptan	Intercol C1203	202

Interfloat® F236, a mixture of hexanols, pentanols, and glycol ethers was employed as the frother throughout the study, while pH modification in model mineral experiments was accomplished using 1% HCl and NaOH; lime was utilized for pH adjustment in real ore studies.

2.3 Flotation of model minerals

Single mineral flotation experiments were conducted separately on 10 g samples of chalcopyrite and pyrite using a 300 ml IMN flotation cell operated at 720 rpm. The pulp pH was carefully adjusted to the desired level using 1% HCl or NaOH solutions, followed by conditioning with collector for 3 minutes and frother for 1 minute. Flotation was performed for a total of 10 minutes with air introduced at a rate of 1.5 L/min, and concentrates were collected at 15-second intervals. At the conclusion of the tests, both the collected concentrates and remaining tailings were oven-dried, and their masses were used to calculate the overall flotation recovery of each mineral under the tested conditions. All tests were conducted in duplicate, and the average values along with error bars are presented on the graphs.

2.4 Zeta Potential Measurement

The zeta potential in the absence and presence of various collectors was measured using a Malvern Zetasizer Nano Series meter. 500 mg of -38 µm size fraction of chalcopyrite model mineral was added to 250 ml of 1×10^{-3} KNO_3 and agitated for 10 min on a magnetic stirrer. For measurement where collectors were added, they were allowed 3 min conditioning time. The suspension was left to stand for 5 min to allow relatively coarse particle to settle. 15 ml of the suspension was picked using a syringe from the surface and introduced into the cell of the Zetasizer, operated in titration mode. Automatic pH adjustment was carried out using 0.25 M KOH and HNO_3. An average of three measurement was recorded for each pH unit and presented.

2.5 Flotation in HydroFloat™

2.5.1 The Laboratory HydroFloat™

The laboratory HydroFloat™ used features a 140 mm diameter and has a dry solids capacity of approximately 30 kg/h. It is equipped with a pressure transducer that monitors the pressure load at the base of the fluidized bed. This measurement enables regulation of bed height by automatically opening the bottom discharge valve, ensuring optimal operational control.

2.5.2 Desliming of feed

The HydroFloat™ requires its feed be deslimed to remove finer particles before flotation. To achieve this, the feed was introduced into the HydroFloat™ cell, which was operated in crossflow mode, in the absence of air or reagents. The cell was run at a superficial water velocity (SWV) of 0.43 cm/s to wash out the fines as overflow, performing a particle size cut at 75 µm. This setup produces a "deslimed" feed, minimizing interference from fine particles while optimizing coarse particle recovery.

2.5.3 Flotation

The deslimed feed was conditioned to a pH of 9 by the addition of hydrated lime. Each feed was separately conditioned with 300 mmol/t collector at 70% solids while being stirred with a handheld mixer for about 3 minutes. The conditioned feed was then introduced into the HydroFloat cell using a vibratory feeder to ensure a controlled feed rate. Concentrates were collected from the overflow launder, while tailings were collected from the dewatering cone through the underflow tube. The superficial water velocity was varied, starting at 0.24 cm/s for the first run, followed by 0.28 cm/s and 0.32 cm/s for the second and third runs, respectively. After each run, concentrates were collected, and tailings were recycled to generate three separate concentrates. Throughout all runs, the gas flow rate was maintained at 20% of the superficial water velocity. After flotation, the resulting concentrates and tails were filtered and analysed by ICP-OES to determine recoveries and grades. Pyrite recovery was calculated based on the stoichiometric composition of sulphide minerals present in the ore, using Cu, Fe, and S assay data. Concentrates and tails were further sized into +250 µm, -250 µm +150 µm, -150 µm +75 µm, and -75 µm fractions and each fraction was subsequently analysed by ICP-AES. All tests were done in duplicate, with average values and error bars reported on the graphs.

3 Results and discussion

3.1 Single mineral studies in mechanical cell

3.1.1 Effect of pH on flotation performance

The recovery of chalcopyrite with respect to pH for the various collector types is shown in Figure 1a. Chalcopyrite flotation performance was relatively stable across the tested pH range with all collectors, with recovery values generally between 75% and 83%. C1203 achieved highest recovery at pH 7 (80%) but showed a slight decline with increasing pH, reaching 77% at pH 11. C6523 exhibited the highest recovery of 83% at pH 9, reflecting optimal chelation conditions, but a slight decrease at pH 11. C4450 showed consistent recovery of ~80% at pH 7 and 9 but declined to 77% at pH 11. PAX maintained stable recoveries, slightly increasing from 75% at pH 7 to 77% at pH 11, suggesting limited sensitivity to pulp chemistry conditions tested.

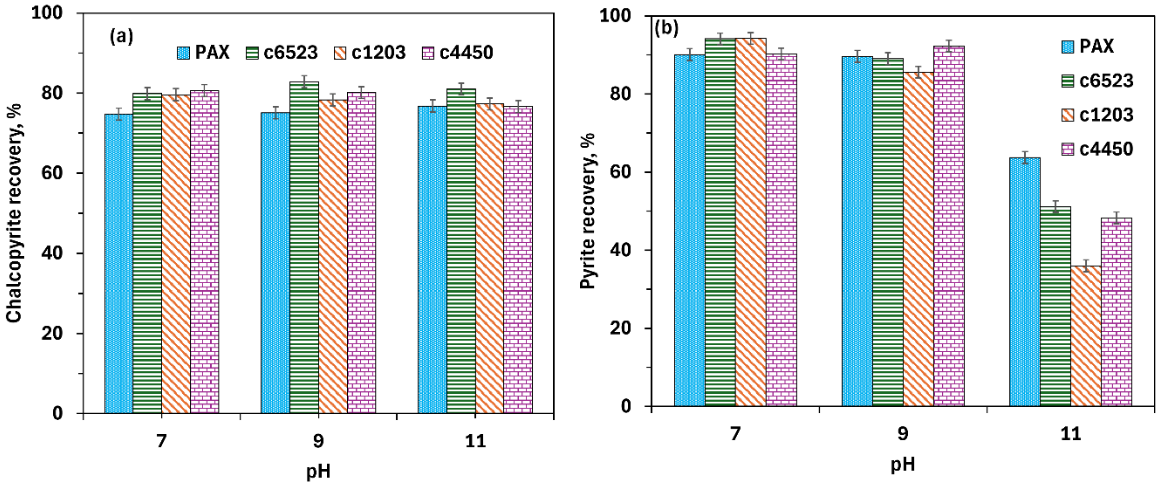

Figure 1 Chalcopyrite (a) and pyrite (b) recoveries at various pH values

Pyrite recovery with the various collectors is shown in Figure 1b. At pH 7, all collectors achieved high recoveries above 90%, with C1203 and C6523 reaching over 94%. A noticeable drop occurs at pH 9 for C1203 where recovery decreased from 94% to 86% indicating early onset of pH influence for the collector. At pH 11, a significant decrease in recovery was observed for all collectors, with values falling between 36% (C1203) and 64% (PAX). C6523 and C4450 showed intermediate recoveries of 51% and 48%, respectively. These results indicate poor pyrite recovery at high pH, consistent with known behaviour where alkaline conditions favour surface oxidation and collector incompatibility on pyrite, demonstrating the potential for selective flotation control via pH adjustment (Lee and Peng, 2024).

3.1.2 Zeta potential

The zeta potential measurements of chalcopyrite in the presence of different collectors across a pH range is shown in Figure 2. The measurements indicated that chalcopyrite surface was negatively charged under the flotation conditions in the absence of collectors (control), ranging from −1.5 mV at pH 7 to −25.3 mV at pH 11. Among the collectors, PAX induced the largest negative shift at pH 7

(−5.9 mV) and pH 9 (−7.5 mV), suggesting stronger adsorption. C1203 was slightly more negative than the control at pH 7 (−6.7 mV) and pH 11 (−26.8 mV), but slightly less negative at pH 9. C4450 and C6523 showed smaller modifications across the pH range, with shifts closer to the unconditioned chalcopyrite values. Overall, PAX appears to have the most consistent effect in enhancing surface negativity in the flotation range. Since the zeta potential changes are small, with unconditioned chalcopyrite constantly negative in flotation relevant range, flotation performance is likely governed primarily by collector-surface interactions and hydrophobicity rather than large changes in electrostatic forces.

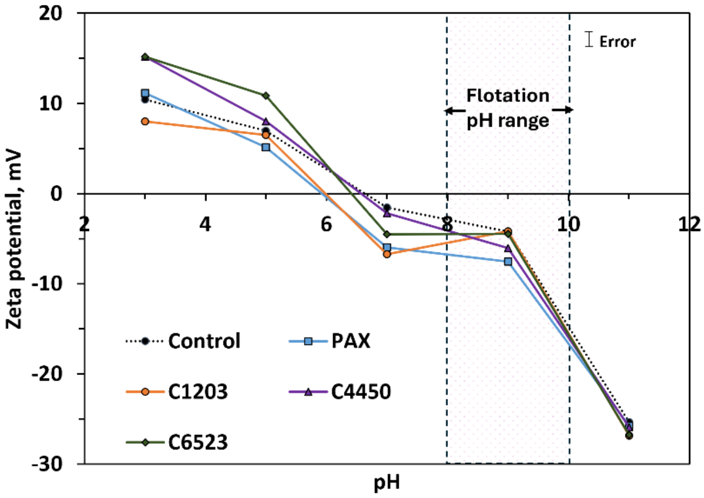

Figure 2 Zeta potential of chalcopyrite when conditioned with the various collectors.

3.1.3 Effect of collector concentration on flotation

The recovery of chalcopyrite as a function of collector concentration at pH 9 is presented in Figure 3. Collector dosage range was selected to match the typical operating ranges reported in prior HydroFloat™ sulphide flotation studies (Awatey et al., 2013; Dadzie et al., 2025; Zanin et al., 2021). Across the tested dosage range, PAX showed a more pronounced increase in chalcopyrite recovery with increase in collector concentration compared to the other collectors. For C1203, a slight drop in chalcopyrite recovery was observed at 450 mmol/t, accompanied by noticeable froth instability. This suggests that C1203 achieves good froth stability and flotation performance within a narrow dosage range. In contrast, both C4450 and C6523 maintained relatively stable recoveries across all dosages tested.

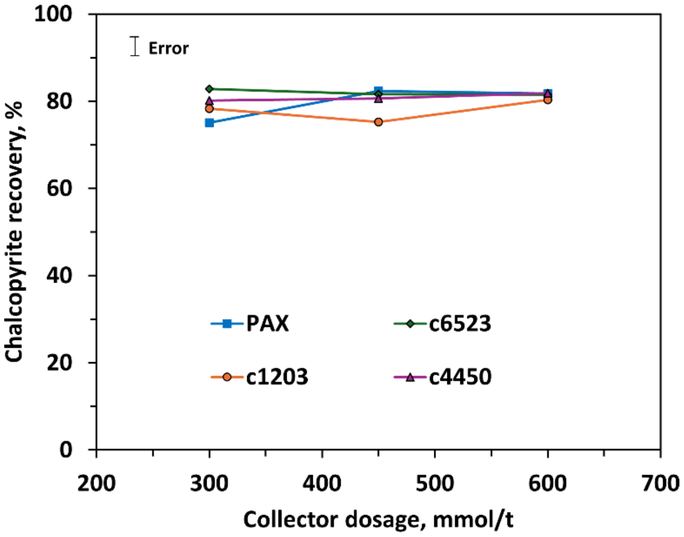

Figure 3 Chalcopyrite recovery at various collector concentrations at pH 9

3.2 Flotation performance in HydroFloat™

The cumulative copper recovery and copper grade observed at increasing water velocity for all collectors are presented in Figure 4a. Across all collectors, copper recovery increased with increasing water flow rate. At the highest water flow rate of 3.2 L/min, the cumulative copper recoveries were 75%, 74%, 61%, and 70% for PAX, C1203, C6523, and C4450 respectively. Copper grades remained relatively low, below 1.3% across all collectors, with PAX and C1203 showed minimal variation with flow rate, despite increasing recovery. In contrast, C6523 and C4450 exhibited a gradual decline in grade from 0.9% to 0.7% and from 1.3% to 0.9%, respectively, as recovery increased. The low grade can be explained by the finely disseminated mineralisation of copper in the ore. Composite particles with very little exposed copper, report to the HydroFloat™ concentrate, which is good for recovery, but inevitably produces low concentrate grade.

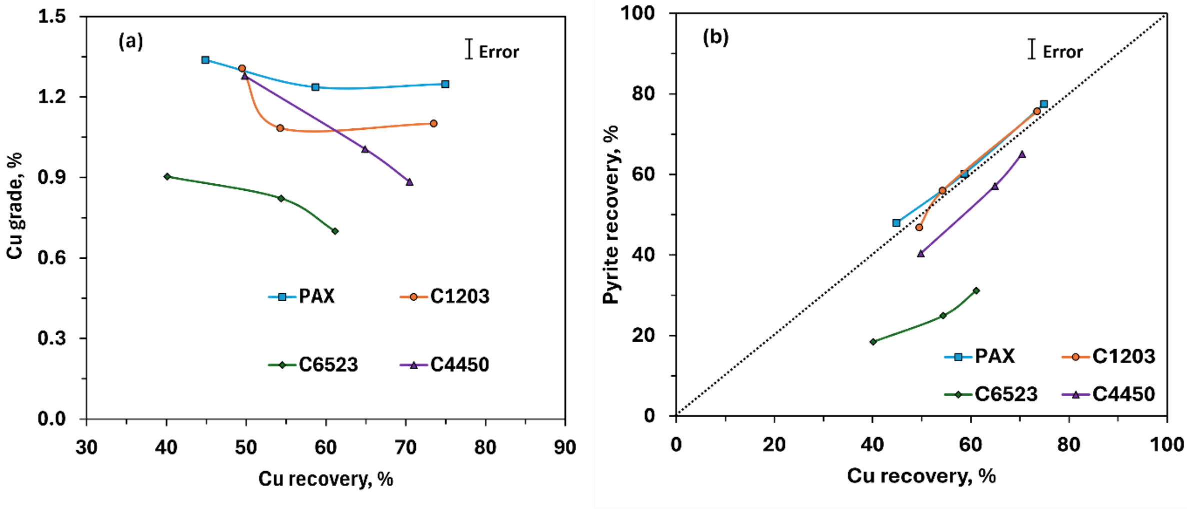

Figure 4 Cumulative Cu grade versus recovery (a) and pyrite recovery versus copper recovery (b) at increasing water flowrates in the HydroFloat™ at 300 mmol/t collector concentration

Pyrite recovery followed Cu recovery (poor selectivity) in the tests with PAX and C1203 (Figure 4b). In contrast, C6523 exhibited markedly higher selectivity (pyrite recovery 31% at 63% Cu recovery), although chalcopyrite was also depressed to an extent. C4450 displayed intermediate behaviour, with moderate pyrite recovery (65.1%) at 72% Cu recovery. Mineralogy, and poor liberation of Cu at such coarse grind size, is also an obvious limiting factor to selectivity in HydroFloat™.

4 Conclusions

The performance of PAX, C1203, C6523, and C4450 in coarse flotation of chalcopyrite and pyrite was evaluated under varying pH and collector dosage. Chalcopyrite recovery was generally stable across pH 7–11, with PAX and C4450 showing limited sensitivity, while C1203 and C6523 exhibited slight variations. Pyrite recovery decreased markedly at high pH (>11), demonstrating effective gangue depression and the potential for selective flotation. Collector dosage influenced recovery differently among collectors. PAX showed a consistent increase in recovery with dosage, C1203 displayed non-linear behaviour likely linked to froth instability, and C6523 and C4450 maintained stable performance, reflecting consistent adsorption and selectivity. In the HydroFloat™, Cu recovery increased with increase in the teeter water flowrate, which enhances the drag force on bubble/particle aggregates and allows for higher mass pull, with PAX achieving the highest cumulative recovery. Pyrite recovery was lowest for C6523, which however also produced the lowest Cu recovery and grade at the concentration used. Cu grade for both PAX and C1203 was relatively higher compared to the other collectors. These preliminary results highlight that collector type, and operating conditions critically affect coarse particle flotation. Further optimisation is however needed.

5 Acknowledgements

The authors would acknowledge the funding support from the Advanced Flotation Project and the ARC Centre of Excellence for Enabling Eco-Efficient Beneficiation of Minerals, grant number CE200100009. The authors gratefully thank InterChem for providing the flotation reagents used in this study.

6 References

Awatey, B., Thanasekaran, H., Kohmuench, J.N., Skinner, W. and Zanin, M., 2013. Optimization of operating parameters for coarse sphalerite flotation in the HydroFloat fluidised-bed separator. Minerals Engineering, 50: 99-105.

Awatey, B., Thanasekaran, H., Kohmuench, J.N., Skinner, W. and Zanin, M., 2014. Critical contact angle for coarse sphalerite flotation in a fluidised-bed separator vs. a mechanically agitated cell. Minerals Engineering, 60: 51-59.

Brill, C., Verster, I., Franks, G. and Forbes, L., 2023. Aerosol Collector Addition in Coarse Particle Flotation–A Review. Mineral Processing and Extractive Metallurgy Review, 44(7): 522-531.

CAO, F., SUN, C.-y., WANG, H.-j. and CHEN, F.-w., 2014. Effect of alkyl structure on the flotation performance of xanthate collectors. Chinese Journal of Engineering, 36(12): 1589-1594.

Castellón, C.I. et al., 2022. Froth flotation of chalcopyrite/pyrite ore: a critical review. Materials, 15(19): 6536.

Crawford, R. and Ralston, J., 1988. The influence of particle size and contact angle in mineral flotation. International Journal of Mineral Processing, 23(1-2): 1-24.

Dadzie, R.A., Zanin, M., Skinner, W. and Abaka-Wood, G.B., 2025. HydroFloat™ Flotation of Fine Copper Tailings: Performance Analysis, Hydrodynamics, and Reagent Optimisation, 11th World Congress on Mechanical, Chemical, and Material Engineering (MCM'25), Barcelona, Spain.

Dankwah, J., Asamoah, R., Zanin, M. and Skinner, W., 2021. A brief review on fluidized bed flotation: Enhancing coarse particle flotation. Chemeca 2021: Advance, Disrupt and Sustain: Advance, Disrupt and Sustain: 1-11.

Dankwah, J., Asamoah, R., Zanin, M. and Skinner, W., 2022. A Simple Analysis Showing the Limits of Coarse Particle Flotation, Proceedings of 7th UMaT Biennial International Mining and Mineral Conference, 2022a Tarkwa, Ghana, pp. 1-7.

Dzinza, L., 2018. An investigation into the effect of potential modifiers on the flotation of a copper sulphide ore.

Forson, P., Skinner, W. and Asamoah, R., 2021. Decoupling pyrite and arsenopyrite in flotation using thionocarbamate collector. Powder Technology, 385: 12-20.

Forson, P., Skinner, W. and Asamoah, R., 2023. Investigating the selective flotation of auriferous arsenian pyrite from refractory ores using thionocarbamate. Powder Technology, 426: 118649.

Fosu, S., Skinner, W. and Zanin, M., 2015. Detachment of coarse composite sphalerite particles from bubbles in flotation: Influence of xanthate collector type and concentration. Minerals Engineering, 71: 73-84.

Fuerstenau, D.W., 2007. A century of developments in the chemistry of flotation processing. Froth flotation: A century of innovation: 1-13.

Göktepe, F., 2002. Effect of pH on pulp potential and sulphide mineral flotation.

Hassanzadeh, A. and Karakaş, F., 2017. Recovery improvement of coarse particles by stage addition of reagents in industrial copper flotation circuit. Journal of Dispersion Science and Technology, 38(2): 309-316.

Jameson, G.J., 2010. Advances in fine and coarse particle flotation. Canadian Metallurgical Quarterly, 49(4): 325-330.

Kohmuench, J., Mankosa, M., Thanasekaran, H. and Hobert, A., 2018. Improving coarse particle flotation using the HydroFloat™(raising the trunk of the elephant curve). Minerals Engineering, 121: 137-145.

Lee, R.L.J. and Peng, Y., 2024. Assessing the depression of high-concentration pyrite in copper flotation by high pH. Minerals Engineering, 209: 108651.

McFadzean, B., Moller, K. and O'Connor, C., 2015. A thermochemical study of thiol collector surface reactions on galena and chalcopyrite. Minerals Engineering, 78: 83-88.

Muzenda, E., Afolabi, A.S., Abdulkareem, A.S. and Ntuli, F., 2011. Effect of pH on the Recovery and grade of base metal sulphides (PGMs) by flotation, Proceedings of the World Congress on engineering and Computer Science, pp. 2.

Özün, S. and Ergen, G.l.a., 2019. Determination of optimum parameters for flotation of galena: effect of chain length and chain structure of xanthates on flotation recovery. ACS omega, 4(1): 1516-1524.

Ralston, J., 1991. Eh and its consequences in sulphide mineral flotation. Minerals Engineering, 4(7-11): 859-878.

Santana, R.C., Farnese, A.C., Fortes, M.C., Ataíde, C.H. and Barrozo, M.A., 2008. Influence of particle size and reagent dosage on the performance of apatite flotation. Separation and Purification Technology, 64(1): 8-15.

Shannon, L. and Trahar, W., 1986. The role of collector in sulphide ore flotation. Advances in Mineral Processing: A Half-Century of Progress in Application of Theory to Practice: 408-425.

Taguta, J., O'Connor, C. and McFadzean, B., 2017. The effect of the alkyl chain length and ligand type of thiol collectors on the heat of adsorption and floatability of sulphide minerals. Minerals Engineering, 110: 145-152.

Vianna, S.M., Franzidis, J., Manlapig, E.V., Silvester, E. and Fu, P., 2003. The influence of particle size and collector coverage of the floatability of galena particles in a natural ore, 22nd International Mineral Processing Congress, Cape Town, pp. 816-826.

Wark, E.E. and Wark, I.W., 2002. The Physical Chemistry of Flotation. III. The Relationship between Contact Angle and the Constitution of the Collector. The Journal of Physical Chemistry, 37(6): 805-814.

Wills, B.A. and Finch, J.A., 2016. WIll's Mineral Processing Technology: An introduction to the Practical Aspects of Ore Treatment and Minerals Recovery Eight Edition. Elsevier.

Zanin, M., Chan, E. and Skinner, W., 2021. Modelling the fluidised bed in HydroFloat™ for improved process control. Powder Technology, 388: 241-250.

Zanin, M., Lambert, H. and Du Plessis, C., 2019. Lime use and functionality in sulphide mineral flotation: A review. Minerals Engineering, 143: 105922.