Determination of Optimum Parameters for Flotation of Galena: Effect of Chain Length and Chain Structure of Xanthates on Flotation Recovery

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ABSTRACT: The structure of the xanthates’ hydrocarbon (C−H) chain is one of the major factors which affect flotation recovery. The effectiveness and the collecting power of xanthates increase with increasing chain length and vary depending on the chain structure: branched and straight chains. In this regard, the influences of length (2−5 carbon) and structure (straight: normal and branched: iso) of xanthate’s hydrocarbon chain on flotation recovery of galena were investigated under different experimental conditions: xanthate concentration, conditioning time, air flow rate (AFR), and air bubble size. Because of the steric effects of the chain structure, the branched chain xanthates gave lower flotation recoveries with shorter conditioning times compared to those with straight chain xanthates. Over-conditioning with straight chain xanthates resulted in hydrophobic aggregation of galena particles which resulted in the detachment of galena particles from air bubbles due to increasing weight, leading to lower flotation recoveries. In the case of flotation with different AFRs, the flotation recoveries increased with increasing AFR to 7 lph and further increase in AFR (10 lph) negatively affected the flotation recoveries when particles had insufficient hydrophobic surfaces. The maximum flotation recoveries were obtained with the addition of MIBC (methyl isobutyl carbinol) as a frother; the size of the air bubbles deceased with increasing MIBC concentration which increased higher encounter/collision probability of air bubbles with galena particles, resulting in higher flotation recoveries.

1. INTRODUCTION

Lead is defined as a chalcophile element according to Goldschmidt’s classification. Chalcophile elements are elements such as Zn, Pb, As, Sb, Ag, Hg, Cd, and so forth which preferentially bond with sulfur to form sulfides. Thus, lead is rarely present in the environment in its free form. Instead, it is generally found in combination with other elements in the form of minerals. Galena (PbS) and its oxidized forms cerussite (PbCO₃) and anglesite (PbSO₄) are the most common forms of lead in the earth’s crust. Of these minerals, galena has the highest lead content, and it coexists in nature with sphalerite (ZnS), chalcopyrite (CuFeS₂), pyrite (FeS₂), quartz (SiO₂), calcite (CaCO₃), fluorspar (CaF₂), silver, and so forth, thus, froth flotation can be applied selectively in order to obtain high-grade concentrates.¹²³

Sulfide minerals are weakly polar due to their covalent bonding, which makes their surfaces hydrophobic when they have freshly crushed/ground surfaces. Thus, sulfide minerals having fresh and less oxidized surfaces show natural floatability and readily float without a collector.¹⁴ The natural floatability of sulfide minerals under appropriate conditions has been reported in the descending order as chalcocytite > galena > pyrrhotite > sphalerite > pyrite > arsenopyrite.⁶⁷ However, the hydrophobic behavior of their surfaces, and thus the flotation recovery responses in the presence/absence of xanthates, decreases with surface oxidation. Oxidation often occurs when minerals are exposed to open atmosphere and/or an aqueous environment during mining and mineral-processing operations.⁸⁻¹⁰ The oxidation rates of sulfide minerals in air and aqueous solutions have been visualized by scanning electron microscopy, scanning tunneling microscopy, scanning auger microscopy, atomic force microscopy, and so forth.¹¹⁻¹⁴ From these experiments, the oxidation rate of galena was found to be less than that of chalcopyrites and pyrites.¹⁵ Even though sulfide minerals with fresh surfaces may easily float and/or rapid oxidation on their surfaces may prevent flotation (i.e. galena), the hydrophobicity is mostly enhanced by the use of xanthates.⁴¹⁶

Among the numerous factors which affect the collecting power of xanthates,¹⁷ the structure of nonpolar (C−H) chain plays a crucial role during selective separation of sulfide minerals by flotation.¹⁸ If the ore contains multiple sulfide minerals, two strategies can be applied for the recovery of sulfide minerals. In the first case, as the collecting power of the xanthates increases with increasing C−H chain length,¹⁸ the long chain xanthates are preferentially selected to collect all

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sulfide minerals as a bulk concentrate. Furthermore, upgrading of an ore having finely ground sulfide minerals can be possible with the use of long-chain xanthates, resulting in better flotation recovery by inducing aggregation and hydrophobization of the fine sulfide particles. In the second case, if selectivity is more important than flotation recovery alone, the less powerful xanthate derivatives are selected in order to form separate concentrates at successive flotation stages. In either case, the selection of C–H chain length is generally limited to 2–5 carbon atoms because xanthates with longer chain lengths have much lower solubility in an aqueous environment than xanthates with shorter chain lengths. Therefore, the use of xanthates with longer chains results in a decrease in the concentration of xanthate species adsorbed on mineral surfaces. The structure of C–H chain is another important factor, which affects the flotation recovery and selective separation of sulfide minerals. It indirectly affects the adsorption capability of a xanthate on the mineral surface, thus promoting the floatability of mineral particles. For example, the adsorption capabilities of iso-xanthates with branched chains on mineral surfaces have been reported to be much higher than α-xanthates having straight chains. Broadly speaking, this problem has attracted a lot of attention in the field of mineral processing. However, most of the earlier studies have focused on the usage of xanthates for the recovery of single or multisulfide minerals from sulfide ores in ideal flotation conditions. One of the major aims of this study, therefore, was to analyze and investigate the effects of hydrocarbon chain length (2–5 carbon atoms) and hydrocarbon chain structure (straight chain and branched chain) of xanthates to contribute to a greater understanding of the flotation recovery of galena. Furthermore, the effects of different variables, such as collector concentration, conditioning time, air flow rate (AFR), and air bubble size on flotation recovery of galena were also investigated in the presence of each xanthate with different chain lengths and structures.

2. RESULTS AND DISCUSSION

2.1. Effect of Collector Concentration on Flotation Recovery. Xanthates are the salts of xanthic acid (alkyl/aryl dithiocarbonic acid) and are formed through the replacement of two oxygen atoms in carbonic acid by sulfur and replacement of one hydrogen atom by an alkyl/aryl group. They are commonly used as a standard collector for sulfide minerals, and their collecting power varies with C–H chain length and the C–H chain structure they carry. This part of the study therefore aimed to compare the effects of xanthate concentration (1–50 ppm) on flotation recovery of galena, with variations depending in the hydrocarbon chain (2–5 carbon) and hydrocarbon chain structure (straight and branched chain) of xanthates (PEX, SIPX, SIBX, and PAX). The microflotation tests were conducted below the critical micelle concentration of each collector at four different pH values between highly acidic and alkaline conditions (pH 2–11.5), a function of concerned parameters (Table 1), at ambient temperature. The zeta potential values and the collector concentration versus flotation recovery profiles of microflotation tests are given in Figures 1 and 2a–d, respectively.

In Figure 1, the results show that the zeta potential values of galena in water vary depending on pH. It shows slightly positive zeta potentials at highly acidic values and shows negative zeta potential values through alkaline pHs with increasing magnitude by displaying isoelectric point (pHiep) at about pH 2.8. In the case of microflotation tests, the results given in Figure 2a–d show that the flotation recovery galena increases with increasing collector concentration at certain pH values and changes depending on the chain length and chain structure of the xanthate used. While the minimum flotation recoveries were obtained at highly alkaline pH values (pH > 11) for each xanthate, the highest flotation recoveries were obtained at moderately alkaline pH conditions (pH 9–9.5) with straight-chain xanthates (over 90% with PEX and PAX). Because of the shape factor that governs the effectiveness of adsorption of xanthates on the surface, the molecules with branched or ring chains showed tendencies to poorer adsorption layer formation as compared to straight-chain xanthates. Therefore, the flotation recoveries obtained with branched-chain xanthates (over 65% with SIBX and over 55% with SIPX) were found to be less than those with straight-chain xanthates.

It is worth mentioning here that prior to the microflotation tests with each collector, the microflotation tests were first performed in distilled water in order to determine the natural floatability of the galena sample. According to the results, after cleaning and drying stages, the mineral surfaces were oxidized, resulting in less than 10% flotation recoveries over the entire pH range. It is also worth indicating that the reactions between sulfide minerals and xanthates are complex, and many mechanisms have been proposed. Xanthates are assumed to adsorb mostly by irreversible chemical bonds to the OCSS group in the polar heads forming insoluble metal xanthates with a high degree of hydrophobicity which changes depending on the metallic compounds that exist on the mineral surface. The species distribution diagram of Pb ion as a function of pH given in Figure 3 shows that Pb is found dominantly as Pb in the

| Table 1. Experimental Conditions in Microflotation Tests |
|-----------------------------------------------|
| particle size range | −106 + 75 μm |
| mineral amount | 1 g |
| stirring speed | 400 rpm |
| conditioning time | 5 min |
| pH | 2–11.5 |
| AFR | 4 lph |
| flotation time | 2 min |
| collector concentration | 1–50 ppm |

Figure 1. Zeta potentials of galena.
acidic–neutral pH range and predominantly as Pb(OH)$^+$ in the neutral–basic (pH 7.5–9.5) pH range. Their concentrations decrease while the concentrations of Pb(OH)$_2$ and Pb(OH)$_3$$^-$ increase with increasing pH. Moreover, xanthates consist of anionic monomers (X$^-$) dominated at neutral–alkaline pH conditions. The monomer concentrations of xanthates, and thus their collecting ability, decrease with decreasing pH at neutral–acidic pH values where xanthates hydrolyze to form xanthic acid (HX) and form dixanthogene when exposed to an open atmosphere (Figure 3b).$^{27}$

Considering the species distribution diagrams given in Figure 3a,b, and the zeta potential values of galena given in Figure 1, the high flotation recoveries of galena at 2–2.5 pH (Figure 2a) were mostly caused by Coulombic forces: the interaction between oppositely charged xanthate species (X$^-$) and mineral surfaces (Pb$^{2+}$). With increasing pH, the magnitude of negative zeta potential values of galena increased and the concentration of Pb$^{2+}$ in the pulp decreased which resulted in lower flotation recoveries especially for PEX, SIPX, and SIBX in the pH range of 6–6.5 (Figure 2b). Galena had increasing stability of surface charge with increasing pH and displayed net negative zeta potentials ($-30$ mV) at pH 9–9.5, and the xanthate dominated as ionic monomers (X$^-$) in the pulp. Even so, the flotation recoveries with each collector increased to maximum values at given pH values. The results indicated that an adsorption occurred between galena and each xanthate sample was mostly by the chemical interaction of xanthate monomers$^{24,25}$ with Pb(OH)$^+$. However, a further increase in pH (>pH 11) resulted in the minimum flotation recoveries (<15% with PEX, SIPX, and SIBX) even in the presence of the highest collector concentration used. The pH-dependent flotation recovery results in this study were similar to those obtained by Ma et al., 2017.$^{28}$

According to the molecular orbital theory proposed first by Fukui et al., 1952,$^{31}$ the energy gap ($\Delta E$) between the highest occupation molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is considered an important stability index. The higher the gap, the higher the

Figure 2. Flotation recovery of galena with xanthate at (a) pH 2–2.5, (b) pH 6–6.5, (c) pH 9–9.5, and (d) pH 11–11.5.

Figure 3. Species distribution diagram of (a) Pb$^{2+}$ and (b) xanthate.$^{27,30}$
stability of a molecule and the lower the reactivity. The results given in Table 2 showed that when two straight-chain xanthates were compared, PAX, having higher $\Delta E_{\text{HOMO-LUMO}}$ value, displayed higher reactivity than PEX. Similarly, SIBX displayed higher reactivity value than SIPX when branched-chain xanthates were compared. These results were compatible with the flotation recovery results obtained. The lower HOMO and higher LUMO values of PEX and SIPX indicated that they had a weaker ability to donate and accept electrons as compared to the abilities of PAX and SIBX. Furthermore, the results also indicated that an increase of the alkyl in the carbon chain resulted in an increase in reactivity, which was similar to the results obtained in the zinc oxide flotation using an amine collector. The lower flotation recoveries seen in the presence of branched xanthates compared to those with $n$-xanthates might be due to the greater steric hindrance caused by the branched structure, resulting in the lower surface coverage on the mineral surface and thereby lower hydrophobicity.

### 2.2. Effect of Conditioning Time on Flotation Recovery

The success of the flotation process is largely determined by the interaction of xanthates with the target mineral particles and is mainly dependent on the characteristics of the xanthate and mineral, pH, conditioning time, collector concentration, and so forth. Thus, in order to determine the effect of conditioning time on flotation recovery, the flotation recovery responses of galena with 2.5–10 min conditioning intervals were investigated in the presence of 2.5 ppm collector concentration (100 mL) above neutral pH conditions, with over variables held constant. The results of flotation tests are shown in Figure 4a–c for 2.5, 5, and 10 min conditioning intervals.

The results given in Figure 4a–c show that flotation recoveries of galena can change depending on the conditioning time, pH, and collector chain structure. From the results obtained, the conditioning time had a marked effect on the collector uptake, and the maximum flotation recoveries were obtained above pH 7 and dropped rapidly through highly alkaline pH values. For 2.5 min of conditioning, the maximum flotation recoveries were about 20% with SIPX, 25% with SIBX, and 35% with PEX and above 50% with PAX. The adsorption capabilities of each xanthate on galena increased with increasing conditioning time as reported by Aktas et al., 2008, which resulted in approximately 10–15% higher flotation recoveries after 5 min of conditioning. Up to 5 min of conditioning, the straight-chain xanthates (PEX and PAX) provided higher flotation recoveries than branched-chain xanthates (SIPX and SIBX). However, longer conditioning time (10 min) had a slightly negative influence on the flotation recoveries obtained with the straight-chain xanthates, while the flotation recovery values with SIPX and SIBX enhanced more than those obtained with 5 min of conditioning. It has been previously reported by Kuopanportti et al., 2000 that the adsorption of xanthates on a mineral surface is a rapid process and takes place in a few minutes. Thus, overconditioning in the presence of straight chain xanthates resulted in hydrophobic aggradation of galena particles. Then, the galena particles detached easily from the air bubbles due to the increasing weight of aggregated particles, resulting in lower flotation recoveries.

In the case of branched chain xanthates, the steric hindrance caused by the branched structure of SIPX and SIBX negatively affected interactions of xanthate species with the galena surface. Thus, the shorter conditioning time intervals (2.5 and 5 min) resulted in lower flotation recoveries, whereas the longer conditioning time (10 min) enhanced adsorption capability of branched chain xanthates which therefore indirectly prevented them to aggregate, resulting in higher flotation recoveries.

### 2.3. Effect of AFR on Flotation Recovery

In the flotation process, air bubbles are primarily responsible for carrying the hydrophobic mineral particles to froth zone and then transferring them over the flotation cell lip. A higher number of air bubbles in the flotation cell increases the encounter/collision probability of particles with air bubbles, which increases with increasing AFR. Hence, this part of the study aimed to investigate the effect of AFR on flotation recovery of galena with different AFRs between 4 and 10 lph using 2.5 ppm collector concentration (100 mL) above neutral pH conditions. According to the results given in Figure 5a–c, the minimum flotation recoveries of galena were obtained with AFR of 4 lph. As the AFR increased from 4 to 7 lph (Figure 5a,b), the number of air bubbles and thus the flotation recoveries increased to maximum values over 80% flotation recoveries for PEX, SIBX, and PAX, as was expected. However, a further increase in AFR to 10 lph resulted in the lowest flotation recoveries obtained (<40%) for each xanthate used.

![Figure 4](image_url) **Figure 4.** Flotation recovery of galena after (a) 2.5, (b) 5, and (c) 10 min of conditioning steps.
Figure 5. Flotation recovery of galena in the presence of 2.5 ppm with (a) 4, (b) 7, and (c) 10 lph of AFRs.

AFR has also a significant impact on bubble size and the probability of coalescence of air bubbles. The air bubble sizes formed due to the higher AFR were reported to be much bigger than that obtained with slower AFR for the same test conditions. Furthermore, it is also worth mentioning here that the velocities of the rising air bubbles increase with the bubble diameter, resulting in higher drag forces. Therefore, from the results obtained without methyl isobutyl carbinol (MIBC), it might be suggested that as the size of air bubbles increased, their rising velocities also increased, leading to the detachment of insufficiently hydrophobic galena particles (with the use of 2.5 ppm xanthate). This occurred when the detachment forces exceeded the adhesive forces. The other forces which negatively affected the flotation recoveries might also be the unstable conditions by oscillation, coalescence of air bubbles, and/or helical action of the air bubbles while they were rising up.

Considering previously obtained flotation response of galena with each xanthate, a further investigation was also performed in order to determine the effect of higher AFR (10 lph) on flotation recovery of galena conditioned in the presence of the higher xanthate concentration (25 ppm). According to the results given in Figure 6, the flotation recovery values obtained clearly indicated that when galena particles had sufficiently hydrophobic surfaces, their attachment to air bubbles was stronger than that with lower xanthate concentrations (Figure 7). This, therefore, resulted in much higher flotation recoveries even with higher AFR (10 lph) compared to those obtained with low xanthate concentrations (Figure 5c).

Figure 6. Flotation recovery of galena in the presence of 25 ppm xanthate with 10 lph AFR.

Figure 7. Schematic representation of the interaction of an air bubble with (a) sufficient and (b) insufficient hydrophobic particles.

2.4. Effect of Air Bubble Size on Flotation Recovery. Frothers are added to the pulp when the surfaces of the target mineral particles have been rendered hydrophobic after conditioning with an appropriate flotation collector. They play an important role in flotation by building up small and stable air bubbles which are responsible for carrying the hydrophobic particles to the froth zone. It has been reported that the amount of frother and the air bubble diameter are inversely proportional to each other and that the air bubble size decreases with increasing frother concentration. Considering the fact that xanthates containing less than 6 carbon atoms do not exhibit frothing properties; in this part of the study, the effect of air bubble size formed by frother addition (0.8–4 ppm of MIBC) on the flotation recovery of galena was investigated in the presence of each xanthate sample. The tests were applied using 2.5 ppm xanthate concentration (100 mL) and 4 lph AFR. The Hallimond tube images are given in Figures 8 (no/0.8 ppm of MIBC) and Figure 9 (4 ppm of MIBC), and their corresponding flotation recovery results are presented in Figure 10.

The efficiency of the flotation process is accomplished mainly by three stages: encounter/collision of particles and air bubbles, attachment of particles on air bubbles, and detachment. In Figures 8 and 9, the Hallimond tube images show that air bubbles sizes decrease with increasing concentration of MIBC addition. According to Yoon and Luttrell, 1989, and Tao’s fundamental analysis and, Sobhy and Tao, 2013, it was indicated that the mineral particle–air bubble collision probability with smaller air bubbles is higher than that with larger ones under similar conditions. It was also indicated that the detachment probability of particles from air bubbles
decreases with decreasing size of the air bubbles. Furthermore, the smaller the air bubble sizes, the lower their rising velocity, resulting in longer residence time in the flotation cell.

According to the results given in Figure 10, the maximum flotation recoveries with each xanthate were obtained below pH 9.5. With the addition of 0.8 ppm of MIBC, nearly 60% and 80% of the galena test sample were recovered with PEX and PAX respectively while the flotation recoveries increased over 90% for both straight-chain xanthates with the addition of 4 ppm of MIBC. In the case of branched-chain xanthates, the effect of bubble size on flotation recoveries was much more effective than it was with straight-chain xanthates. The flotation recoveries with the addition of MIBC increased gradually from about 35% to over 80% with SIPX and from 40% to over 90% with SIBX. Thus, with decreasing air bubble size in a flotation cell, the residence time and total surface area of air bubbles per unit time increased, leading to both higher collision probability of air bubbles with galena particles and carrying of a single galena particle by multiple air bubbles (Figure 9e). It was also reported by Leja and Schulman, 1954 that the addition of frother enhanced the interaction of the bubble with mineral particles, leading to stronger and faster attachment. The flotation recoveries of galena with 2.5 ppm of each xanthate sample, therefore, increased gradually with increasing MIBC concentration (Figure 10a–c) compared to those without MIBC.

3. CONCLUSIONS

On the basis of this study, the following conclusions can be made regarding the effects of C–H length and structure of xanthates on flotation recovery of galena under various experimental conditions:

The flotation recovery of galena varied with C–H chain length and structure of xanthate, xanthate concentration, and pH. Observed steric effects due to the branched-chain structure of xanthates (SIPX and SIBX) decreased their interaction rate with the galena surface which prevented the hydrophobic aggregation of galena particles even with longer conditioning time (10 min). Thus, branched-chain xanthates resulted in the higher flotation recovery values compared to those obtained with straight-chain xanthates (PEX and PAX) causing hydrophobic aggregation of galena particles for the over-conditioning times.

AFR had a crucial effect on flotation recovery of galena. The observed flotation recoveries increased to the maximum values obtained and then dropped sharply with further increase in AFR (10 lph). However, for the same experimental conditions...
much higher flotation recoveries with higher AFRs were obtained with the addition of MIBC.

The flotation recoveries seen with branched-chain xanthates were affected more by the air bubble size than straight-chain xanthates. The maximum flotation recoveries were obtained depending on both the presence and concentration of MIBC which increased higher encounter/collision probability of air bubbles with galena particles and lead to stronger and faster attachment, resulting in higher flotation recoveries.

4. MATERIALS AND METHODS

The high quality galena sample used in this experiment was obtained from the Dursunbey/Balkesir region in Turkey. The sample was wet-screened and rinsed with dilute HCl solution to clean the surface of mineral particles. Then, the galena sample was rinsed again with distilled water and dried in an oven for 48 h. The ~106 ± 75 μm-sized sample was used in microflotation studies in order to minimize the effect of particle size on flotation recovery. According to results of X-ray fluorescence analysis, the sample has over 73% Pb with minor quantities (>3%) of sphalerite, pyrite, and chalcopyrite.

The number of isomers of xanthates varies and increases with increasing chain length. The most common and important xanthates are found in forms with both straight chains (n-xanthates) (Figure 11a,b) and branched chains (iso-xanthates) (Figure 11c,d). The collector samples in this study were obtained from ECS mining chemical company depending on their chain length and structure as potassium amyl xanthate (K-AX; PAX), sodium isobutyl xanthate (Na-IBX; SIBX), and ethyl xanthate (K-EX; PEX), sodium isopropyl xanthate (Na-IPX; SIPX), and potassium amyl xanthate (K-AX; PAX). Their molecular structures and molecular orbitals were calculated by the Gaussian 09 program57 using geometry optimization at the HF/6-31G(D) level. The visual molecular dynamics graphics tool58 was used to build each collector.

Prior to the analyses, 250 ppm of stock solutions were prepared freshly by dissolving each collector sample in distilled water, was conditioned at the target pH and surfactant conditions by a stirrer with adjustable conditioning and placed into a Hallimond tube. Next, a microflotation test was performed at constant stirrer speed, AFR, and bubble collecting time period. Flotation recovery under various flotation conditions was then calculated by weighing the filtered and dried concentrate and tailing.

Figure 11. Structure of xanthate with (a,b) straight (ethyl and amyl xanthates) and (c,d) branched hydrocarbon chains (iso-propyl and iso-butyl xanthates).

Figure 12. Schematic diagram of Halimond tube test unit.

constituting 1 g of mineral sample, chemical compounds, and distilled water, was conditioned at the target pH and surfactant conditions by a stirrer with adjustable conditioning and placed into a Hallimond tube. Next, a microflotation test was performed at constant stirrer speed, AFR, and bubble collecting time period. Flotation recovery under various flotation conditions was then calculated by weighing the filtered and dried concentrate and tailing.

4.1. Zeta Potential Measurement and Microflotation Tests. The zeta potential values (ζ) of the galena particles were measured at ambient temperatures with the Malvern Zetasizer Nano-Z meter. The instrument measures the zeta potential of the particles having size range of 5 nm to 10 μm using a laser doppler velocimeter. For the zeta potential measurement, 10 mg of representative mineral sample (~10 μm) was stirred in 100 mL of distilled water for 5 min after pH adjustment, and the pulp was then transferred to a Zetasizer sample cell for the measurement. An average potential of 3 measurements was taken as a zeta potential value.

Microflotation tests were done using the Hallimond tube microflotation test apparatus, which was assembled in the depicted configuration (Figure 12). The pulp of 100 mL,
(4) Ralston, J. The chemistry of galena flotation: principles & practice. Miner. Eng. 1994, 7, 715–735.

(5) Ozun, S.; Hassas, B. V.; Miller, J. D. Collectorless flotation of oxidized pyrite. Colloids Surf., A 2019, 561, 349–356.

(6) Trahar, W. I. The influence of pulp potential in sulphide flotation. In Principles of Mineral Flotation, The Wark symposium; Jones, M. H., Woodcock, I. T., Eds.; Australasian Institute of Mining and Metallurgy: Parkville, Victoria, Australia, 1984; pp 117–135.

(7) Guy, P. J.; Trahar, W. J. The effects of oxidation and mineral interaction on sulphide flotation. In Flotation of Sulphide Minerals, Developments in Mineral Processing 6; Forssberg, K. S. E., Ed.; Elsevier: Amsterdam, Netherland and New York, NY, 1985; pp 91–109.

(8) Chandra, A. P.; Gerson, A. R. The mechanisms of pyrite oxidation and leaching a fundamental perspective. Surf. Sci. Rep. 2010, 65, 293–315.

(9) Klassen, V. I.; Mokrousov, V. A. Section IV-Collectors. An Introduction to the Theory of Flotation; Butterworths: London, 1963; pp 209–221.

(10) Santos, E. C. D.; Silva, J. C. d. M.; Duarte, A. Pyrite oxidation mechanism by oxygen in aqueous medium. J. Phys. Chem. C 2016, 120, 2760–2768.

(11) Eggleston, C. M.; Hochella, M. F., Jr. Scanning tunneling microscopy of galena (100) surface oxidation and sorption of aqueous gold. Science 1991, 254, 983–986.

(12) Shapter, J. G.; Brooker, M. H.; Skinner, W. M. Observation of the oxidation of galena using Raman spectroscopy. Int. J. Miner. Process. 2000, 60, 199–211.

(13) Vaughan, D. J.; Patrick, R. A. D.; Wogelius, R. A. Minerals, metals and molecules: ore and environmental mineralogy in the new millennium. Mineral. Mag. 2002, 66, 653–676.

(14) Smart, R. S. C.; Amarantidis, J.; Skinner, W. M.; Prestidge, C. A.; La Vanier, L.; Grano, S. R. Surface analytical studies of oxidation and collector adsorption in sulphide mineral flotation. In Solid—Liquid Interfaces; Macroscopic Phenomena-Macroscopic Understanding (Topics in Applied Physics 85); Wandelt, K., Thurgate, S., Eds.; Springer: Berlin, Heidelberg, 2003; pp 3–62.

(15) Brion, D. Photoelectron spectroscopy of the superficial degradation of FeS, CuFeS2, ZnS and PbS in air and in water. Appl. Surf. Sci. 1980, 17, 401–414.

(16) Vills, B. A.; Napier-Munn, T. Wills’ Mineral Processing Technology: An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery, 7th ed.; Butterworth-Heinemann: Oxford, London, 2006.

(17) Wang, D. Flotation Reagents: Applied Surface Chemistry on Minerals Flotation and Energy Resources Beneficiation; Springer: Singapore, 2016.

(18) Gaudin, A. M. Flotation, 2nd ed.; McGraw-Hill Book Company: New York, 1957.

(19) Trahar, W. J.; Warren, L. J. The floatability of very fine particles - a review. Int. J. Miner. Process. 1976, 3, 103–131.

(20) Trahar, W. J. A rational interpretation of the role of particle size in flotation. Int. J. Miner. Process. 1981, 8, 289–327.

(21) Hamilton, I. C.; Woods, R. Surfactant properties of alkyl xanthates. Int. J. Miner. Process. 1986, 17, 113–120.

(22) Rao, S. R. Xanthates and Related Compounds; Marcel Dekker Inc.: New York, 1971.

(23) Yoon, R. H.; Basilio, C. I. Adsorption of thiol collectors on sulphide minerals and precious metals—a new perspective. In XVIII International Mineral Processing Congress; The Australasian Institute of Mining and Metallurgy: Sidney, 1993; pp 611–617.

(24) Kartio, I.; Laajalehto, K.; Suoninen, E. Characterization of the ethyl xanthate adsorption layer on galena by synchrotron radiation excited photoelectron spectroscopy. Colloids Surf., A 1999, 154, 97–101.

(25) McFadzean, B.; Castelyn, D. G.; O’Connor, C. T. The effect of mixed thiol collectors on the flotation of galena. Miner. Eng. 2012, 36–38, 211–218.

(26) Haixhaj, A.; Fan, M.; Haixhaj, B. The Management of Lead Concentrate Acquisition in ”Trepa”. Int. J. Miner. Process. Extr. Metall. 2016, 1, 1–7.

(27) Yongxin, L.; Changgen, L. Selective flotation of scheelite from calcium minerals with sodium olate as a collector and phosphates as modifiers. I. selective flotation of scheelite. Int. J. Miner. Process. 1983, 10, 205–218.

(28) Ma, X.; Xia, L.; Wang, S.; Zhong, H.; Jia, H. Structural modification of xanthate collectors to enhance the flotation selectivity of chalcopyrite. Ind. Eng. Chem. Res. 2017, 56, 6307–6316.

(29) Qin, W.; Wang, X.; Ma, L.; Jiao, F.; Liu, R.; Yang, C.; Gao, K. Electrochemical characteristics and collectorless flotation behavior of galena: with and without the presence of pyrite. Miner. Eng. 2015, 74, 99–104.

(30) Somasundaran, P.; Wang, D. Solution chemistry: minerals and reagents. In Developments in Mineral Processing 17; Elsevier Science: Amsterdam, 2006.

(31) Fukui, K.; Yonezawa, T.; Shingyo, H. A Molecular Orbital Theory of Reactivity in Aromatic Hydrocarbons. J. Chem. Phys. 1952, 20, 722–725.

(32) Hu, Y.; Liu, X.; Xu, Z. Role of crystal structure in flotation separation of diaspore from kaolinite, pyrophyllite and illite. Miner. Eng. 2003, 16, 219–227.

(33) Chen, J.; Chen, Y.; Li, Y. DFT calculation of amine cation collectors for zinc oxide flotation. J. Guangxi Univ., Nat. Sci. Ed. 2009, 34, 67–72.

(34) Taguta, J.; O’Connor, C. T.; McFadzean, B. The effect of the alkyl chain length and ligand type of thiol collectors on the heat of adsorption and floatability of sulphide minerals. Miner. Eng. 2017, 110, 145–152.

(35) Kuopanportti, H.; Suorsa, T.; Dahl, O.; Niinimäki, J. A model of conditioning in the flotation of a mixture of pyrite and chalcopyrite ores. Int. J. Miner. Process. 2000, 59, 327–338.

(36) Aktas, Z.; Cilliers, J. J.; Banford, A. W. Dynamic froth stability: Particle size, airflow rate and conditioning time effects. Int. J. Miner. Process. 2008, 87, 65–71.

(37) Gursoy, Y. H.; Otyekaya, B. Effects of air-to-pulp ratio and bias factor on flotation of complex Cu-Zn sulphide ore in the Jameson cell. Physicochem. Probl. Miner. Process. 2015, 51, 511–519.

(38) Cole, K. E. Bubble size, coalescence and particle motion in flowing foams, Ph.D. Thesis, Imperial College, London, 2010.

(39) Alkhalidi, A. A. T.; Amano, S. S. Factors affecting fine bubble creation and bubble size for activated sludge. Water Environ. J. 2014, 29, 105–113.

(40) Wang, L. K.; Shammas, N. K.; Selke, W. A.; Aulenbach, D. B. Gas dissolution, release, and bubble formation in flotation systems. In Flotation Technology: Handbook of Environmental Engineering 12; Wang, L., Shammas, N., Selke, W., Aulenbach, D., Eds.; Humana Press: Totowa, New Jersey, 2010.

(41) Hassanzadeh, A.; Hassas, B. V.; Kouachi, S.; Brabecova, Z.; Celik, M. S. Effect of bubble size and velocity on collision efficiency in chalcopyrite flotation. Colloids Surf., A 2016, 498, 258–267.

(42) Sutherland, K. L. Physical chemistry of flotation: XI. Kinetics of the flotation process. J. Phys. Chem. 1948, 52, 394–425.

(43) Schubert, H.; Bischofberger, C. On the optimization of hydrodynamics in flotation processes. Proceedings of 13th International Mineral Processing Congress: Warszawa, 1979; Vol. 2, pp 1261–1287.

(44) Cheng, T.-W.; Holtham, P. N. The particle detachment process in flotation. Miner. Eng. 1995, 8, 883–891.

(45) Ata, S. The role of frother on the detachment of particles from bubbles. Miner. Eng. 2011, 24, 476–478.

(46) Cho, Y. S.; Laskowski, J. S. Effect of flotation frothers on bubble size and foam stability. Int. J. Miner. Process. 2002, 64, 69–80.

(47) Cho, Y. S.; Laskowski, J. S. Bubble coalescence and its effect on dynamic foam stability. Can. J. Chem. Eng. 2002, 80, 299–305.

(48) Goodall, C. M.; O’Connor, C. T. Residence time distribution studies in a flotation column, Part 2-The relationship between solids residence time distribution and metallurgical performance. Int. J. Miner. Process. 1992, 36, 219–228.
(49) Tuteja, R. K.; Spottiswood, D. J.; Mishra, V. N. Recent progress in the understanding of column flotation—a review. The AusIMM Proceedings, No. 2, 1995; pp 25–31.

(50) Sam, A.; Gomez, C. O.; Finch, J. A. Axial velocity profiles of single bubbles in water/frother solutions. Int. J. Miner. Process. 1996, 47, 177–196.

(51) Kursun, H. The effect of air hold-up (\(\varepsilon_g\)), superficial air flow rate (\(V_h\)) and frother dosage in two-phase (air/water) and three-phase system (air/water/minerals) on the performance of column flotation. SDU J. Nat. Appl. Sci. 2005, 9, 1–8.

(52) Bulatovic, S. M. Frothers. In Handbook of Flotation Reagents; Chemistry, Theory and Practice; Flotation of Sulfide Ores; Bulatovic, S. M., Ed.; Elsevier Science: Petersborough, Ontario, Canada, 2007; pp 43–51.

(53) Tao, D. Role of bubble size in flotation of coarse and fine particles—a review. Sep. Sci. Technol. 2005, 39, 741–760.

(54) Yoon, R. H.; Luttrell, G. H. The effect of bubble size on fine particle flotation. Miner. Process. Extr. Metall. Rev. 1989, 5, 101–122.

(55) Sobhy, A.; Tao, D. Nanobubble column flotation of fine coal particles and associated fundamentals. Int. J. Miner. Process. 2013, 124, 109–116.

(56) Leja, J.; Schulman, J. H. Flotation theory: Molecular interactions between frothers and collectors at solid-liquid-air interfaces. Trans. AIME 1954, 199, 221–228.

(57) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, E. J.; Ogliaro, F.;Bearpark, M.;Heyd, J. J.; Brothers, E.;Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.;Normand, J.;Raghavachari, K.; Rendell, A.;Burant, J. C.;Iyengar, S. S.;Tomasi, J.;Cossi, M.; Rega, N.;Millam, J. M.;Klene, M.;Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.;Jaramillo, J.;Gomperts, R.; Stratmann, R. E.; Yazyev, O.;Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.;Morokuma, K.;Zakrzewski, V. G.;Voth, G. A.;Salvador, P.; Dannenberg, J. J.;Dapprich, S.;Daniels, A. D.;Parkas, Ö.;Foreman, J. B.; Ortiz, J. V.;Cioslowski, J.;Fox, D. J. Gaussian 09; Gaussian, Inc.: Wallingford CT, 2009.

(58) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. J. Mol. Graphics 1996, 14, 33–38.

(59) Liu, W.; Wang, X.; Xu, H.; Miller, J. D. Lauryl phosphate adsorption in the flotation of Bastnaesite, \((\text{Ce,La})\text{FCO}_3\). J. Colloid Interface Sci. 2017, 490, 825–833.

(60) Liu, W.; Wang, X.; Xu, H.; Miller, J. D. Physical chemistry considerations in the selective flotation of bastnaesite with lauryl phosphate. Miner. Metall. Process. 2017, 34, 116–124.