

Special Issue Reprint

Surface Chemistry and Reagents in Flotation

Edited by
Shiva Mohammadi-Jam

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Surface Chemistry and Reagents in Flotation

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Guest Editor

Shiva Mohammadi-Jam



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About the Editor

Shiva Mohammadi-Jam

Shiva Mohammadi-Jam is a Research Associate in the Department of Mining and Materials Engineering at McGill University. She holds a Ph.D. in Materials Engineering from McGill University and an M.Sc. in Inorganic Chemistry from the Iran University of Science and Technology. Her research focuses on the intersection of surface chemistry and froth flotation, with specific expertise in surface energy characterization. Beyond traditional mineral processing, she is actively involved in life cycle assessment and the recycling of lithium-ion batteries. Dr. Mohammadi-Jam contributes to the field through the collaborative supervision of research projects within the McGill Mineral Processing Group, with a focus on advancing sustainable practices in the industry.

Editorial

Surface Chemistry and Reagents in Flotation

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For over a century, froth flotation has been a cornerstone of the global mining industry, responsible for concentrating base-metal sulfide ores and underpinning the production of copper, zinc, lead, nickel, and associated metals worldwide. Today, its role is evolving rapidly as we look towards the “green revolution”. We are no longer just chasing base metals; flotation is now central to the supply of lithium, rare earths, and graphite, the building blocks of renewable energy. This shift is driving a new wave of innovation in surface chemistry and reagent design, aiming for a process that is not only highly selective but also environmentally responsible.

Recent progress in the field has been impressive, largely driven by advances in interfacial science and materials engineering. High-resolution techniques such as atomic force microscopy (AFM) [1–3] and time-of-flight secondary ion mass spectrometry (ToF-SIMS) [4–6] have unveiled the atomic-scale interactions between reagents and mineral surfaces, revealing how collector molecules form self-assembled monolayers or how they chemisorb via specific functional groups. At the same time, the industry’s force for sustainability has led the development of “green” reagents: biosurfactants, plant-derived fatty acids, and ionic liquids that maintain high recovery while solving toxicity and biodegradability issues [7–9]. Moreover, computational tools such as density functional theory (DFT) have accelerated reagent design by predicting adsorption energies and reducing the need for endless trial-and-error experiments [10–12]. These developments have extended flotation applicability to challenging feeds, such as low-grade polymetallic ores and battery black mass from recycling, where traditional collectors fail due to poor selectivity or environmental risks [13–16].

Despite these progresses, significant challenges remain. Traditional reagents often struggle with complex mineralogy, leading to excessive reagent consumption, froth instability, and environmental impacts. We still do not fully understand the molecular dynamics of these interactions in real-world pulp conditions, where pH, ionic strength, and dissolved species are constantly in flux, especially for non-sulfide minerals such as silicates and phosphates. Furthermore, as mining operations move into water-scarce regions, we urgently need reagents that can perform in saline or recycled water without compromising performance, and for strategies that integrate flotation with downstream processes such as bioleaching or hydrometallurgy.

This Special Issue brings together ten peer-reviewed articles that bridge fundamental insights with practical mineral processing applications. The collection opens with an exploration of the correlation between the electronic structures of pyrite and arsenopyrite active sites and their xanthate adsorption capacities (contribution 1). This is followed by an investigation into surfactant effects on the column flotation performance of apatite (contribution 2) and a study on the separation of gold-pyrite from barren pyrite using

a dithiophosphate-based gold collector and sodium metabisulfite as a pyrite depressant (contribution 3). The issue also addresses the flotation separation of hematite from quartz using 4-Tert-butyl-catechol, a novel collector (contribution 4). Regarding coal processing, researchers examine how three different depressants (starch, dextrin, and humic acid) impact the desulfurization of meta-bituminous coal during reverse flotation (contribution 5). An innovative reagent strategy is demonstrated in a paper on mixed fatty acid synergy with sodium alginate for selective apatite flotation from calcite and quartz (contribution 6), while another study evaluates the influence of gas holdup on the column flotation of a low-grade apatite ore (contribution 7).

Rounding out the issue, the influence of particle size and dodecylamine concentration on lepidolite flotation in alkaline media is addressed (contribution 8), alongside a comparative study evaluating how structurally distinct frothers, such as 2-ethylhexanol, PPG250, and MIBC affect the surface properties and recovery of galena (contribution 9). Finally, a particular highlight is the investigation of various depressant types for pyrochlore flotation, utilizing microflotation and surface chemistry to understand the underlying mineral-reagent interactions (contribution 10).

Looking ahead, the future of flotation lies in interdisciplinary work that aligns with global sustainability goals. The next breakthroughs, I believe, will come from AI-driven reagent discovery and bio-inspired collectors that mimic natural enzymes for ultra-selective separations in low-water systems. Furthermore, the entire life cycle of these materials must be considered to ensure the processes align with emerging regulations, such as the EU's Critical Raw Materials Act (CRMA).

This collection is intended to be a practical resource for both researchers and operators. I hope these articles offer a fresh perspective on how surface chemistry is shaping the next generation of flotation. My sincere thanks go to the authors, reviewers, and the Minerals team for their hard work in bringing this issue to life.

Conflicts of Interest: The author declares no conflict of interest.

List of Contributions

1. Cui, Q.; Liu, C.; Gao, Z.; Lu, T.; Zhao, Z.; Zhu, Y.; Wu, G. First Principle Study of the Relationship between Electronic Properties and Adsorption Energy: Xanthate Adsorption on Pyrite and Arsenopyrite. *Minerals* **2024**, *14*, 749. <https://doi.org/10.3390/min14080749>.
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Article

First Principle Study of the Relationship between Electronic Properties and Adsorption Energy: Xanthate Adsorption on Pyrite and Arsenopyrite

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Abstract: This study investigates the correlation between the electronic structure of the active sites on mineral surfaces and their adsorption capacity. Density functional theory (DFT) and flotation experiments are employed to examine the bonding behavior and adsorption enthalpy of ethylxanthate on pyrite (1 0 0) and arsenopyrite (0 0 1) surfaces. The results indicate that ethylxanthate adsorbs more significantly on pyrite than on arsenopyrite. The adsorption is chemical, primarily occurring through the orbitals of sulfur in the ethylxanthate and iron on the mineral surface. Compared to arsenopyrite, the d-band center of the iron atoms on the surface of pyrite is closer to the Fermi level; thus, the adsorption strength of ethylxanthate on the pyrite surface is greater than on arsenopyrite. The d-band centers of pyrite and arsenopyrite exhibit a direct relationship with their adsorption capacity.

Keywords: d-band center; pyrite; arsenopyrite; DFT; COHP

1. Introduction

The mineral arsenopyrite, which contains arsenic, is commonly found in abundance on Earth. Arsenopyrite, a sulfide mineral, is typically associated with other non-ferrous metal minerals. During flotation, the primary method used to improve and recover these non-ferrous metal minerals, collectors are also adsorbed onto the surface of arsenopyrite [1,2]. This results in significant amounts of arsenic in the flotation concentrate, which can seriously contaminate the metallurgical process [3,4]. Therefore, it is necessary to separate arsenopyrite from valuable minerals during the flotation process to enhance the mineral processing efficiency and protect the environment.

Despite the importance of separating arsenopyrite from pyrite, this task remains challenging due to the analogous structures and similar flotation behaviors of pyrite and arsenopyrite, coupled with the limited understanding of crucial aspects regarding reagent adsorption on their surfaces. These factors pose significant challenges in the flotation-based separation of pyrite and arsenopyrite.

To achieve effective mineral separation through flotation, the collector must exhibit distinct differences in the adsorption characteristics among various minerals. The chemical adsorption of the collector onto the surface of sulfide ores results in the varying adsorption capacities of the active sites due to their different electronic structures. Therefore, analyzing the electronic structure of the active sites on mineral surfaces and designing collectors accordingly is crucial for developing superior flotation separation performance.

Previous studies have explored the impact of the coordination structure of iron on the surface of marcasite (1 0 1) on its oxidation properties. Chen found that the presence of copper alters the orbital symmetry matching between collectors and sphalerite [5,6].

The electronic characteristics of bulk sphalerite containing 14 different types of impurities were investigated to assess their impact on flotation performance [7]. Li examined how the spatial and electrical structure of Z200 affects its adsorption on mineral surfaces [8]. Additionally, Long extensively investigated the difference in the density of states (DOSs) between sphalerite and copper-activated sphalerite, analyzing the underlying reasons for the variations in the xanthate adsorption capacity on mineral surfaces [9].

While extensive research has been conducted on the electronic structure of mineral surfaces, these studies have primarily focused on qualitative analyses of active sites. Consequently, there is no accurate method to quantify the variations in the chemical properties among different mineral surface active sites. In 2009, Nørskov introduced a highly valuable parameter known as the d-band center (DBC), which serves as an effective measure [10]. A larger DBC indicates a lower electron density in the antibonding orbitals, enhancing the bond stability and increasing adsorption capacity on mineral surfaces. Numerous research groups have validated this model through experimental and theoretical studies [11–14].

As the most commonly used collector in the flotation of sulfide minerals, understanding the adsorption characteristics of xanthate on pyrite and arsenopyrite surfaces is crucial for enriching the theoretical understanding of flotation reagent adsorption. In this research, we propose using a simulation approach to comprehensively examine the variations in the coordination structures of the active sites on the surfaces of arsenopyrite and pyrite. The aim is to investigate the effects of these variations in the electronic characteristics on adsorption. By utilizing the hypothesis of DBCs, validated through single-mineral flotation and adsorption enthalpy, we aim to establish a connection between the electronic properties of the active sites on mineral surfaces and the adsorption capacity of the reagents on these surfaces. The design of flotation reagents for arsenopyrite and pyrite could be guided by quantitatively describing the structural differences between the two minerals using the DBC.

2. Materials and Methods

2.1. Minerals and Reagents

Pure mineral samples of pyrite and arsenopyrite were obtained from Yunnan Province, China, and crushed to a size of -0.0074 nm. Figure 1 shows the XRD patterns of pyrite and arsenopyrite before and after adsorption, as well as the XRD patterns obtained from the crystal structure calculations. As can be seen from Figure 1, the purity of pyrite and arsenopyrite is high, and the data align well with the calculated results. The ethylxanthate used in the experiments was acquired from Tieling Flotation Reagent Factory in China, and all the water used was deionized.

2.2. Micro-Flotation Experiments

In the micro-flotation test, 5.0 g of ore and 40 milliliters of water were added to a 40-milliliter flotation cell (XFG-II, Jilin Prospecting Machinery Factory, Changchun, China). The pH was adjusted using 0.01 M NaOH or 0.01 M HCl, which were sourced from Sinopharm. After adding the capturing agent and stirring for 3 min, a foaming agent (MIBC) was added and stirred for an additional 2 min. Air was introduced throughout the test, and the stirring speed was maintained at 1850 rpm. The resulting flotation foam samples and tailings were collected, dried, and weighed.

2.3. Adsorption Experiments

The 50 mL pulp samples of pyrite or arsenopyrite were prepared by mixing the materials with 0.5 g ethylxanthate solutions and distilled water. The pulp was adjusted to the required pH values using 0.01 M NaOH and 0.01 M HCl. The samples were then stored at a predetermined temperature for 12 h in a shaker bath with a constant temperature. After centrifugation, the remaining concentration of ethylxanthate in the supernatant was quantified using an ultraviolet spectrophotometer (Cary 100 UV-Vis, Agilent, Australia).

The quantity of ethylxanthate adsorbed onto the surfaces of pyrite and arsenopyrite was determined using Equation (1):

$$Q_e = \frac{V(C_0 - C_e)}{1000 \text{ ms}} \quad (1)$$

where Q_e is the equilibrium adsorption capacity of ethylxanthate on the pyrite and arsenopyrite surfaces (mol/m^2), C_0 and C_e are the initial and equilibrium concentrations of ethylxanthate, respectively (mol/L), V is the volume of the solution (mL), S is the specific surface area of pyrite and arsenopyrite (m^2/g), and m is the mass of pyrite and arsenopyrite (g).

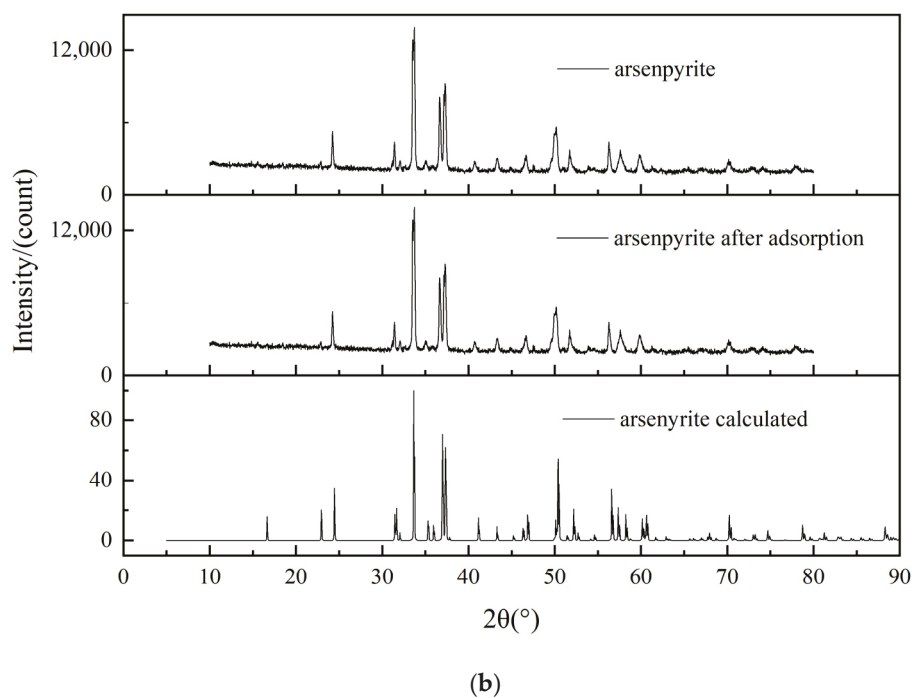
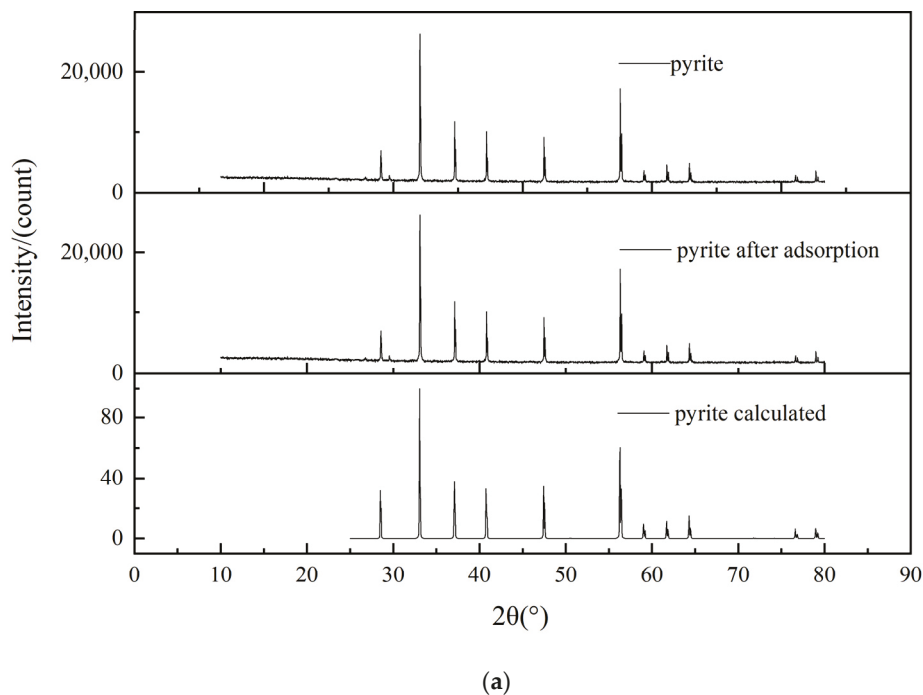


Figure 1. XRD patterns of (a) pyrite and (b) arsenopyrite.

2.4. Computation Approach

The molecular simulation computations were performed using the Dmol3 module within Material Studio software, version 2017, utilizing density functional theory. The calculated parameters included the GGA correlation parameters for exchange using PW91 [15–18], a cut-off energy of 660 eV, k-points of $2 \times 2 \times 2$, maximum force of 1.0×10^{-5} Ha, maximum displacement of 2.0×10^{-3} Ha, maximum step size of 5.0×10^{-3} , and a self-consistent field value of 1.0×10^{-6} eV/atom. All the calculations included all the electrons and were performed with spin-polarization [19,20].

The equilibrium geometric structures of pyrite and arsenopyrite, calculated using DFT, are shown in Figure 2. Pyrite, with its cubic symmetry form and space group Pa3, and the cell parameter 5.417 Å [21], was used in our computations. For arsenopyrite, with triclinic symmetry, we used the crystal space group P-1 and the cell parameters $a = 5.743$ Å, $b = 5.669$ Å, and $c = 5.787$ Å [22]. The arsenopyrite (0 0 1) plane and pyrite (1 0 0) plane were determined as their most stable surfaces [23,24], leading to the creation of (2×2) supercells for each surface, separated by a vacuum of 15 Å, with only the top two atomic layers allowed to relax.

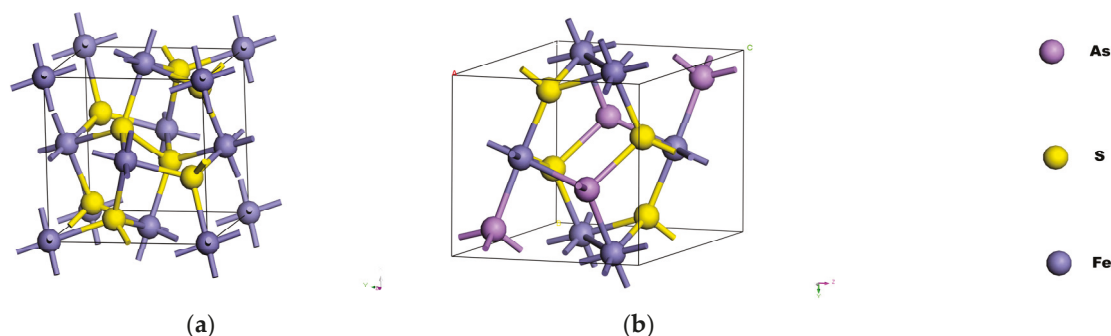


Figure 2. Equilibrium geometries of (a) pyrite and (b) arsenopyrite.

For the optimization of ethylxanthate, a cubic box of $15 \times 15 \times 15$ Å³ was chosen at the gamma point. Figure 3a–c show the equilibrium geometries of ethylxanthate on the surfaces of arsenopyrite (0 0 1) and pyrite (1 0 0).

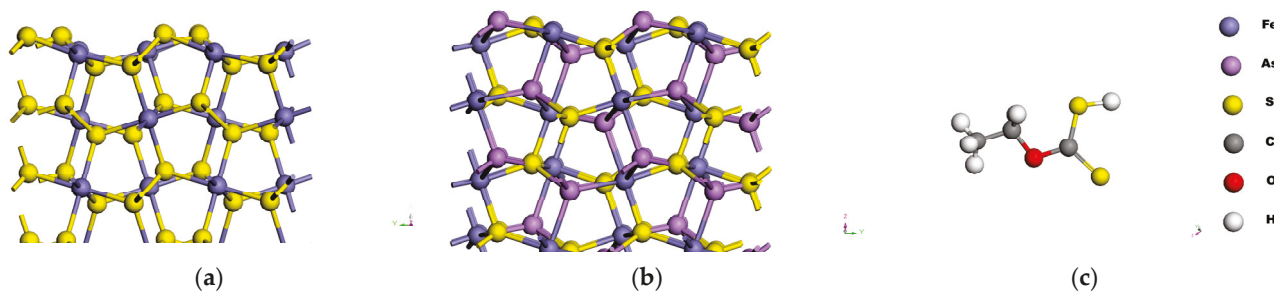


Figure 3. Equilibrium geometries of the (a) pyrite (1 0 0) surface, (b) arsenopyrite (0 0 1) surface, and (c) ethylxanthate.

The adsorption energy (E_{ads}) was calculated using Equation (2):

$$E_{ads} = E_{adsorbates/surface} - E_{surface} - E_{adsorbates} \quad (2)$$

where E_{ads} is the adsorption energy, $E_{adsorbates/surface}$ is the computed energy of the ethylxanthate adsorbed on the arsenopyrite/pyrite surface, $E_{surface}$ is the energy of the arsenopyrite/pyrite surface, and $E_{adsorbates}$ is the energy of the ethylxanthate.

The d-band center (DBC) was calculated using Equation (3) [25]:

$$\epsilon_d = \frac{\int_{-\infty}^{\infty} n_d(\epsilon) \epsilon d\epsilon}{\int_{-\infty}^{\infty} n_d(\epsilon) d\epsilon} \quad (3)$$

where ε_d is the d-band center, n_d is the energy, and ε is the density of states.

3. Results and Discussion

3.1. Micro-Flotation Experiments for Single Mineral

Figure 4 illustrates the impact of the ethylxanthate dosage and pH on the flotation recovery of arsenopyrite and pyrite. Both pyrite and arsenopyrite exhibit higher flotation recovery rates with an increase in the collector dosage. At a collector dosage of 4 mg/L, the flotation recoveries of pyrite and arsenopyrite reach 92.45% and 82.96%, respectively. Beyond this dosage, further increases do not significantly affect the flotation recovery of either mineral, suggesting that 4 mg/L is the optimal dosage for evaluating pH effects.

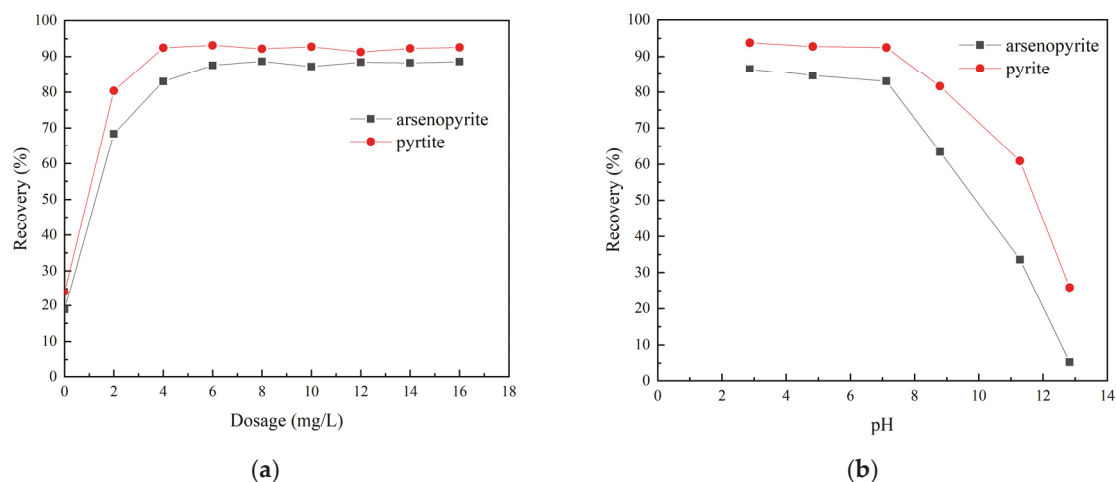


Figure 4. Effects of different reagent dosages at (a) pH = 7.12, C_{MIBC} = 2 mg/L and (b) pH C_{MIBC} = 2 mg/L, $C_{collector}$ = 4 mg/L on the flotation recovery of arsenopyrite and pyrite.

As shown in Figure 4b, as the pH increases from 3 to 12, the flotation recovery of pyrite decreases from 93.74% to 25.87%, while the recovery of arsenopyrite declines from 86.52% to 5.26%. Throughout the entire pH range, the recovery rate of pyrite when using ethylxanthate as the collector consistently exceeds that of arsenopyrite. This demonstrates that pyrite has a higher adsorption capacity for ethylxanthate compared to arsenopyrite.

3.2. Adsorption Thermodynamics

Figure 5 clearly shows that as the adsorption temperature increases, the ability of ethylxanthate to bind to the surfaces of pyrite and arsenopyrite also increases significantly. This indicates that ethylxanthate adsorption on pyrite and arsenopyrite surfaces is endothermic. The thermodynamic parameters of ethylxanthate adsorption on pyrite and arsenopyrite were determined by fitting the isothermal adsorption data using the Langmuir and Van't Hoff equations [26,27].

Table 1 presents the collected adsorption thermodynamic data. According to the data, the adsorption enthalpy of ethylxanthate on pyrite is 59.25 kJ/mol, whereas the adsorption enthalpy on arsenopyrite is 38.99 kJ/mol. Based on the adsorption energy calculations, it can be seen that within the tested temperature range, the adsorption energy of ethylxanthate on the surface of pyrite is greater than that on the surface of arsenopyrite.

Table 1. The parameters of the adsorption thermodynamics.

	ΔH (kJ·mol ^{−1})	ΔS (J·mol ^{−1} K ^{−1})	ΔG (kJ·mol ^{−1})			
			293.15 K	298.15 K	303.15 K	308.15 K
Pyrite	59.25	276.45	−21.79	−23.17	−24.55	−25.94
Arsenopyrite	38.99	191.38	−17.11	−18.06	−19.03	−19.98

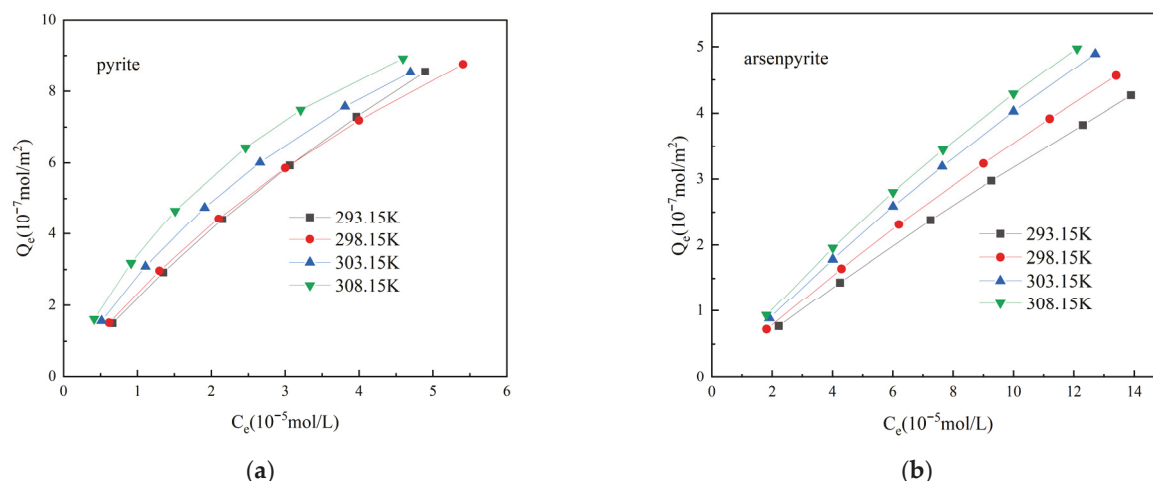


Figure 5. Adsorption isotherms of ethylxanthate on (a) pyrite surfaces and (b) arsenopyrite surfaces ($t = 6 \text{ h}$ and $\text{pH} = 8.0$).

3.3. COHP Analysis

Figure 6a shows the equilibrium configuration of ethylxanthate adsorption on the surface of pyrite. It is evident that xanthate is adsorbed onto two Fe atoms on the (1 0 0) surface of pyrite through two S atoms, with an adsorption energy of -326.53 kJ/mol . The bond length of S1-Fe1 is $2.317 \text{ \AA}$, which is similar to the bond length of S2-Fe2. Both bond lengths are smaller than the van der Waals radii sum of the Fe and S atoms ($3.85 \text{ \AA}$) [28], indicating that the adsorption of xanthate on the pyrite (1 0 0) surface is chemisorption.

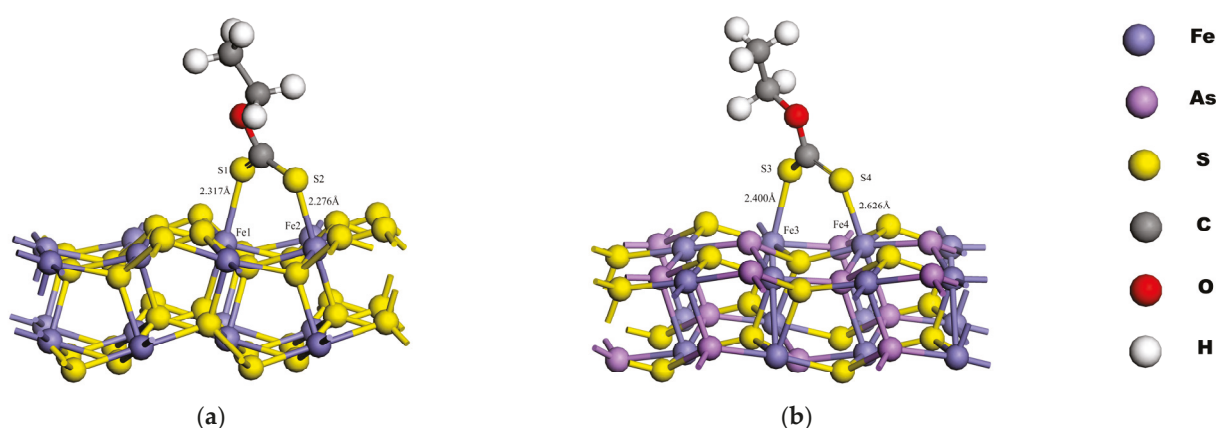


Figure 6. Adsorption model of ethylxanthate on the surface of (a) pyrite and (b) arsenopyrite.

Similarly, ethylxanthate adsorption on the surface of arsenopyrite (0 0 1) involves two S atoms from the collector binding with two Fe atoms on the arsenopyrite surface. The adsorption energy of ethylxanthate on arsenopyrite is -253.99 kJ/mol . The figure shows that the Fe3 on the arsenopyrite surface is coordinated with three S atoms and two As atoms. The bond length of S3-Fe3 is $2.400 \text{ \AA}$, which is longer than the S1-Fe1 bond length. The bond length of the S4-Fe4 bond is $2.626 \text{ \AA}$, which is also longer than the S2-Fe2 bond length but is still smaller than the van der Waals radius sum of the Fe and S atoms. This suggests that the adsorption of ethylxanthate on the arsenopyrite (0 0 1) surface is also chemisorption, but it is weaker than its adsorption on the pyrite (1 0 0) surface.

Since the adsorption of ethylxanthate on the surfaces of pyrite and arsenopyrite is chemical, it can be analyzed using molecular orbital theory. As shown in Figure 7, bond orbitals and antibond orbitals are formed after adsorption. Stable chemical bonds can be created when only the bonding orbitals are occupied. Conversely, stable chemical bonds cannot form if both the bonding and antibonding orbitals are occupied.

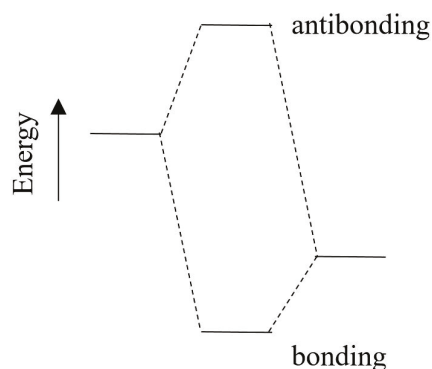


Figure 7. Molecular orbital model.

The Crystal Orbital Hamiltonian Population (COHP) method is used to analyze the chemical bonding in periodic systems through electronic structure calculations [29]. The COHP is an extension of the Crystal Orbital Overlap Population (COOP) method [30], which utilizes the overlap matrix as a weight for the density of states (DOSs). Instead of the overlap matrix, the COHP uses the Hamiltonian matrix, which reflects the energy contribution of each orbital interaction. The COHP values can be negative (indicating bonding) or positive (indicating antibonding). The integral of the COHP over a specific energy range can indicate the bond strength between groups. The COHP can be calculated using different types of basis sets, such as localized atomic orbitals or plane waves.

To study the differences between pyrite and arsenopyrite, the adsorption of ethylxanthate on the (1 0 0) surface of pyrite and the (0 0 1) surface of arsenopyrite was investigated using COHP analysis. This approach provides insights into the bond strength and electronic interactions involved in ethylxanthate adsorption on these mineral surfaces.

Figure 8 presents a COHP graph illustrating the bonds between the S in the ethylxanthate and the Fe on the mineral surfaces. The Crystal Orbital Hamiltonian Population (COHP) calculations provide a clear picture of the interactions between ethylxanthate and the minerals [31]. The intensity of the interaction between S and Fe can be observed from these graphs. Compared to xanthate adsorption on the pyrite surface, the antibonding orbitals have higher occupancy when xanthate is adsorbed on the arsenopyrite surface.

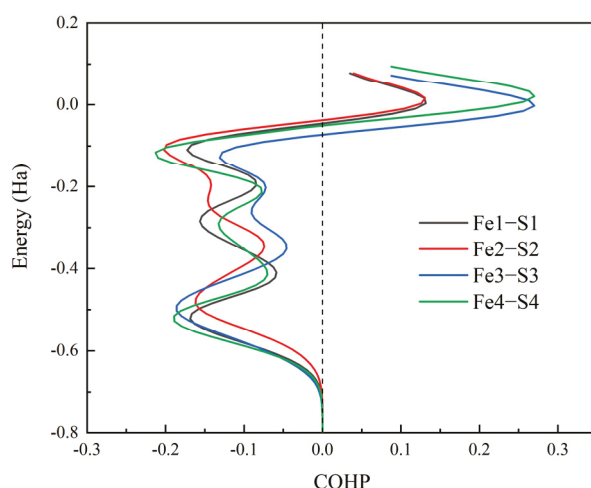


Figure 8. COHP curves of ethylxanthate adsorption on the mineral. The Fermi level is set at 0 eV.

The COHP values and bond order for the Fe–S bonds resulting from ethylxanthate adsorption on the surfaces of pyrite and arsenopyrite are presented in Table 2. As shown in Table 2, the COHP values for the Fe–S bonds formed by ethylxanthate adsorption on the surface of pyrite are -0.064 Ha and -0.062 Ha, respectively. In contrast, the COHP values for the Fe–S bonds formed by ethylxanthate adsorption on the surface of arsenopyrite

are -0.0482 Ha and -0.042 Ha, respectively. These results indicate the higher adsorption capacity of the pyrite surface for ethylxanthate compared to that of the arsenopyrite surface. This is evidenced by the lower COHP values for the Fe–S bonds formed on the surface of pyrite through ethylxanthate adsorption. Based on the bond order, it can be seen that chemical bonds are formed between Fe1–S1, Fe2–S2, Fe3–S3, and Fe4–S4, with the bond strength decreasing sequentially. This observation is consistent with the conclusions obtained from the COHP analysis.

Table 2. The COHP of ethylxanthate adsorbed on the pyrite (1 0 0) surface and arsenopyrite (0 0 1) surface.

Adsorbate	Mineral Surface	Bond	COHP/Ha	Bond Order
Ethylxanthate	Pyrite (1 0 0)	S1-Fe1	-0.064	0.57
		S2-Fe2	-0.062	0.49
	Arsenopyrite (0 0 1)	S3-Fe3	-0.048	0.42
		S4-Fe4	-0.042	0.40

3.4. The Analysis of the Density of States

Figure 9a shows the PDOS of the Fe atoms on the pyrite surface before and after ethylxanthate adsorption. Since the Fe atoms on the pyrite surface are all in a five-coordinate structure and have consistent chemical properties, only the PDOS of one Fe atom before and after adsorption is presented. When ethylxanthate is adsorbed on the surface of pyrite, the interaction between the 3p orbit of S and the 3d orbit of Fe in the ethylxanthate is also mainly in the range of 0.2 to 0 Ha.

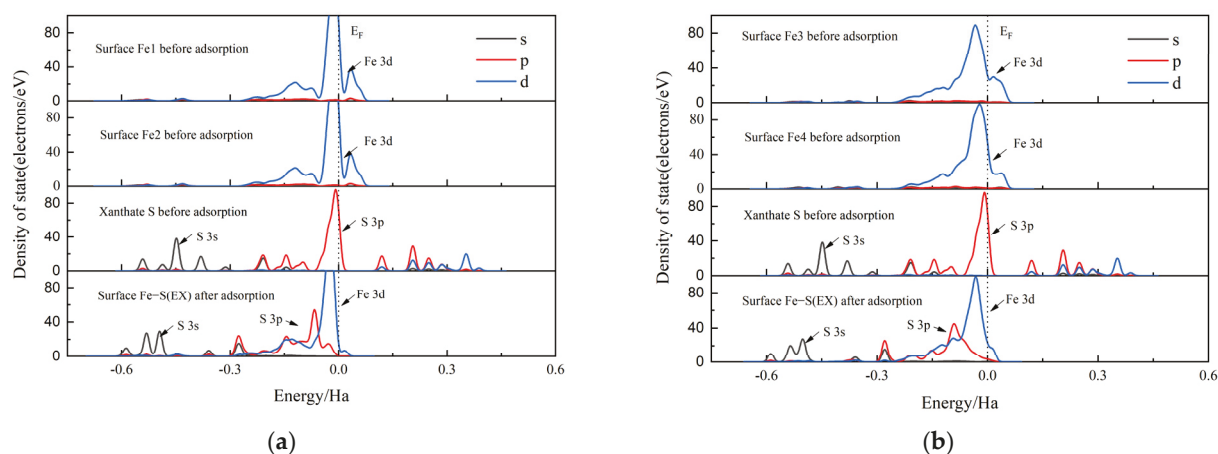


Figure 9. DOS of the S of the ethylxanthate, pyrite (a) and arsenopyrite (b) surface Fe before and after.

As shown in Figure 9b, Fe3 is coordinated with three sulfur atoms and two arsenic atoms, while Fe4 is coordinated with two sulfur atoms and three arsenic atoms. The distribution of Fe3 above the Fermi level is greater than that of Fe4 above the Fermi level. When ethylxanthate is adsorbed on the surface of arsenopyrite, the interaction between the 3p orbit of the S and the 3d orbit of the Fe in the ethylxanthate is primarily in the range of 0.2 to 0 Ha.

Comparing Figures 9 and 10, it can be seen that the 3d orbit of the Fe in pyrite is closer to the Fermi level than the 3d orbit of the Fe in arsenopyrite, indicating that the 3d orbit of the Fe in pyrite has fewer electrons than the 3d orbit in arsenopyrite. Consequently, after ethylxanthate is adsorbed to form a bond, the antibonding orbit formed by the 3p orbit of the S in the ethylxanthate and the 3d orbit of the Fe on the surface of pyrite has fewer electrons than the antibonding orbit formed by the 3p orbit of the S in the ethylxanthate and the 3d orbit of the Fe on the surface of arsenopyrite. Therefore, ethylxanthate exhibits a stronger adsorption capacity on the surface of pyrite.

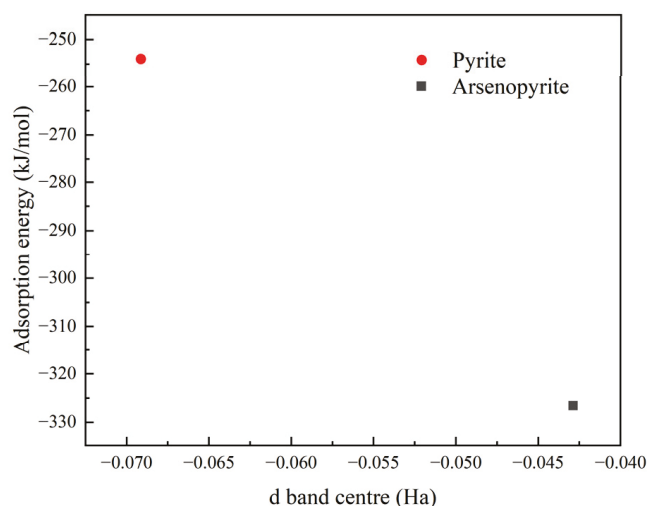


Figure 10. Relationship between adsorption energy and DBC.

Table 3 shows the changes in the Mulliken charges of the Fe on the surfaces of pyrite and arsenopyrite before and after the adsorption of ethylxanthate. As listed in Table 3, after the adsorption of ethylxanthate, the s, p, and d orbitals of the Fe gain electrons, with the d orbitals gaining significantly more electrons than the s and p orbitals. The PDOS analysis indicates that the interaction between the electrons in the Fe 3d orbitals and the S 3p orbitals of the ethylxanthate is crucial for influencing the adsorption of ethylxanthate on the surfaces of pyrite and arsenopyrite. This finding is consistent with Norskov's research [32].

Table 3. Changes in the Mulliken charges before and after the adsorption of ethylxanthate on the pyrite and arsenopyrite.

	Adsorption State	Atom	s	p	d	Total	Charge
Pyrite	Before	Fe1	0.277	0.485	6.855	7.617	0.383
	After		0.289	0.505	6.956	7.75	0.250
	Change		0.012	0.02	0.101	0.133	
	Before	Fe2	0.277	0.485	6.855	7.617	0.383
	After		0.286	0.503	6.943	7.732	0.268
	Change		0.009	0.018	0.088	0.115	
Xanthe (adsorbed on pyrite)	Before	S	1.86	4.46	0	6.31	−0.31
	After		1.81	4.15	0	5.96	0.04
	Change		−0.05	−0.29	0	−0.35	
Arsenopyrite	Before	Fe3	0.344	0.548	6.926	7.818	0.182
	After		0.365	0.561	6.944	7.87	0.130
	Change		0.021	0.013	0.018	0.052	
	Before	Fe4	0.408	0.505	6.921	7.834	0.166
	After		0.425	0.521	6.953	7.899	0.100
	Change		0.017	0.016	0.032	0.065	
Xanthe (adsorbed on arsenopyrite)	Before	S	1.86	4.46	0	6.31	−0.31
	After		1.82	4.19	0	6.01	−0.01
	Change		−0.04	−0.27	0	−0.30	

Additionally, the data show that pyrite gains more electrons than arsenopyrite, which further indicates that the interaction between ethylxanthate and pyrite is stronger than the interaction between ethylxanthate and arsenopyrite.

3.5. Correlation between the Adsorption Energy and DBC

In the context of adsorption, a higher d-band center (DBC) implies a greater availability of empty d-states for chemical bonding, leading to stronger molecule–substrate interactions and higher adsorption energies. This significantly affects the adsorption energy as molecules interact with these empty states during the adsorption process.

The presence of As and S in the coordination structure of the arsenopyrite surface causes Fe to adopt a different coordination structure compared to the pyrite surface, where Fe is solely coordinated with S. This disparity in the coordination structure results in variations in the DBC of Fe on the mineral surfaces. Analysis of Figures 9 and 10 reveals that the DBC of Fe on pyrite surfaces is -0.043 Ha, whereas that on arsenopyrite surfaces is -0.069 Ha. The substitution of S atoms with As atoms in the mineral leads to a reduction in the DBC of the surface metal atom, consequently diminishing the adsorption capacity of the mineral surface toward the adsorbent.

Figure 10 presents a graph illustrating the correlation between the DBC and the adsorption energy. The graph demonstrates that the DBC of Fe on the surface of pyrite surpasses that on arsenopyrite. Furthermore, the adsorption energy of Fe on pyrite with ethylxanthate is higher compared to Fe on arsenopyrite.

This research indicates that the location of the DBC can function as a marker for the collector's adsorption at different active sites on mineral surfaces. This discovery could significantly benefit the development of flotation reagents.

4. Conclusions

This study investigates the influence of the active site electronic structures on the adsorption characteristics of mineral surfaces using flotation tests, thermodynamic data fitting, and density functional theory (DFT) simulations. Micro-flotation experiments reveal that pyrite exhibits a higher adsorption capacity for ethylxanthate compared to arsenopyrite, with adsorption enthalpies of 59.25 kJ/mol and 38.99 kJ/mol, respectively.

The findings concerning the bond lengths and adsorption energies indicate that ethylxanthate exhibits superior adsorption on pyrite surfaces. The Covalent Orbital Hamilton Population (COHP) analysis shows that ethylxanthate forms stronger bonds with pyrite than with arsenopyrite. The density of states (DOSs) and Mulliken charge evaluations reveal that, during the adsorption process, electron transfer occurs more frequently within the Fe d orbitals of pyrite compared to arsenopyrite.

Further investigation using the d-band center (DBC) theory indicates that the adsorption capacity of Fe on pyrite surfaces is greater than that on arsenopyrite because the DBC of the Fe atoms on pyrite is closer to the Fermi level. This study demonstrates that ethylxanthate adsorbs more readily on pyrite surfaces. Therefore, in flotation process design, floating pyrite while depressing arsenopyrite flotation proves to be a more advantageous approach.

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Article

Analysis of the Effect of Surfactants on the Performance of Apatite Column Flotation

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Abstract: Given that particle and bubble size, as well as their surface properties, are pivotal in froth flotation, surfactants have been extensively employed due to their impact on bubble size and froth stabilization. This study aimed to investigate the influence of surfactants on the performance of apatite flotation in column. Three different categories of surfactants were examined: anionic, amphoteric, and nonionic, specifically Lupromin, Genagen, and Triton X-100, respectively. The critical coalescence concentration (CCC) and surface tension of each surfactant were determined. The impact of these surfactants on reducing bubble size was quantified, and their subsequent effects on apatite flotation in a column were assessed. The most favorable flotation response for Genagen was achieved at CCC and pH 11, resulting in the highest apatite recovery and the smallest bubble size. For Triton X-100, the best condition was attained at $\frac{1}{4}$ CCC and pH 11. However, overall, Lupromin was the surfactant that yielded the best flotation results (at $\frac{1}{4}$ CCC and pH 11). The superior performance of this anionic surfactant was corroborated by chemical adsorption results, as demonstrated by FTIR analyses.

Keywords: bubble size; surfactant; apatite; flotation

1. Introduction

Phosphate rocks serve as the primary global reservoirs of phosphorus used in the production of phosphatic fertilizers [1]. Phosphorus fertilizers play a crucial role in enhancing agricultural productivity and ensuring food security for a growing global population. Its application extends to the food, pharmacy, and chemical industries, and produces phosphoric acid, detergents, food additives, etc., [1]. Phosphorus is also critical in a host of industrial applications and is a nonrenewable resource that is sourced primarily from the phosphatic mineral apatite, hosted in either sedimentary deposits or igneous ores [2]. Phosphorus within phosphate rocks is consistently bound to other elements in the form of phosphate minerals, with the most prevalent and widely distributed minerals belonging to the apatite group [2].

Igneous deposits, primarily extracted in Russia, South Africa, Brazil, Finland, and Zimbabwe, consist of fluorapatite ores predominantly associated with carbonatites and various types of alkaline intrusions [2]. However, these igneous phosphate ores typically have a low grade. With global reserves of high-grade phosphorus ore rapidly diminishing, there is an increasing reliance on low-grade phosphate ores, which depends on the development of efficient processes to yield high-quality apatite concentrates. This has made the study of phosphorus ore flotation an essential method for upgrading ore quality. A deep understanding of flotation techniques can significantly enhance the efficiency of phosphorus recovery, ensuring a more sustainable supply to meet global demands.

Froth flotation is a common technique in the mining industry used to separate and concentrate ores. In this process, target particles are separated from a liquid phase based on

the varying ability of air bubbles to selectively adhere to their surfaces due to differences in hydrophobicity [3]. Consequently, the hydrophobic particles, referred to as “floatable”, preferentially attach to the surface of air bubbles. These bubbles ascend from the pulp zone to the foam zone, where they are collected in the concentrate stream. In contrast, the gangue material, consisting of more hydrophilic particles, remains in the pulp phase and is gathered in the tailings [3].

Due to the progressive depletion of igneous deposits, processing plants have resorted to extensive grinding to increase the release of phosphorus. This practice, however, has led to the production of a significant amount of fines [4]. Particle size is a crucial parameter in the flotation process, as it significantly impacts flotation performance. Inefficient flotation can result in substantial revenue loss and the unnecessary depletion of reserves. In this context, understanding the interaction between bubbles and particles and finding ways to enhance it become exceptionally important for improving the efficiency of the apatite flotation process [5,6].

The collection of particles by bubbles in the pulp involves bubble–particle collision, attachment, and detachment [7]. The relationship between particle size and bubble diameter plays a pivotal role in determining the likelihood of particles colliding with bubbles, adhering to bubbles after collision, and remaining attached within the pulp phase [7]. However, the mineral particles of interest often lack inherent hydrophobic properties, and the use of reagents can enhance flotation performance. Therefore, the judicious selection of reagents such as collectors, depressants, frothers, and pH modifiers is a fundamental step to enhance the selectivity of this process [8].

Various factors can influence the distribution of bubble sizes, including gas flow rate, solid concentration, temperature, and the addition of surfactants [9]. Surfactants are compounds with both a polar group and a hydrocarbon chain and are generally introduced into the process to regulate bubble size distribution and facilitate froth stabilization [10,11]. Additionally, frothers exhibit characteristics similar to collectors, with the primary distinction being the functionality of the polar group. Collectors tend to have greater adsorption on mineral surfaces, while frothers possess a lyophilic radical that is more attracted to water [12].

Given the significant impact of bubble size in froth flotation, various researchers have investigated this variable [13–20]. For instance, Reis et al. [18] explored the effect of bubble size on the flotation of fine particles in a low-grade Brazilian apatite ore and found that the optimal bubble size range for the particle sizes under investigation was 800–1000 μm . Li et al. [19] examined bubble size distribution in the presence of a surfactant and observed that the Sauter mean diameter (d_{32}) significantly decreased when Triton X-100 was introduced into the air–water system (without ore). The frother’s role was to prevent coalescence by adsorbing onto the surface of the bubbles [20]. However, most of these studies were conducted in the context of an air–water system, as obtaining precise data on bubble size distribution becomes challenging when ore is introduced into the system. Therefore, assessing the influence of various categories of surfactants on bubble size within a system containing ore and its subsequent impact on flotation performance can offer a means to enhance the process for different particle sizes [20].

The objective of this study was to examine the impact of three distinct categories of surfactants (anionic, amphoteric, and nonionic) on the reduction in bubble diameter and, consequently, their influence on the performance of apatite flotation in a column. The critical coalescence concentration and surface tension were determined for each surfactant. The findings presented here may offer insights into identifying the most suitable type of surfactant for achieving optimal apatite froth flotation results.

2. Materials and Methods

2.1. Experimental Apparatus

The batch flotation tests were conducted in an acrylic column divided into three sections: a cylindrical section with a diameter of 4 cm and a length of 150 cm, followed by a

frustoconical section with a height of 9.5 cm, and, finally, another cylindrical section with a length of 12 cm and a diameter of 10 cm (Figure 1). At the base of the column, an air sparger was installed. This sparger consisted of a porous cone made of sintered bronze, designed by MetalSinter (São Paulo, Brazil) to generate the desired distribution of bubble sizes. The column was fed from the top, where a froth washer water system was also located. Additionally, there was a recirculation load at the bottom of the column to ensure that the feed particles passed through the collection zone.

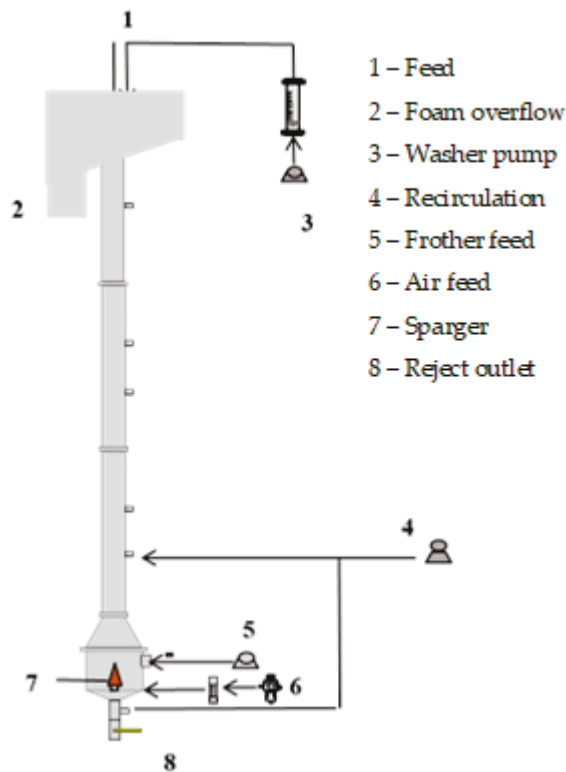


Figure 1. Experimental apparatus.

2.2. Bubble Size Measurements

Bubble sizes were assessed using a Fastec IL5 high-speed digital camera (Fastec Imaging, San Diego, CA, USA). The bubbles were recorded in a dynamic state (1000 frames per second), and the acquired images were analyzed with the assistance of ImageJ software 1.49 (National Institutes of Health, New York, NY, USA). This software allowed us to measure the diameter sphere with the same projected area. Detailed descriptions of the measurement procedures can be found in our previous publication [21]. The Sauter mean diameter (d_{32}) was determined from the bubble size distribution obtained in each test using Equation (1).

$$d_{32} = \frac{\sum_{i=1}^N n_i d_i^3}{\sum_{i=1}^N n_i d_i^2} \quad (1)$$

where n is the number of measured bubbles, d_i is the bubble diameter of bubble i , and n_i is the number of bubbles with diameter d_i . In each test, around 500 bubbles were measured.

2.3. Surfactants and Air–Water System

In this study, the surfactants utilized included Lupromin (sodium sulfosuccinate from BASF, Ludwigshafen, Germany), Genagen (from Clariant, Muttens, Switzerland), and Triton X-100 (polyethylene glycol tert-octylphenyl ether from Sigma Aldrich, St. Louis, MO, USA) at concentrations of 5, 10, 20, 30, 40, and 50 ppm. These specific surfactants were selected because apatite exhibits negative surface activity. Lupromin is categorized as an anionic surfactant, Genagen as an amphoteric surfactant, and Triton X-100 as a nonionic

surfactant. The surface tension of all surfactant solutions was determined using a Krüss K6 tensiometer (Krüss, Hamburg, Germany).

The impact of these surfactants on bubble size in the air–water system was studied under the operating conditions specified in Table 1.

Table 1. Fixed operating conditions for the air–water system.

Parameters	Operating Conditions
Air pressure	3 bar
Surfactant flow rate	50 mL/min
Recirculation flow rate	0.5 L/min
Air flow rate	80 L/h

The critical coalescence concentration (CCC) for each surfactant was determined by plotting the d_{32} of the bubbles against the concentration of the surfactant solution. The CCC was considered reached when the bubble sizes remained relatively unchanged across different concentrations [22,23].

2.4. Characterization of the Phosphate Ore Sample

The igneous apatite samples for this study were sourced from the Barreiro carbonatite complex in Araxá, Minas Gerais state, Brazil, which is owned and operated by Mosaic Fertilizantes do Brasil Ltd., São Paulo, Brazil. These samples were collected from the feed circuit of the apatite flotation column.

The particle size distribution of the ore was determined using a laser diffraction technique with a Mastersize Microplus MAF 5001[®] particle size analyzer from Malvern Panalytical Ltd., Malvern, UK. The Rosin–Rammler–Bennet (RRB) model (Equation (2)) provided the best fit to the experimental data, with estimated parameter values of $d_{63.2} = 87.63 \mu\text{m}$ and $n = 1.83$ ($r^2 = 0.9984$). The particle size distribution curve is presented in Figure 2.

$$X = 1 - \exp \left[- \left(\frac{d_p}{d_{63.2}} \right)^n \right] \quad (2)$$

where d_p is the particle diameter and X is the cumulative fraction.

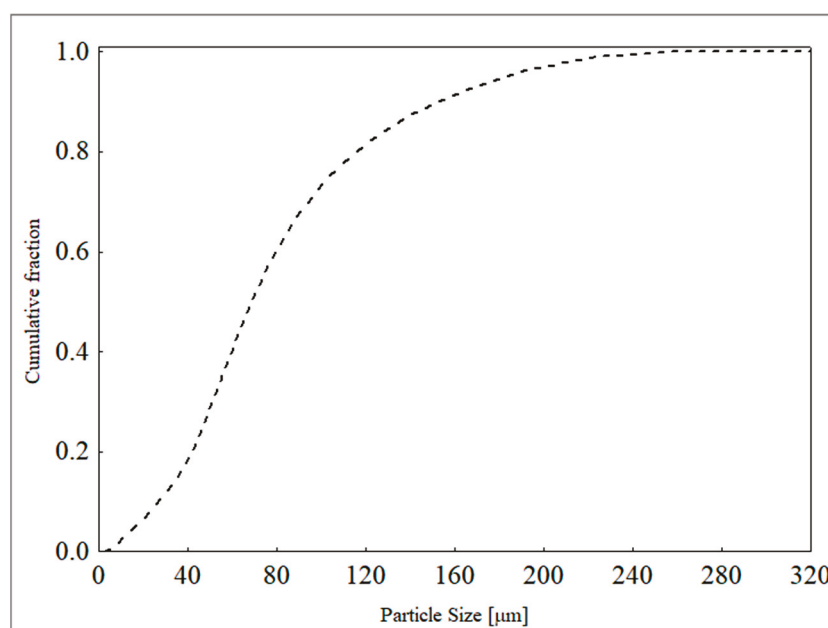


Figure 2. Particle size distribution of the feed samples.

The chemical composition of the fed sample was determined by X-ray fluorescence spectrometry using an S8 Tiger spectrometer (Bruker, Germany). It was mainly composed of 20.66% of P_2O_5 , 27.57% of CaO, 24.45% of Fe_2O_3 , 12.44% of SiO_2 , 8.41% of TiO_2 , 2.74% of BaO, and 1.27% of Al_2O_3 . Then, the highest proportion of gangue minerals combined with apatite were iron and silicate minerals.

2.5. Reagents and Flotation Test Procedures

In the ore-conditioning step, flotation reagents were introduced, including a collector, which was a fatty acid soap derived from rough rice oil, which was saponified with NaOH at 60 °C and applied at a concentration of 360 g/t. Additionally, a gangue depressant was employed, consisting of gelatinized cornstarch, which was used at a concentration of 100 g/t. Both the collector and depressant were diluted in water to reach concentrations of 2.5% and 3%, respectively. The pH was controlled by using 10% NaOH and 1 M HCl solutions. These reagents were chosen based on prior investigations related to apatite froth flotation [24–27]. Additionally, a solution of Lupromin, Genagen, or Triton X-100 was included in the flotation tests as a surfactant to control the bubble size distribution. Tests were conducted for each type of surfactant, with their concentrations varying between $\frac{1}{4}$ CCC and CCC, and at pH levels of 9 and 11. The remaining flotation parameters remained consistent across all experiments.

The batch tests were conducted in the column depicted in Figure 1. After setting the air flow rate at 80 L/h and the wash water flow at 0.15 L/min using flow meters, the preconditioned pulp, consisting of 13.68% solids, was introduced at the top of the column. The equipment operated with a circulating load of 0.50 L/min, ensuring the suspension of ore particles and allowing them to pass through the collection zone. Both the concentrate and the tailings were discharged from the flotation column. Subsequently, the products of each flotation experiment, namely, the concentrate and the tailings, underwent oven-drying at 110 ± 0.5 °C for 24 h. They were then weighed, and their chemical composition was analyzed through X-ray fluorescence spectrometry. Table 2 outlines the fixed operating conditions, which were determined based on prior studies [18,21,24–26] and preliminary tests. For each test, the size of bubbles was measured, and the corresponding d_{32} value was calculated.

Table 2. Fixed operating conditions in the flotation.

Parameters	Operating Conditions
Ore mass	340 g
Solid percentage	13.68%
Conditioning time	5 min (each reagent)
Collector dosage	360 g/t
Depressant dosage	100 g/t
Wash water flow rate	0.15 L/min
Air pressure	3 bar
Surfactant flow rate	50 mL/min
Recirculation flow rate	0.5 L/min
Air flow rate	80 L/h

The quality of the concentrated product was assessed based on the P_2O_5 grade, while the productivity of the flotation process was determined by the apatite recovery. For phosphate flotation of igneous ores, the industrial benchmark for satisfactory results is typically defined as having a minimum of 30% apatite grade and a 60% recovery [26].

To examine the adsorption of the surfactant within the system, the product from each flotation process was analyzed using Fourier transform infrared spectroscopy (FTIR) with a Miracle ATR/Spectrum Two FT-IR spectrometer from Pike Technologies, USA. FTIR spectra of apatite, both with and without surfactant, were recorded within the range of 400 to 1900 cm^{-1} .

2.6. Index of Flotation Response

The performance of apatite flotation was assessed using the index of flotation response, which factors in both the P_2O_5 grade and the apatite recovery. This index considers the industrial benchmarks for grade and recovery, as represented by Equation (3):

$$\text{Index of flotation response} = \frac{P_2O_5 \text{ grade}}{30} + 2 \times \left(\frac{\text{Apatite recovery}}{60} \right) \quad (3)$$

In cases where the P_2O_5 grade and apatite recovery were both below 30% and 60%, respectively, i.e., falling short of the industrial reference values, the index of flotation response was assigned a value of zero

3. Results

3.1. Effect of Surfactant on the Air–Water System

It is an undeniable fact that mineral flotation, as we understand it today, relies heavily on the essential role of reagents [27]. These flotation reagents include collectors, depressants, frothers, and pH regulators, which serve to control the physical and chemical conditions of the three phases involved in the process.

Surface-active agents, commonly referred to as frothers, are amphipathic compounds capable of adsorbing at the air–water interface. These surfactants accumulate at the interface between water and air bubbles, forming a protective layer around the bubbles to prevent their collapse [28,29]. The arrangement of surfactant molecules at the air–water interface involves positioning the hydrophilic or polar groups towards the water phase, while the hydrophobic or nonpolar chains face the air phase [30]. Surfactants exhibit various charge characteristics depending on their properties, which can be anionic, cationic, amphoteric, or nonionic, with the type of surfactant determined by their hydrophilic chain [30].

In this study, three types of surfactants were chosen due to the active surface of apatite being characterized by an excess of negative charges. These surfactants included anionic (Lupromin), amphoteric (Genagen), and nonionic (Triton X-100), while the cationic surfactant was not tested because it carries an excess of positive charges, which would hinder its adsorption onto apatite [31].

Initially, the impact of varying the concentration of these three surfactants on bubble sizes in a system without ore (air–water system) was examined. Figure 3 illustrates the relationship between the d_{32} of the bubbles and the concentration of each surfactant. The data indicate that the d_{32} decreased linearly with increasing concentrations of Lupromin and Genagen until the critical coalescence concentration (CCC) was reached at 40 ppm. Beyond this concentration, the bubble size remained constant, with slight fluctuation in the Sauter mean diameter falling within the margin of measurement error. Preliminary tests indicated that the CCC for Triton X-100 was approximately 50 ppm.

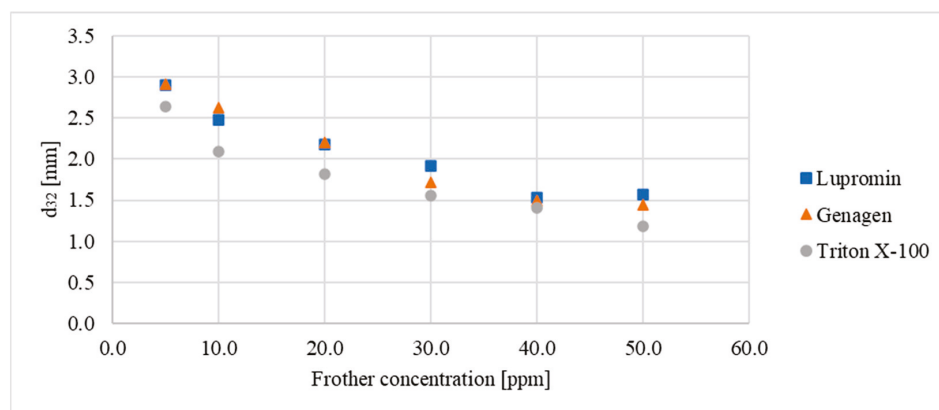


Figure 3. Relationship between Sauter mean diameter and surfactant concentration for each surfactant for the air–water system.

Figure 4 displays the reduction in surface tension with increasing surfactant concentration for all three surfactants under investigation. It is evident that the effect of these surfactants on bubble size reduction corresponds to the same behavior on respective surface tension. Triton X-100 resulted in the lowest surface tension and the smallest d_{32} , followed by Lupromin and Genagen, which exhibited very similar responses.

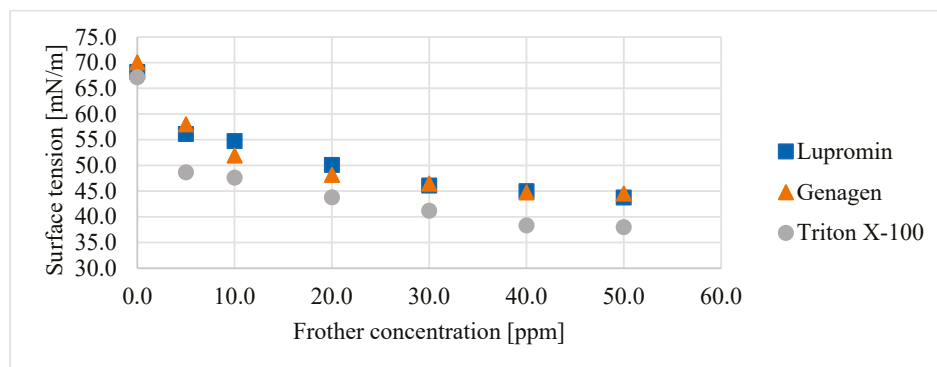


Figure 4. Relationship between surface tension and surfactant concentration for each surfactant for the air–water system.

3.2. Influence of Surfactant in Apatite Flotation

Each of the surfactants used in this study, namely, Lupromin (an anionic surfactant), Genagen (an amphoteric surfactant), and Triton X-100 (a nonionic surfactant), was assessed for its impact on flotation performance. Table 3 provides details of the conditions and results for each apatite flotation test. It is evident that all the conditions investigated achieved a P_2O_5 grade and apatite recovery exceeding 30% and 60%, respectively, surpassing the industrial reference values. The most favorable flotation outcome was attained at a pH of 11 using a surfactant concentration equivalent to $\frac{1}{4}$ CCC (test F4). Under these conditions, the highest flotation response index was recorded, with a value of 3.58. Moreover, this condition led to the highest apatite recovery at 74.73%, with a P_2O_5 grade of 32.57%. The d_{32} value of the bubbles decreased by a factor of 1.27 compared to the system without surfactant, transitioning from coarse to medium-sized bubbles.

Table 3. Conditions and results of each apatite flotation test.

Test	Surfactant	Surfactant Concentration (ppm)	pH	P_2O_5 Grade (%)	Apatite Recovery (%)	d_{32} (mm)	Index of Flotation Response
F1	Without surfactant	0	9	33.98	70.27	1.31	3.47
F2	Without surfactant	0	11	32.54	70.17	1.13	3.42
F3	Lupromin	10 = $\frac{1}{4}$ CCC	9	33.87	69.46	0.98	3.44
F4	Lupromin	10 = $\frac{1}{4}$ CCC	11	32.57	74.73	0.89	3.58
F5	Lupromin	40 = CCC	9	33.76	70.05	0.98	3.46
F6	Lupromin	40 = CCC	11	32.46	71.29	0.96	3.46
F7	Genagen	10 = $\frac{1}{4}$ CCC	9	33.34	68.57	0.78	3.40
F8	Genagen	10 = $\frac{1}{4}$ CCC	11	33.28	71.07	0.84	3.48
F9	Genagen	40 = CCC	9	32.23	66.44	0.75	3.29
F10	Genagen	40 = CCC	11	32.37	74.41	0.66	3.56
F11	Triton X-100	12.5 = $\frac{1}{4}$ CCC	9	32.40	64.10	0.78	3.22
F12	Triton X-100	12.5 = $\frac{1}{4}$ CCC	11	33.39	70.63	0.83	3.47
F13	Triton X-100	50 = CCC	9	31.84	69.51	0.77	3.38
F14	Triton X-100	50 = CCC	11	33.78	67.85	0.83	3.39

This study involved a statistical quantification of the effects of independent variables on the index of flotation response for each surfactant. This analysis revealed that when Lupromin and Genagen were used, the effect of pH was six times more significant than the

effect of surfactant concentration. However, in the tests using Triton X-100 as the surfactant, the effect of pH was twice as prominent as the effect of surfactant concentration. Hence, it becomes evident that a more comprehensive examination of the interaction between the collector and surfactant is required to gain a deeper understanding of this phenomenon. This investigation could provide valuable insights for identifying the optimal conditions for the apatite flotation process.

As evident from the results presented in Table 3, the type of surfactant had varying impacts on the selectivity and efficiency of apatite flotation. The index of flotation response ranged from highest to lowest in the following order: anionic (Lupromin), amphoteric (Genagen), and nonionic (Triton X-100). This suggests that the choice of surfactant can significantly influence the performance of the apatite flotation process, with anionic surfactants demonstrating the most favorable outcomes in this case. A deeper analysis for each surfactant is presented below.

3.2.1. Lupromin

The results from the first six tests (F1 to F6) reveal that the addition of Lupromin to the process led to a reduction in the d_{32} of the bubbles and an increase in apatite recovery. However, the P_2O_5 grade did not exhibit a significant change compared to the test without surfactant (F1 and F2). Since Lupromin is classified as an anionic surfactant, it is possible that it competed with the collector and influenced the hydrophobicity of apatite. This suggests that there might be an interaction between the collector and the surfactant. The most favorable flotation outcome was achieved at pH 11, using a surfactant concentration equivalent to $\frac{1}{4}$ CCC (test F4). Under these conditions, the highest index of flotation response was recorded, along with the smallest d_{32} of the bubbles.

Figure 5 presents the infrared absorption spectra of the floated samples for the experiments conducted with the anionic surfactant ($\frac{1}{4}$ CCC of Lupromin) at both pH 9 and 11, as well as without surfactant under the same conditions. Theoretical analysis indicates the presence of four vibrational modes for phosphate ions, namely, ν_1 , ν_2 , ν_3 , and ν_4 .

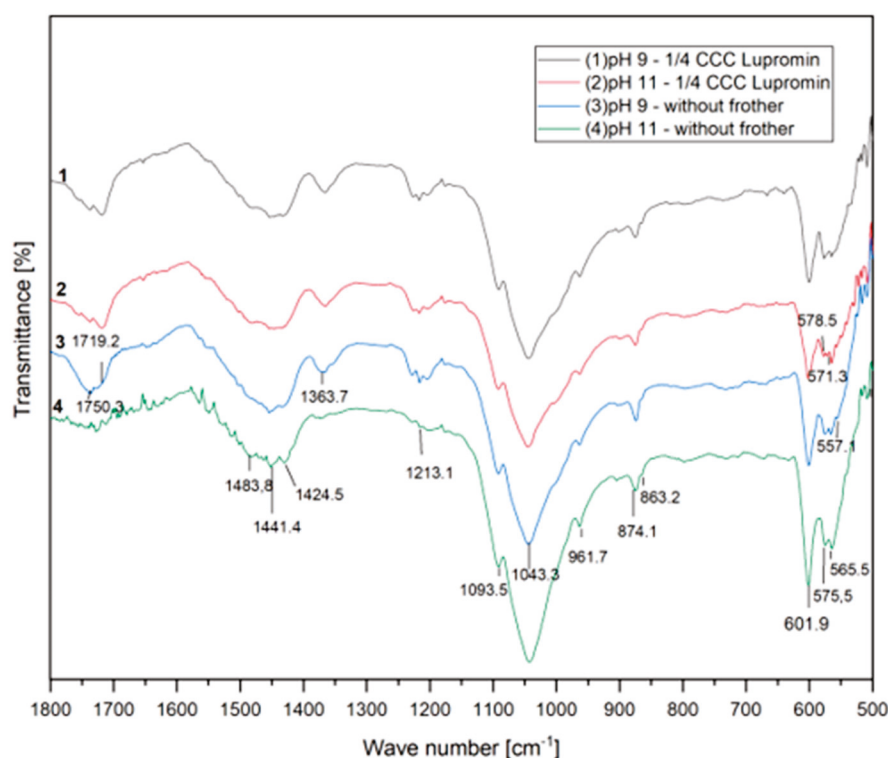


Figure 5. FTIR spectra with Lupromin.

In the spectra related to flotation without surfactant, characteristic phosphate bands within the apatite domain are observable. These bands correspond to the vibration of PO_4^{3-} ions, including asymmetric bending of P–O in ν_4 at 601.9 and 575.5 cm^{-1} , symmetric valence oscillation of ν_1 at 961.7 cm^{-1} , and asymmetric valence oscillations of ν_3 attributed to the asymmetric stretching of P–O at 1093.5 and 1043.3 cm^{-1} [32,33].

At pH 9, no chemical or physical adsorption of Lupromin was observed. However, at pH 11, a different behavior was noted, characterized by the appearance of new peaks at 571.3 and 578.5 cm^{-1} within the vibrational mode ν_4 of phosphate. This suggests the occurrence of chemical adsorption because the P_2O_5 grade remained nearly constant, while apatite recovery increased, attributed to true flotation and entrainment caused by the addition of Lupromin at pH 11. It is also important to mention that no adsorption was observed in the domain ranging from 1750 to 1400 cm^{-1} , which pertains to the carboxylate group. This implies that Lupromin may have interacted with the active surface of apatite after the conditioning process, subsequently enhancing the flotation process.

The observed behaviors provide an explanation for the superior result obtained in test F4. This enhanced performance can be attributed to true flotation, brought about by the chemical adsorption of the surfactant. Furthermore, this process was facilitated by the smaller d_{32} of the bubbles and the entrainment mechanism. The highest apatite recovery achieved in this condition may also be linked to the formation of a more stable froth, as visually observed during the test, which inhibited the detachment mechanism. All these results collectively demonstrate that the anionic surfactant (Lupromin) was chemically adsorbed onto the apatite surface and that its presence also influenced the stability of the froth.

3.2.2. Genagen

The results obtained with the addition of Genagen to the flotation tests (tests F7 to F10 in Table 3) indicate that, in all the studied conditions, the P_2O_5 grade and apatite recovery exceeded the industrial reference values of 30% and 60%, respectively. The most favorable index of flotation response was achieved in test F10, conducted at pH 11 with a surfactant concentration equivalent to the CCC value.

Table 3 provides clear evidence of the amphoteric surfactant's effect on reducing bubble size. Test F10, which exhibited the best flotation performance for this surfactant, also resulted in the smallest d_{32} value for the bubbles (0.66 mm). At alkaline pH levels, this amphoteric surfactant behaves similarly to anionic surfactants [34] and possesses more frothing properties, evident from its stability and the smaller d_{32} of the bubbles.

The infrared absorption spectra of the floated samples from the experiments conducted with and without the amphoteric surfactant (at CCC of Genagen) at pH 9 and 11 are presented in Figure 6. These spectra clearly demonstrate that the addition of Genagen had a significant impact on the behavior of apatite flotation.

In all the curves, bands corresponding to the apatite domain of PO_4^{3-} ions can be observed. However, when Genagen was introduced into the system, there were noticeable changes in the shape of the curves, and new peaks appeared at 605, 598, 592, 578, and 571 cm^{-1} . These new peaks are associated with the vibration of PO_4^{3-} ions, particularly between asymmetric formations of ν_4 related to P–O bonds. Additionally, new peaks were identified in the region corresponding to the symmetric valence oscillation of ν_1 and the asymmetric valence oscillations of ν_3 at 1046.5, 1043, 1000, 988, and 981.6 cm^{-1} . The peak at 874 cm^{-1} , attributed to HPO_4^{2-} , disappeared when Genagen was added to the system, and the peaks in the range of 1750 to 1400 cm^{-1} , corresponding to CO_3^{2-} ion oscillations, also vanished. These observations suggest that Genagen did not adsorb onto the calcium mineral surface and point to the existence of chemical adsorption of Genagen on the active surface of apatite, as indicated by the region where the new peaks appeared.

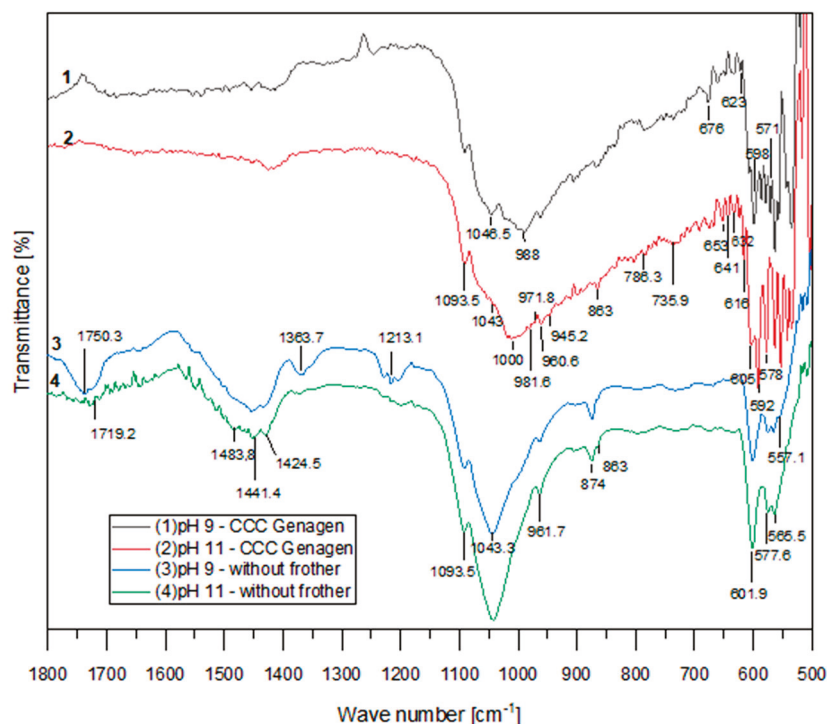


Figure 6. FTIR spectra with Genagen.

3.2.3. Triton X-100

The conditions and results of each flotation test using Triton X-100 are provided in Table 3, encompassing tests F11 to F14. Notably, the addition of the nonionic surfactant substantially reduced the d_{32} of the bubbles. However, it is evident that neither the surfactant concentration nor the pH had a significant impact on the bubble size distribution.

In terms of the P_2O_5 grade, there was a slight increase in this response when the experiments were conducted at pH 11 for Triton X-100. This increase might be attributed to the physical adsorption of the surfactant and the potential interaction between the collector and the surfactant under these conditions. The most favorable flotation outcome was achieved at pH 11 using a surfactant concentration equivalent to $\frac{1}{4}$ CCC (test F12).

Figure 7 presents the FTIR spectra for each test conducted without and with the nonionic surfactant (at $\frac{1}{4}$ CCC of Triton X-100) at pH 9 and 11. The curves appear very similar, indicating the absence of chemical adsorption of Triton X-100 in the system. This figure also highlights the regions associated with the carboxylate and apatite groups, as previously described [32,33].

Nonionic surfactants are commonly incorporated into the flotation process due to their ability to reduce bubble size and stabilize mineralized froths. Furthermore, they are known for generating robust and stable foams without engaging in ionic interactions with surfaces, a characteristic that aligns with the findings of our FTIR analyses.

3.3. Effect of Surfactant on Bubble Size for Both Systems

This section provides a comparison of the impact of the three investigated surfactants on bubble size for systems both without ore (air–water) and with ore (air–water–ore). Figure 8 illustrates the bubble size distribution in the air–water system for each type of surfactant at a concentration of 50 ppm, which corresponded to the CCC of Triton X-100. As depicted, each type of surfactant (anionic, amphoteric, and nonionic) had varying effects on reducing bubble size, resulting in distinct bubble size distributions.

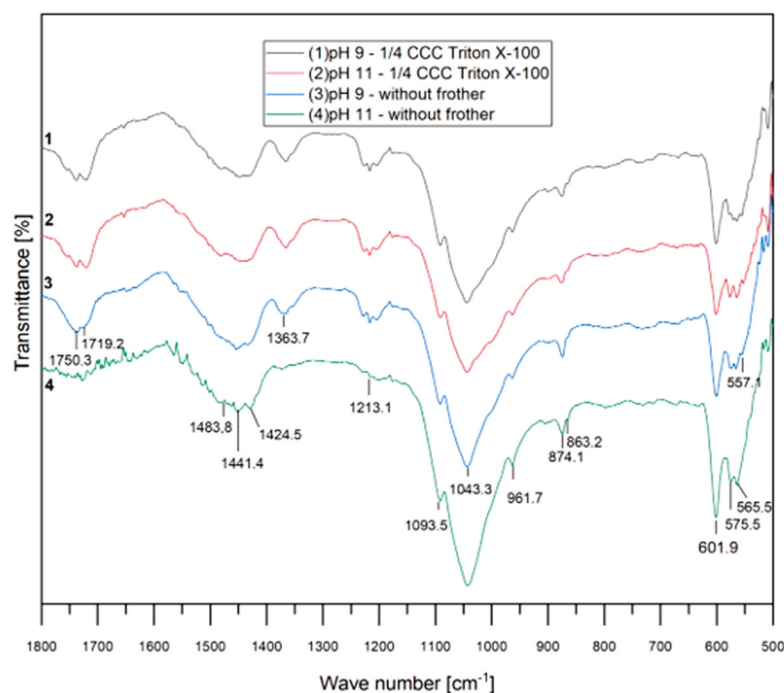


Figure 7. FTIR spectra with Triton X-100.

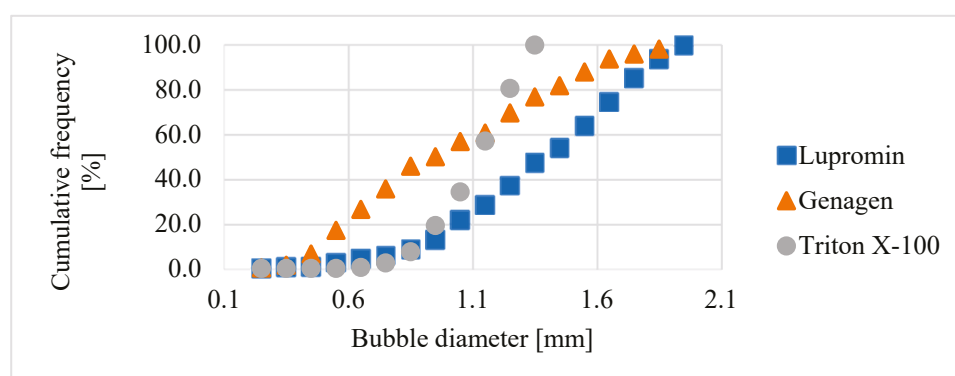


Figure 8. Bubble size distribution for the air–water system at 50 ppm.

The effect of the surfactant on bubble size in the system with ore was notably different compared to the system without ore (the air–water system). In the presence of ore particles, the mineralized bubbles had their size reduced compared to the system without ore. This reduction in bubble size occurred because the presence of ore particles attached to the surface of the bubbles prevented coalescence, which was a result of the lower surface tension under these conditions [34]. It is known that the concentration of surfactants has a considerable impact on bubbles size, likely due to the adsorption of the surfactant at the gas–liquid interface. Within a pulp, these molecules adsorb at this interface, with their polar groups facing the liquid phase, thereby forming a structured molecular layer. This layer covers the surface of the aqueous solution with nonpolar groups. As the concentration of surfactant increases, there is a corresponding rise in the accumulation of nonpolar groups on the surface, resulting in a reduction in surface tension until a minimum value is achieved. This behavior is consistently observed [35,36].

Figure 9 shows the bubble sizes in the air–water system using Lupromin at $\frac{1}{4}$ CCC, while Figure 10 illustrates the system with ore using Lupromin at the same concentration and at pH 11. This particular condition was selected because it yielded the highest index of flotation response (i.e., 3.58) among all the conditions analyzed in this study. It is evident that the air–water system had bubbles with irregular shapes due to the coalescence

phenomenon, while the system with ore featured more uniform and round-shaped bubbles. Additionally, the d_{32} of the bubbles in the system without ore was 2.79 times larger than in the system with ore.

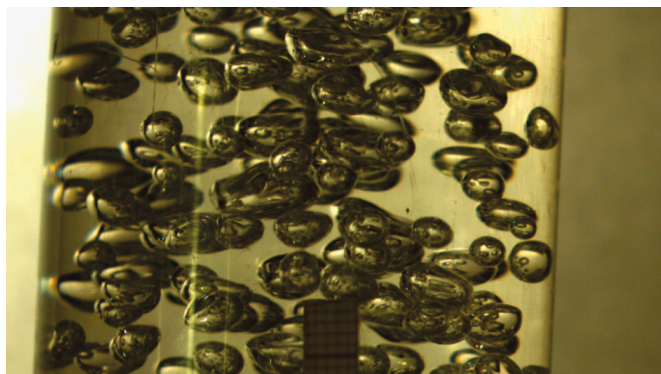


Figure 9. Images of the best condition reached by the addition of Lupromin: $\frac{1}{4}$ CCC for the air–water system.

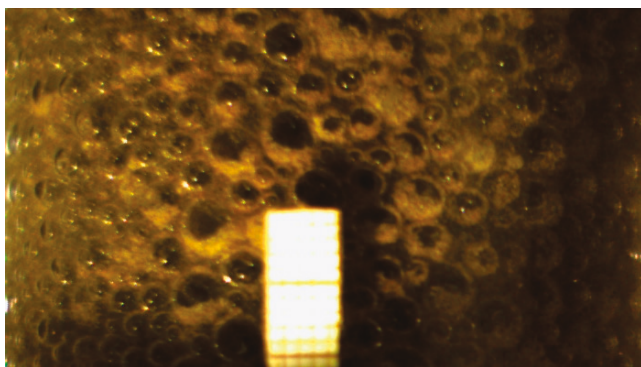


Figure 10. Images of the best condition reached by the addition of Lupromin: $\frac{1}{4}$ CCC and pH 11 for the system with ore.

The results in Table 3 demonstrate that all three surfactants were effective in reducing bubble sizes, a crucial variable that significantly impacts the probability of bubble–particle interactions, attachment, and retention in the pulp phase. This, in turn, has a substantial influence on the flotation performance. However, it is worth noting that the type of surfactant had varying effects on the selectivity and efficiency of apatite flotation. The anionic surfactant (Lupromin) and the amphoteric surfactant (Genagen) proved to be more effective in enhancing the flotation performance, likely due to their chemical adsorption on the active surface of apatite.

3.4. Global Analysis of the Effect of Surfactant on Apatite Flotation

The best results in apatite flotation, i.e., the highest index of flotation response (3.58), were achieved in test F4. In this test, an anionic surfactant (Lupromin) was employed at a concentration equivalent to $\frac{1}{4}$ CCC and a pH of 11. This condition yielded a P_2O_5 grade of 32.57% and an apatite recovery of 74.73%, both significantly exceeding the industrial reference values. In terms of bubble size (d_{32}), it was 32% smaller than that obtained in the best result of the flotation test conducted without a surfactant (test F1).

The superior performance at pH 11 can be attributed to its favoring of chemical adsorption, as indicated in the FTIR analyses (Figures 5 and 6), and likely the collector–surfactant interaction [36].

The impact of surfactants on the flotation process depends on their chemical properties and the applied conditions. Surfactants that reduce superficial tension the most may not necessarily deliver the best performance for the flotation process. In our study, although

Triton X-100 exhibited the lowest surface tension in the air–water system, followed by Lupromin and Genagen, its performance in the air–water–ore system varied significantly. This discrepancy can be attributed to the influence of the collector–surfactant interaction on the formation of bubble–particle aggregates, a factor that cannot be overlooked. The nonionic surfactant (Triton X-100) was found to be physically adsorbed on the active surface of apatite (Figure 7).

4. Conclusions

In this study, we examined the impact of various surfactants on the performance of apatite flotation in a column. In the air–water system, it was evident that all the surfactants tested were capable of significantly reducing surface tension, leading to a reduction in bubble size. Notably, the bubble size in the system without ore (air–water) was 2.79 times larger than that in the system with ore (air–water–ore).

During the flotation tests, it was observed that under all conditions examined, the P_2O_5 grade and apatite recovery exceeded the industrial reference values (30% and 60%, respectively). However, the anionic surfactant (Lupromin) and the amphoteric surfactant (Genagen) demonstrated higher efficiency in enhancing the flotation performance, primarily due to their chemical adsorption onto the active surface of apatite. Furthermore, we observed a collector–surfactant interaction that influenced the formation of bubble–particle aggregates, ultimately favoring true flotation, improved selectivity, and enhanced flotation efficiency.

The current work identified that the best results in apatite flotation, indicated by the highest index of flotation response (3.58), were achieved when utilizing the anionic surfactant (Lupromin) at a concentration equivalent to $\frac{1}{4}$ CCC and a pH of 11. However, to build on these findings and further enhance the understanding of surfactants behavior in flotation process, it is recommended that future research explores the application of a broader range of surfactants. This could involve measuring the surface tension of the pulp associated with each surfactant under controlled conditions, leading to more efficient and cost-effective flotation processes.

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Article

Surface Chemistry and Flotation of Gold-Bearing Pyrite

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Abstract: Gold grains are observed in a variety of forms, such as coarse-liberated native gold grains, and ultra-fine grains associated with sulfide or non-sulfide mineral particles, in the form of solid solution in sulfide minerals, mainly pyrite. In the flotation of gold ores, bulk sulfide mineral flotation is generally applied to maximize gold recovery. This approach gives high gold recoveries, but it also causes the recovery of barren sulfide minerals (i.e., sulfide mineral particles with no gold content), which increases concentrate tonnage and transportation costs and reduces the grade sometimes to below the saleable limit (approx. 10 g/t Au). This study addresses the differences between gold-bearing and barren pyrite particles taken from various ore deposits and utilizes these differences for the selective flotation of gold-bearing pyrite. The laboratory scale flotation tests conducted on three pyrite samples having different cyanide soluble gold contents show that a selective separation between gold-bearing pyrite and barren pyrite particles could be achieved under specific flotation conditions. Gold recovery is correlated directly with the cyanide-soluble gold in the ore samples. Electrochemical experiments were conducted to elucidate the differences in surface properties of the two types of pyrite. The barren pyrite particles were more cathodic and prone to cathodic reduction of OH[−] and depressant ions on the surface, and they could be depressed effectively without significantly affecting the gold-bearing particles.

Keywords: flotation; gold; pyrite; electrochemistry; surface chemistry; cyanide soluble gold; depressants; galvanic interaction

1. Introduction

Gold can exist in visible or refractory (invisible) forms within gold-bearing sulfide minerals, mainly arsenopyrite, pyrite, tetrahedrite, and chalcopyrite. The visible gold is generally observed as native gold, electrum (Au, Ag), and/or gold tellurides (Calaverite (AuTe₂), Sylvanite ((Au,Ag)Te₄), Montbrayite (Au₂Te₃), etc.) associated with the sulfide minerals generally in the forms of nuggets, vein gold, and fracture gold [1,2]). The statistics of 102 types of gold deposits show that approximately 85% of the total gold is extracted from the gold-bearing pyrite in these gold deposits [3]. Therefore, it is important to concentrate pyrite for the recovery of gold.

Pyrite is generally concentrated by flotation, a physico-chemical separation process utilizing the differences in the surface properties of minerals. Pyrite flotation is generally performed at natural or slightly alkaline pH values using a strong xanthate-type collector, such as potassium amyl xanthate (KAX) or sodium isopropyl butyl xanthate (SIBX). Promoters with modified dithiophosphate or thionocarbamate chemistry are generally used to enhance the flotation of gold-bearing minerals and increase gold recovery. Activators, such as CuSO₄, NaHS, and even Pb(NO₃)₂ can also be used according to the type of the sulfide minerals to be floated and the surface state of the sulfide minerals (such as fresh, tarnished, or oxidized) [4–6].

Under these flotation conditions, all the sulfide minerals, both gold-bearing and barren (i.e., sulfide mineral particles with no gold content) sulfide minerals in an ore can be floated to the concentrate. This approach may achieve high gold recoveries but also increase

concentrate tonnage and transportation costs, and reduce the gold grade of the concentrate. The gold grade of a pyrite concentrate should be a minimum of 10 g/t, and the payability for gold increases with the increasing gold grade of the concentrate. Selective flotation of gold-bearing pyrite from barren pyrite can be highly beneficial considering economic, environmental, and technical factors, particularly for low-grade ores with a low Au/S ratio [7].

In the literature, there are several research studies on separating gold and pyrite using selective collectors [4,8] and depressants [9]. The presence of gold in a pyrite particle, either in visible or invisible forms, can change the electronic structure and, hence, floatability of gold-bearing pyrite [10,11]. Gold-bearing pyrite has higher conductivity, oxidation, and stability compared to barren pyrite. It is claimed that the presence of gold may enhance the formation and the adsorption of dioxanthogen on the gold-bearing pyrite surface. Electrum is a very common gold mineral observed in gold-bearing sulfide ore deposits. The presence of Ag in electrum changes the electrochemical and surface characteristics of the pyrite particles. Ag provides active adsorption sites for both xanthate-type strong collectors and also the selective collectors that are generally used as promoters in the flotation of gold-bearing sulfide ores.

The chemical and electrochemical conditions of the flotation pulp can significantly affect the surface characteristics of the sulfide minerals and enhance the differences in the flotation behavior of gold-bearing pyrite and barren pyrite particles [12,13]. Gold is a noble metal and is electrochemically inert, as reflected by its lack of reactivity in air and most aqueous solutions [1]. The presence of dissolved oxygen and redox couples such as $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions can alter pyrite surface properties of gold-bearing pyrite and barren pyrite in different ways, and this could allow the separation of these two types of pyrite by flotation [14,15].

Several electrochemical research studies have been conducted using gold and pyrite electrodes to investigate the influence of gold on the electrochemical characteristics of pyrite. In some of the studies, the two electrodes are connected to simulate the gold-bearing pyrite particles. However, the artificial coupling of gold and pyrite electrodes can be different from the real gold-bearing pyrite particles in the ore. This difference becomes extreme if the gold is in the form of electrum, gold tellurides, or any other mineral form. Given the use of gold-bearing particles from the ore itself or flotation concentrates, a comparison with the barren pyrite becomes more important for understanding the surface characteristics and flotation behavior of gold-bearing pyrite and the selective flotation from the barren pyrite particles.

This research aims to explore the differences between gold-bearing and barren pyrite particles and utilize these differences for the selective flotation of gold-bearing pyrite. This allows the production of pyrite concentrates with higher gold grades and makes low-grade sulfide ore deposits economically feasible. This approach would reduce the processing cost, improve resource efficiency, and minimize the environmental impact. Surface chemistry studies and flotation tests were conducted using samples prepared from gold-pyrite ores and a pyrite concentrate with high gold content.

2. Materials and Methods

2.1. Materials

Three samples, having different chemical and mineralogical characteristics, were used in the experiments. Sample 1 is a flotation concentrate produced by bulk sulfide mineral flotation from a Au-Pyrite ore. Sample 2 and Sample 3 are massive sulfide ore samples containing gold as the valuable metal. These samples were selected according to their cyanide-soluble gold (CNSolAu) content from the same ore deposit, because the CNSolAu value is considered an indicator of the exposed gold in pyrite particles.

The chemical analysis of the test samples is given in Table 1. Sample 1 is a flotation concentrate and contains a higher concentration of Au, Ag, Pb, and Zn than the other two

samples. The gold grades of Sample 2 and Sample 3 are 1.42 g/t and 2.4 g/t, respectively. These two samples were classified according to their CNSolAu content.

Table 1. Chemical analysis of the samples used in the tests.

	Cu	Fe	Pb	Zn	S	Au	Ag	As	CNSolAu
	%	%	%	%	%	g/t	g/t	%	%
Sample 1	0.52	25.8	10.4	10.55	33.8	85	211	2.5	92.0
Sample 2	0.1	23.63	0.05	0.12	25.19	1.42	7.0	0.09	62.72
Sample 3	0.07	25.82	0.06	0.06	26.54	2.40	12.0	0.02	31.93

Mineralogical characterization of the samples was performed using QEMSCAN (Quantitative Evaluation of Minerals by Scanning Electron Microscopy). Particle Mineralogical Analysis (PMA) was used for modal mineralogy and liberation/locking analysis. The gold search was conducted using Trace Mineral Search (TMS) mode with Energy Dispersive Spectrometry (EDS). The distribution of the major minerals of the three samples is summarized in Table 2. Sample 1 contains pyrite (44.9%), galena (19.7%), sphalerite (8.47%), and small amounts of arsenopyrite (1.03%) and chalcopyrite (0.7%). The major non-sulfide minerals were quartz, Mn-Ca silicates, Mn-Ca carbonates, and K-feldspar.

Table 2. Mineral distribution of the samples used in the tests.

Mineral Group	Sample 1	Mineral Group	Sample 2	Sample 3
Pyrite	44.9	Pyrite	52.63	57.28
Arsenopyrite	1.03	Galena	0.06	0.11
Galena	19.7	Sphalerite	0.15	0.07
Sphalerite	8.47	Chalcopyrite	0.05	0.16
Chalcopyrite	0.70	Quartz	15.79	12.90
Cerussite	1.28	Feldspar	1.59	0.71
Coronadite and other Pb	2.91	Muscovite	4.46	1.60
Quartz	7.97	Si-Al Clays	1.95	1.41
K-feldspar	1.62	Calcite	17.05	15.63
Muscovite/biotite/illite	0.73	Rhodochrosite	0.00	5.35
Mn-Ca-silicates	3.30	Sulfide/Silicate Texture	2.67	1.52
Mn-Fe-(Ca)-carbonates	1.85	Other Minerals	3.6	3.26
Mn-Ca-carbonates	1.42	Total	100.00	100.00
Other Minerals	4.12			
Total	100.00			

The gold-bearing phases detected are essentially gold–silver alloys (electrum) with composition of 50%–77% Au and 50%–23% Ag. Gold is usually locked with pyrite or encapsulated within galena/pyrite, but there are also liberated gold particles at coarse particle sizes ($+20\text{ }\mu\text{m}$). Approximately 36% of gold was in the form of liberated particles. Figure 1 shows back-scattered electron (BSE) images of gold-bearing pyrite particles. The CNSolAu content of Sample 1 was measured as 92%. This means that most of the gold is exposed and can interact with the flotation reagents.

Sample 2 and Sample 3 are from the same deposit and have similar mineral distributions. The samples consist of pyrite, quartz, and calcite as the major mineral phases. The gold search was conducted on the HLS (Heavy Liquid Separation) concentrates due to the low head assays. The gold was mainly in the form of native gold with rare Ag–Au–Te grains. The grain size of gold was 1–13 μ in Sample 2 and 1–5 μ in Sample 3. The gold grains were locked in pyrite. Figure 1 shows BSE images of typical gold grains associated with pyrite particles.

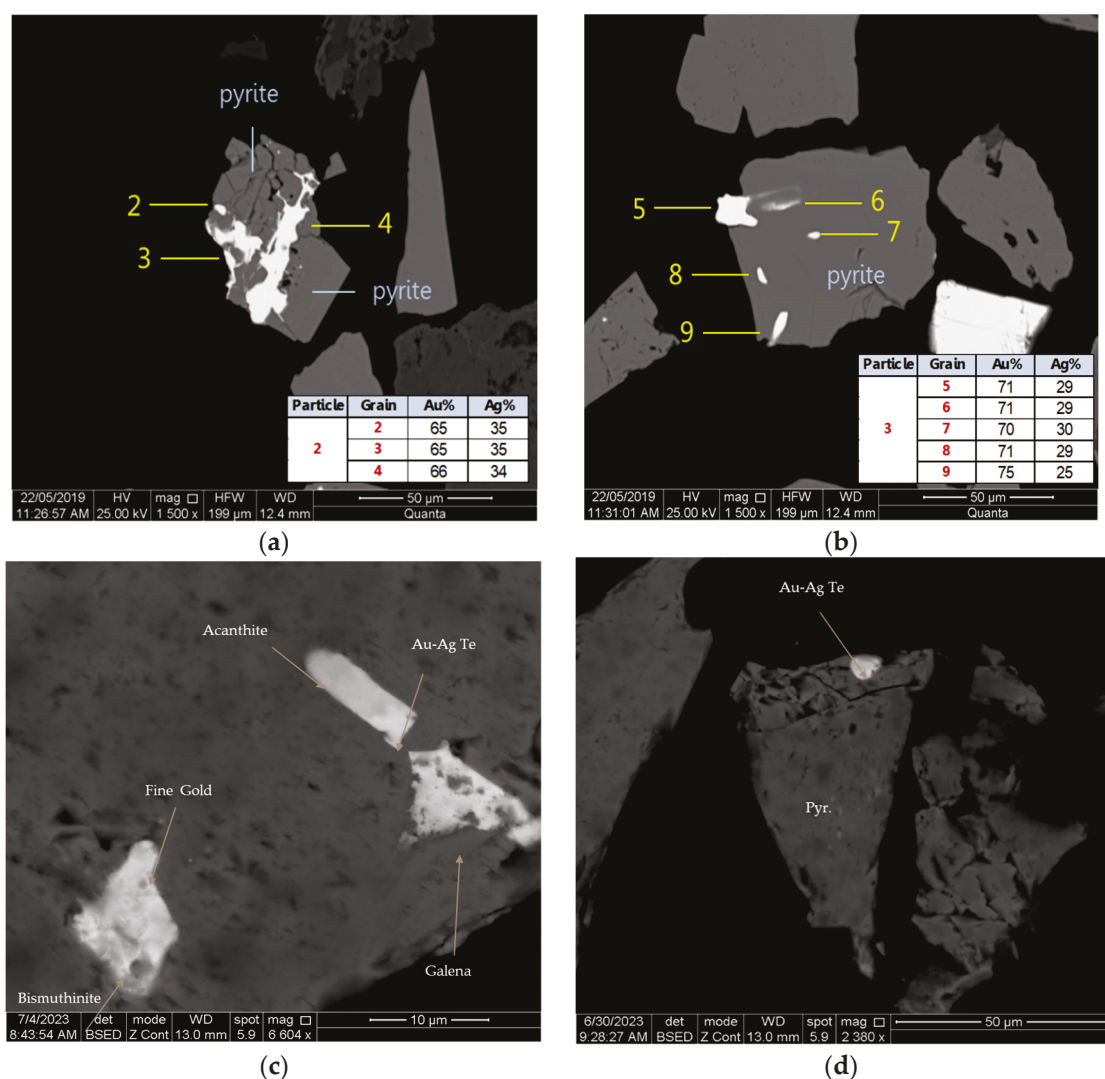


Figure 1. BSE Images of the gold-bearing particles from the test samples: (a) and (b) Sample 1; (c) Sample 2; and (d) Sample 3.

2.2. Experimental Methods

2.2.1. Flotation Tests

Rougher kinetic flotation tests were conducted using a Denver-type flotation machine in a 2.5 L volume flotation cell. The pulp density was adjusted at 30%*w/w*. The agitation speed and the airflow rate were set to 1550 rpm and 4–5 L/min, respectively. Analytical grade H₂O₂, FeSO₄, NaClO, CaClO, NaHS, Na₂S₂O₅, and dextrin from potato starch were used as pyrite depressants in the tests. Sodium Aerofloat (NaAF, ethyl dithiophosphate) and Aero8045 (dithiophosphate formulation) from Syensqo were used as collectors. F-549 (Syensqo) was used as the frother in all the tests. Lime was used as a pH regulator where needed. The sequence of reagent addition was depressant, collector, and frother. The conditioning time was 2 min for the depressants and collectors, and 1 min for the frother. The concentrates were assayed for Au (fire assay with AAS finish for up to 100 g/t gold content and gravity finish for values over 100 g/t), S (Leco), Ag, As, Pb, Zn, and Fe (ICP-MS).

2.2.2. Electrochemical Studies

Two mineral electrodes were used to demonstrate the differences in electrochemical and surface properties of the gold-bearing pyrite (Au-Py) and barren pyrite (B-Py). The Au-Py electrode was manufactured using the pyrite particles concentrated by heavy liquid

separation from a gold-pyrite ore. The B-Py electrode was produced from a high-purity pyrite sample purchased from Wards' Natural Science. The $-212 + 150 \mu\text{m}$ size fraction was used in both electrodes. The pyrite samples were washed with diluted HCl and acetone sequentially, and then rinsed with distilled water to remove any oxidized and organic species from the surface and dried in a vacuum desiccator. The pyrite particles were attached to a copper plate through a conductive silver epoxy. The copper plate with attached pyrite particles was then immersed in an epoxy resin so that only the pyrite particles were exposed. The surface of the mineral electrode was polished using an aluminum paste before the electrochemical experiments. This method allows using the same electrode several times after surface cleaning with aluminum paste. Figure 2 shows a photo of the mineral electrode surface.

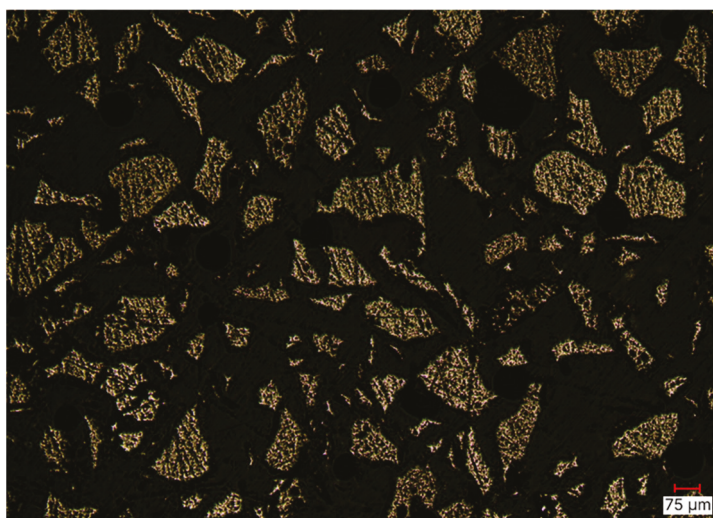


Figure 2. Optical microscope image of polished mineral electrode surfaces of gold-bearing pyrite (Au-Py).

The electrochemical experiments were performed using Gamry Reference 600 Model Potentiostat/Galvanostat. The measurements were performed in a standard three-electrode electrochemical cell with a standard calomel electrode (reference electrode), a platinum wire (counter electrode), and a mineral electrode (working electrode). The open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) measurements were conducted on both pyrite samples. The EIS measurements were performed in the frequency range of 1×10^5 to 1×10^{-2} Hz. The potentials shown in this paper were converted to the standard hydrogen electrode (SHE) scale. A constant polarization potential (100 mV) was applied during EIS measurements. High-purity de-ionized water was used in all experiments. Buffer solution (pH 9.2) of $0.05 \text{ M Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ was used as an electrolyte, and all measurements were carried out at room temperature ($\sim 25^\circ\text{C}$). High-purity nitrogen gas purged through the solution for 15 min to remove the dissolved oxygen in the solution. The pyrite electrodes were polished with alumina and thoroughly rinsed before each experiment.

3. Results

3.1. Flotation Tests

3.1.1. Flotation Concentrate (Sample 1)

Sample 1 is a flotation concentrate containing a high amount of pyrite, galena, and sphalerite. The gold and silver assays were 85 g/t and 211 g/t, respectively. A series of flotation tests was conducted to separate the gold-bearing sulfide minerals from the barren pyrite.

Various types of reagents can be used to depress pyrite in flotation. The type of depressants is selected according to the ore type and mineral content. In the flotation of

copper minerals and copper-activated sphalerite, pyrite is generally depressed at high pH (pH = 11.5) using lime. However, high pH could sometimes negatively affect the flotation of gold and gold-bearing pyrite [5]. In these circumstances, specific depressants should be used. In this study, in addition to the high pH, the effects of different types of depressants and flotation conditions (NaHS, FeSO₄, and Na₂S₂O₅ (Sodium metabisulfite, MBS), high-temperature conditioning followed by flotation at high pH, and oxidizing reagents such as Ca(ClO)₂, NaClO, and H₂O₂ in combination with dextrin) on the selective flotation of gold-bearing pyrite from the barren pyrite were investigated.

Figure 3 shows the gold recovery as a function of mass pull, gold grade vs. recovery curves, and the gold-pyrite selectivity curves. The floatability of both gold-bearing pyrite and barren pyrite was very low at high pH. As it was mentioned above, Sample 1 is a flotation concentrate and both gold-bearing and barren pyrite particles are covered with collector molecules. In order to remove the residual collector molecules and oxidized species from the surface of the minerals, in one of the tests, the material was pre-treated at high temperature, filtered, repulped, and floated at pH 11.5 [16–18]. In another test, NaHS was used for surface cleaning [19]. After conditioning with NaHS, the material was filtered and repulped using fresh water. The flotation was performed at pH 11.5 to depress the barren pyrite particles. The redox potential of the pulp was measured as −47 mV (Ag/AgCl) after repulping with fresh water. The results show that surface cleaning at high temperature improved the gold recovery and the gold/pyrite selectivity to some extent. The use of NaHS, however, depressed both types of pyrite particles. Application of these pre-treatment methods is complicated even in the laboratory scale tests and the flotation performance was not satisfactory. Therefore, alternative reagent schemes were tested using strong pyrite depressants.

The sulfide minerals, particularly pyrite, can strongly be depressed under extreme pulp electrochemical conditions. Pyrite is the most cathodic sulfide mineral [20] and the most affected by changing the pulp electrochemistry. Oxidative conditions form stable and hydrophilic iron oxide/hydroxide species, which inhibit the adsorption of collector molecules on the pyrite surface [16,21]. Surface oxidation can be achieved by pre-aeration or the use of specific oxidizing reagents, such as hydrogen peroxide (H₂O₂) [9,22], sodium hypochlorite (NaClO), or calcium hypochlorite (CaClO₂) [23]. In some of the applications, dextrin (a low-molecular-weight carbohydrate produced by hydrolysis of starch and glycogen) is used as a supporting reagent to improve pyrite depression [23,24]. The dextrin molecules are hydrophilic and adsorb on the iron oxide/hydroxide sites at the surface of the oxidized pyrite. This can prevent collector adsorption even at high dosages and maintain the depression of pyrite particles.

Rougher kinetic flotation tests were performed using H₂O₂ (15 lt/t, 35% purity), NaClO (15 lt/t), and CaClO₂ (750 g/t) as oxidizers and dextrin (300 g/t). The flotation tests were performed at natural pH (pH = 7–8). The redox potential of the pulp increased up to 400 mV (Ag/AgCl) after the addition of the oxidizers and decreased to about 150 mV during the flotation, due to oxidation of pyrite. Both the gold recovery and the selectivity were improved substantially with the use of an oxidizing reagent–dextrin combination. The gold grade of the concentrate increased to 600 g/t with the use of CaClO₂ + Dextrin. The three reagent combinations were effective and achieved high selectivity. These results showed that the flotation behavior and, hence, surface chemistry of gold-bearing pyrite particles are different from the barren pyrite particles under oxidative flotation conditions.

Pyrite can also be effectively depressed using sulfur-based reagents, such as Na₂S₂O₅ and Na₂SO₃ [6]. In this study, Na₂S₂O₅ (sodium metabisulfite, MBS) was used for the depression of barren pyrite particles. After the addition of 3 kg/t MBS, the pulp was pre-aerated for 5 min. The pulp redox potential was about 30 mV (Ag/AgCl) after the pre-aeration stage. Stage addition of collector (NaAF) was applied with 30 g/t addition in each stage. The flotation time was 2 min in each stage and four concentrates were collected in the test. The flotation was conducted at a natural pH (pH 7).

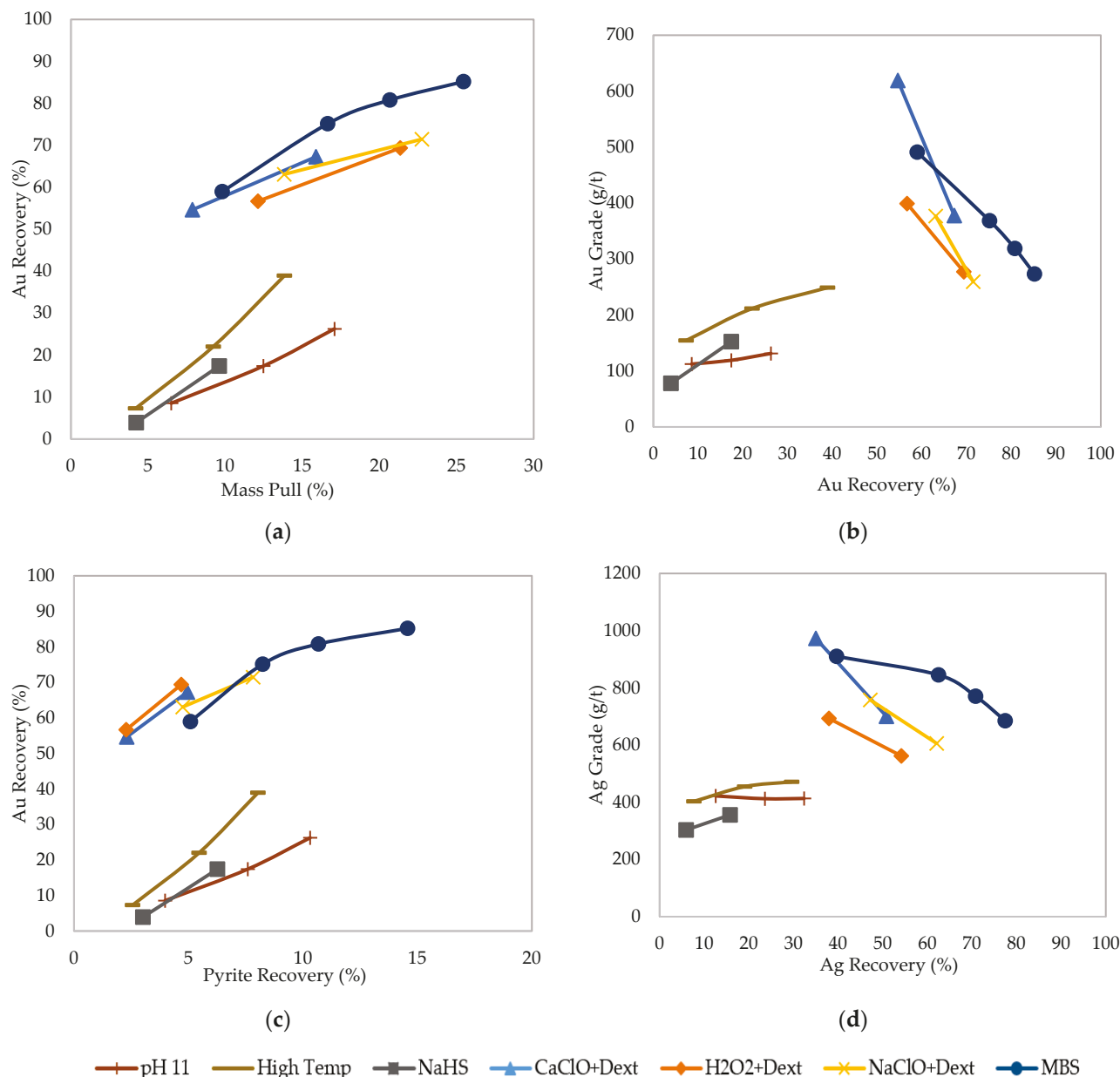


Figure 3. Flotation of gold-bearing pyrite particles from the barren pyrite at different chemical conditions in Sample 1: (a) shows the gold recovery as a function of mass pull; (b) gold grade vs. recovery curves; (c) gold-pyrite selectivity curves; and (d) silver grade vs. recovery curves.

The flotation performance of the MBS test was similar to the tests performed using oxidizers (Figure 3). The gold grade of the first concentrate of the kinetic test was as high as 500 g/t. The silver grade of the concentrate could also be increased up to 900 g/t. At the end of the test, a rougher concentrate was produced assaying 273 g/t Au at 85% gold recovery. The oxidizing conditions produced rougher concentrates with similar gold grade (about 260 g/t) but at lower recoveries (about 70%).

The results showed that MBS can effectively depress the barren pyrite particles without negatively affecting the gold-bearing pyrite particles. The trend of the gold/pyrite selectivity curves is very close in the MBS and oxidizer tests. Both methods can be considered for selective gold flotation from the pyrite concentrates.

The grade and recovery trends of silver were very close to that of gold (Figure 3). The silver content of Sample 1 was about 200 g/t (Table 1) and increased to >600 g/t in the tests performed using the depressants. The use of MBS produced higher silver

grades and recovery. This could be attributed to the flotation of electrum particles, and also galena particles, which may also contain silver [25]. There was a direct correlation between the silver grade and gold and lead grade of the concentrates. The silver grade of the concentrates increases linearly with increasing gold and lead grades. The copper (71%) and lead (81%) recoveries followed the same trend, but not the Zn. MBS is also known as an effective sphalerite depressant and, hence, Zn recovery was only 27% in the absence of copper sulfate.

The chemical and mineralogical analyses of Sample 1 show the presence of arsenopyrite in the material. The effects of pre-treatment methods and the use of different types of depressants on the flotation of arsenopyrite are illustrated in Figure 4. The arsenic grade of the material was about 2.5%, which is presumably in the penalty range. The addition of NaHS obviously removed the oxidized species from the surface of arsenopyrite and produced a concentrate with a higher As grade than the other conditions. The arsenic grade was decreased to <0.5% using oxidizers and to 0.7% with the MBS test. The use of oxidizers and MBS for barren pyrite depression can also depress the arsenopyrite particles effectively and decrease the arsenic content of the concentrate substantially.

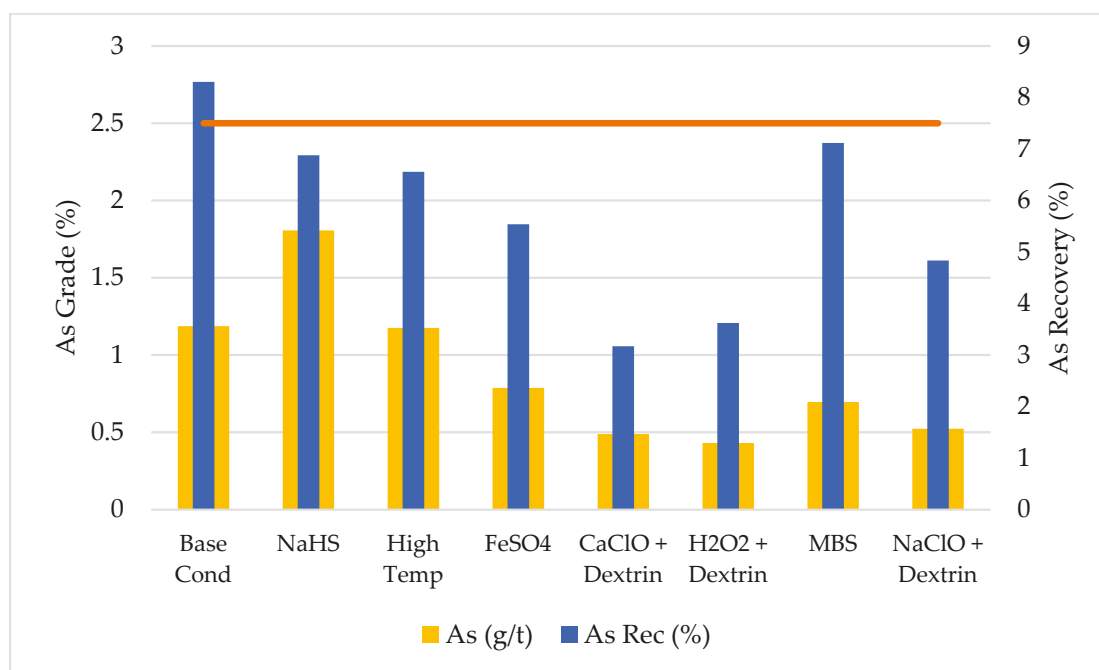


Figure 4. The arsenic grade and recovery of the concentrates produced in the presence of oxidizers and MBS in Sample 1.

3.1.2. Massive Pyrite Ore Samples (Sample 2 and Sample 3)

The gold-bearing pyrite particles could successfully be separated by flotation using MBS or H₂O₂-Dext. Similar depressants were tested on two low-grade massive pyrite ore samples, Sample 2 and Sample 3 (Table 1). Aero8045 produced higher recoveries than that of NaAF and, hence, it was used as the collector in this part of the study. The two samples were prepared from the same ore deposit according to their CNSolAu content to test the hypothesis of this study. The CNSolAu value indicates the exposed gold at the surface of pyrite particles. The higher the CNSolAu, the larger the gold exposed at the surface of the particles. The exposed gold grains may change the electrochemical behavior of these particles and provide active sites for collector adsorption. Figure 5 shows that the highest gold grade and recovery values were obtained with MBS for both samples. The gold recovery of Sample 2 was higher due to its higher CNSolAu content (62.72%).

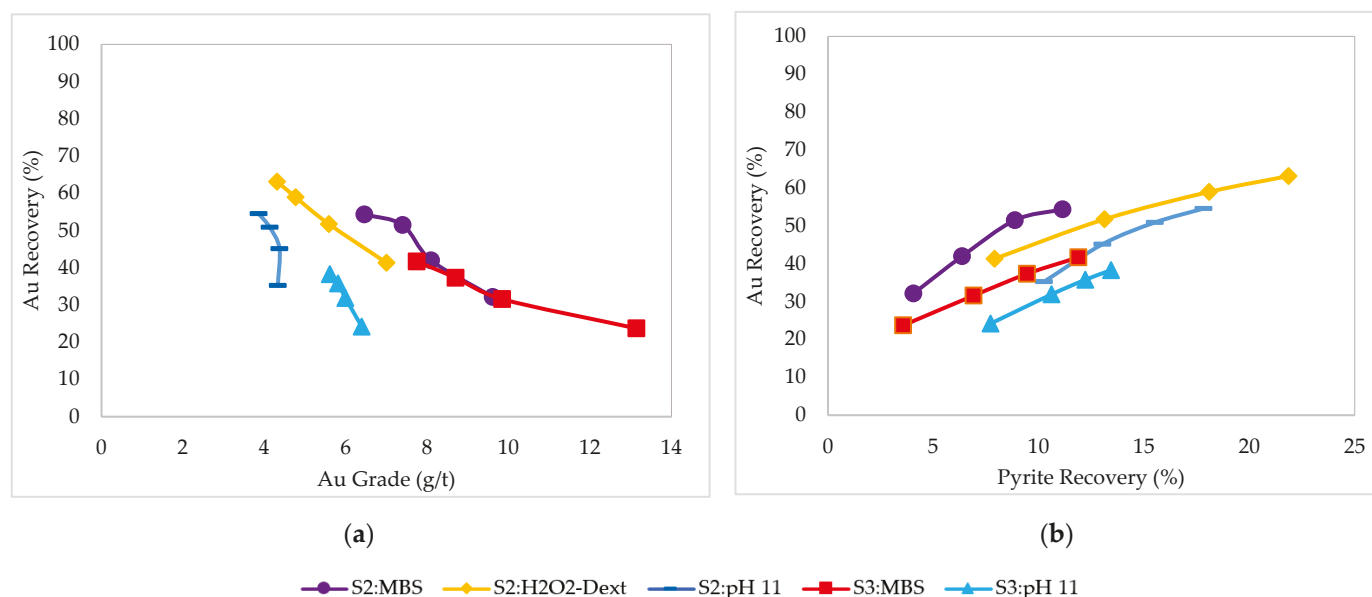


Figure 5. The flotation performance of gold-bearing pyrite particles under different flotation conditions in Sample 2 and Sample 3: (a) shows gold grade vs. recovery curves and (b) gold recovery vs. pyrite recovery curves.

3.2. Electrochemical Experiments

Two mineral electrodes were manufactured using gold-bearing pyrite (Au-Py) and barren pyrite (B-Py) particles. OCP and EIS measurements were performed to demonstrate the influence of gold on the surface characteristics of pyrite. The measurements were performed at pH 9.2.

OCP measurements of the two samples were performed for comparison of their electrochemical reactivity. Figure 6 shows the OCP values measured for 5 min. The measurements performed in an alkaline solution show the response of the pyrite electrodes to oxidation by OH^- ions. B-Py has a higher OCP than Au-Py. This indicates that B-Py is more cathodic and electrochemically more reactive to OH^- ions [26].

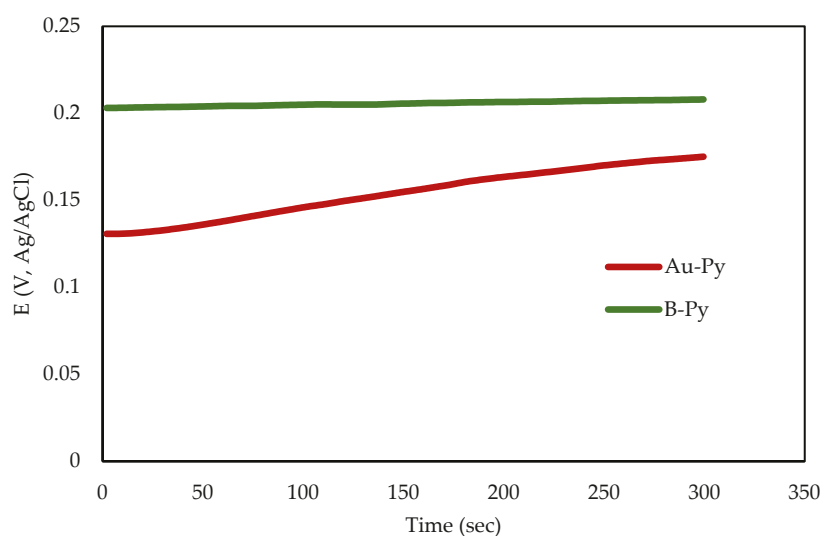


Figure 6. Open Circuit Potential (OCP) of the pyrite samples as a function of time.

The surface characteristics of the two pyrite samples are also compared based on the EIS measurements. The results of the EIS experiments are given in the form of Bode-magnitude and phase angle plots in Figure 7. The results show clearly that there are

significant differences between the surface characteristics of the pyrite samples. The surface coatings of iron oxy/hydroxide and sulfur species are expected on pyrite surface in alkaline solutions. The presence of such coatings increases the resistance to the charge transfer of the surface. Z_{mod} values of B-Py were higher, indicating higher resistance to charge transfer than Au-Py. The differences between the two samples were attributed to the presence of gold in Au-Py.

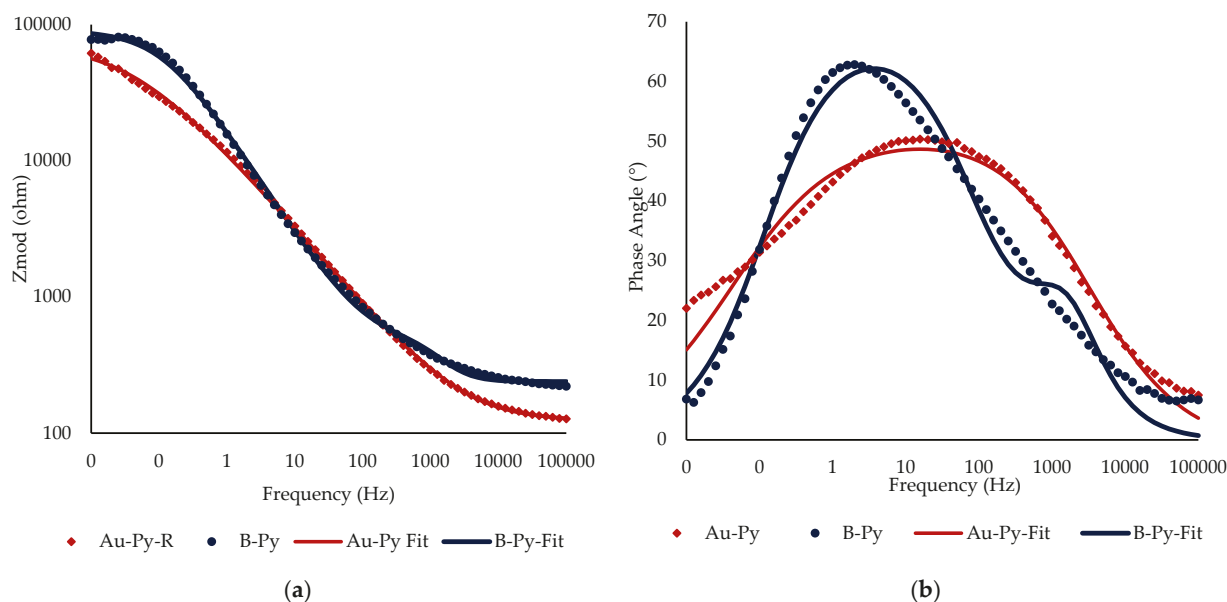


Figure 7. EIS results of Au-Py and B-Py pyrite samples obtained at pH = 9.2 and at 100 mV polarization potential. (a) Bode magnitude (b) Bode-Phase angle plot.

The EIS spectrum of each sample was fitted to an equivalent electrical circuit model to compare the electrochemical properties of the two pyrite electrodes based on conductance and resistance (Figure 8). The proposed model is used to simulate the impedance behavior of the pyrite/electrolyte interface [15,27]. The model parameters were calculated by using Gamry Echem Analyst software Version 6.33. In the electrical circuit model, R_s is the electrolyte resistance and R_{ct} is the charge transfer resistance, representing the resistance of charge transfer through the iron-deficient layer. The pore resistance (R_p) is a measure of the charge transfer in the pores of the product layer, i.e., the Fe-Hydroxide/oxide layer. C_{sl} corresponds to the capacitance of the surface layer consisting of the initial pyrite oxidation species. The double-layer capacitance (Q_{dl}) is represented in terms of the constant phase element that indicates a nonhomogeneous surface. The fitted model parameters and the goodness-of-fit values are given in Table 3. The Chi-squared test gave low values indicating the proposed equivalent electrical circuit simulated the electrical double layer. The “ n ” is the phase angle and represents the surface roughness of the electrode, usually varying between 0.5 and 1.

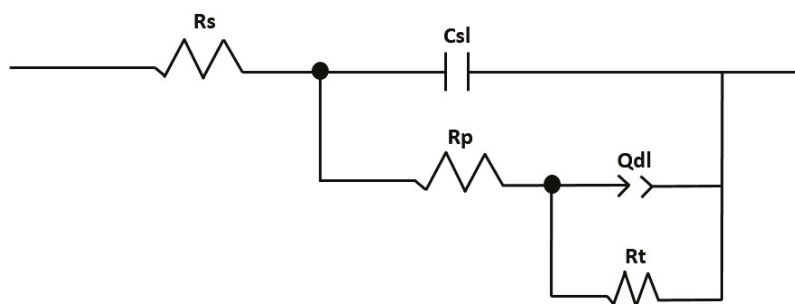


Figure 8. Equivalent electrical circuit for modeling the EIS data [27].

Table 3. The Equivalent electrical circuit model parameters of Au-Py and B-Py samples.

	Rs (Ω)	Rp (Ω)	Rt (kΩ)	Csl (F)	Qdl (S*s ⁿ)	n (°)	Chi-Squared χ ²
Au-Py	126.6	19.39	74.21	1.650×10^{-7}	2.87×10^{-5}	0.57	2.47×10^{-3}
B-Py	238.8	315.2	91.04	5.24×10^{-7}	1.38×10^{-5}	0.76	5.84×10^{-3}

The net rate of electrochemical reactions on electrode surfaces is inversely proportional to the charge transfer resistance (Rct) [28]. Rct and Rp of B-Py were much higher than that of the Au-Py electrode, indicating the formation of a higher amount of oxidation products (iron oxides, iron sulfates, and polysulfides), and resulting in a more electrochemically passive surface layer. The presence of gold obviously changed the electrochemical characteristics of pyrite, which can be utilized for the selective separation of Au-Py particles from B-Py particles.

4. Discussion

The presence of impurities, such as As, Au, Ag, Ni, Co, etc., changes the electrical properties and oxidation behavior of pyrite. The pyrite is classified as p-type and n-type based on its electrical properties. The p-type pyrite is iron deficient ($S/Fe > 2$) and may contain significant quantities of As. The n-type pyrite is sulfur deficient ($S/Fe < 2$) and may be rich in Co and Ni. The conductivity of the p-type is much lower than that of the n-type.

In addition to the presence of fine grains of native gold and/or electrum, in pyrite, particles may change their electrical properties and flotation behavior. Gold is the most noble metal and a galvanic interaction may occur between pyrite and gold. This may change the surface properties of gold-bearing pyrite and barren pyrite, and allow their separation by flotation [14].

In this study, the electrochemical properties of gold-bearing pyrite (Au-Py) and barren pyrite (B-Py) particles were investigated by using the natural material obtained from different ore types. The electrochemical characterization of the Au-Py and B-Py particles shows that B-Py is more cathodic and prone to reduction of OH^- and any other depressant ions on its surface. This resulted in higher charge transfer resistance as shown by the EIS measurements. The Au-Py, on the other hand, is more anodic and allows the adsorption of the collector on the surface. The presence of Ag in electrum may also enhance the adsorption of collector molecules due to the high stability of Ag-X compounds.

Figure 9 shows the galvanic interaction models for a single gold-bearing pyrite particle and for the case when a gold-bearing is in contact with a barren pyrite particle. Huai, et al. [14,15] have studied the single-particle model in detail under ambient and oxygen-enriched conditions. In the single-particle model under oxygen-enriched conditions, the oxygen is reduced at the surface of gold, and the electrons flow from pyrite to gold, which increases the oxidation rate of pyrite (Figure 9a).

In the flotation of gold-bearing pyrite particles, however, barren pyrite particles exist in large quantities affecting the surface overall galvanic interaction mechanism and, hence, the surface properties of the gold-bearing pyrite and barren pyrite particles. Figure 9b shows the galvanic interaction model between a gold-bearing pyrite particle and a barren pyrite particle. The OCP and EIS measurements show that the barren pyrite particles should be the cathodic component in the galvanic interaction model. The electrons flow from Au-Py to B-Py leads to anodic oxidation of Au-Py and oxygen reduction at the surface of B-Py. In addition to the iron-deficient sulfide and polysulfide species, active sites for collector adsorption are formed at the surface of Au-Py. The presence of silver in the electrum particles may enhance the adsorption of collector molecules and increase the degree of hydrophobicity of the Au-Py particles.

The differences in the surface properties of the two-pyrite type were utilized for the selective separation of gold-bearing pyrite from the barren pyrite. The flotation tests show that high pH could not sufficiently expose this difference, and the selective flotation was poor. However, the use of strong oxidizing agents or sulfur-based depressants can

successfully enhance the differences in surface properties of the pyrite particles and allow selective separation by flotation.

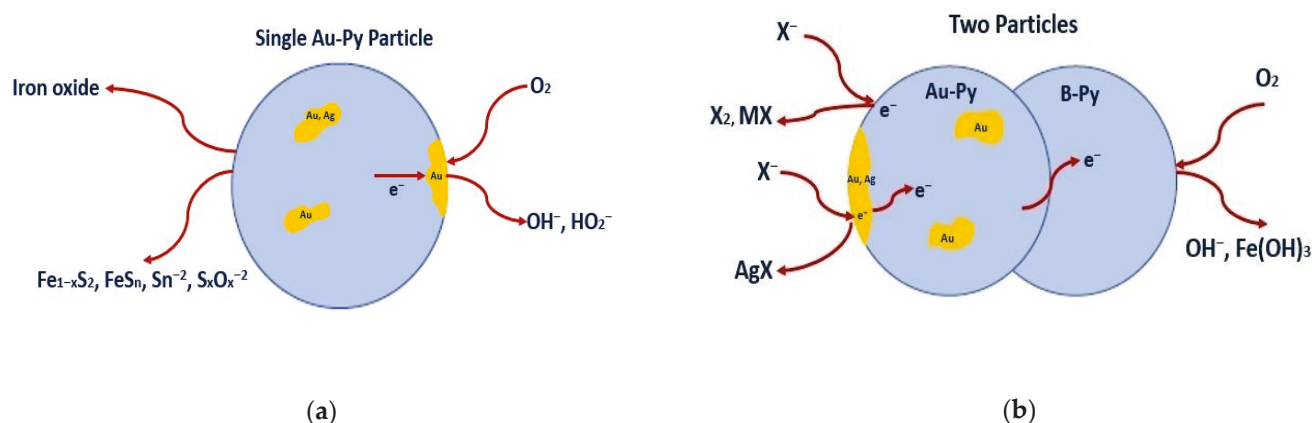


Figure 9. Schematic illustration of the galvanic interaction between gold and pyrite: (a) in a gold-bearing single particle, and (b) when a gold-bearing particle is in contact with a barren pyrite particle.

The flotation results showed that there is a direct relationship between CNSolAu content and gold recovery (Figure 10). The gold recovery increases linearly as a function of CNSolAu. High CNSolAu values indicate the ratio of free gold, i.e., the area of gold/electrum exposed on the surface of pyrite particles. The exposed gold sites are less affected by the depressants compared to the barren pyrite and, hence, the collector molecules can selectively adsorb on these sites.

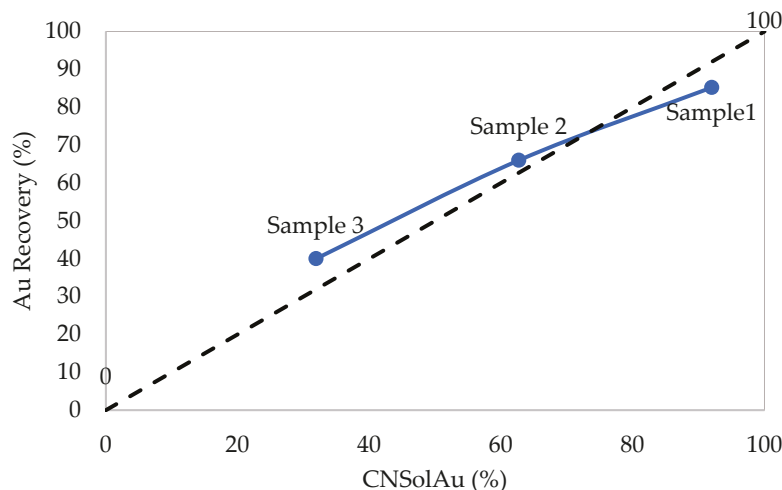


Figure 10. The relationship between CNSolAu and gold recovery.

5. Conclusions

Laboratory scale flotation tests were conducted on three ore samples containing both gold-bearing pyrite (Au-Py) particles and barren pyrite (B-Py) particles. The selective flotation of Au-Py from B-Py was achieved by using strong pyrite depressants and a selective gold collector. MBS (Sodium Metabisulfite) and a dithiophosphate formulation collector were found to be the most effective reagent combination.

There was a direct relationship between CNSolAu and gold recovery, indicating the contribution of free gold on the selective flotation.

Electrochemical studies showed that the presence of gold/electrum in a pyrite particle changes the electrochemical characteristics and surface of the gold-bearing pyrite particles.

According to the galvanic interaction model, the barren pyrite particles are the cathodic component and are prone to cathodic reduction of OH^- and depressant ions on the surface. The Au-Py, on the other hand, goes through anodic oxidation-forming iron-deficient sulfur and polysulfide species, as well as active sites for collector adsorption. Consequently, the B-Py particles can be depressed effectively without significantly affecting the Au-Py particles under specific flotation conditions.

This study shows that low-grade gold-pyrite ores can be enriched by flotation depending on the form of gold in the ore. This allows production of pyrite concentrates with a saleable gold grade and makes the low-grade sulfide ore deposit economically feasible.

Further studies should be performed to investigate the surface properties of pyrite particles containing gold as a solid solution and the possibility of separating these particles by flotation in refractory gold ores.

Author Contributions: Conceptualization, S.Ö. and Z.E.; methodology, S.Ö. and Z.E.; validation, S.Ö. and Z.E.; formal analysis, S.Ö.; investigation, S.Ö. and Z.E.; resources, Z.E.; writing—original draft preparation, S.Ö. and Z.E.; supervision, Z.E.; project administration, Z.E. All authors have read and agreed to the published version of the manuscript.

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Article

Insights on the Flotation Separation of Hematite from Quartz with a 4-Tert-butyl-catechol Collector

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Abstract: Iron ore is the main raw material of the iron and steel metallurgy industry, but quartz in iron ore reduces metallurgical efficiency and increases metallurgical costs. Therefore, iron ore desilicization by flotation plays an important role in the iron and steel metallurgy industry. In this study, 4-tert-butyl-catechol (TBC) was designed as a collector to directly float out hematite from quartz. The micro-flotation tests demonstrated that under pH ~9.0, 1×10^{-5} mol·L⁻¹ TBC recovered 98% hematite from its mixture with quartz, while the recovery of quartz was only about 17%. Zeta potential and contact angle results inferred that the adsorption affinity of TBC toward hematite was greater than that to quartz. The results of FTIR and XPS inferred that TBC adsorbed on the Fe³⁺ sites of hematite interfaced via the O atom of its two adjacent hydroxyl groups to form a stable five-membered chelating ring at pH 9.0. This study offered new research insight on the development of novel collectors for hematite flotation through bionics technology.

Keywords: hematite; 4-tert-butyl-catechol; desilication; flotation separation

1. Introduction

Steel is one of the most important metal materials and it plays a vital role in human development and social progress [1]. With the development of the economy, the steel demand around the world continues to be high [2]. However, due to the depletion of high-quality iron ore resources, the quartz-associated iron ores have to be processed to enrich iron minerals [3]. In the smelting process, quartz significantly increases the consumption of alkaline fluxing agents (limestone) [4], which reduces the blast furnace efficiency and increases energy consumption, the amount of slag produced, and the costs. Therefore, the removal of quartz from iron concentrates is of great significance for the efficient utilization of iron ore resources [5]. As a crucial enrichment technology, the flotation separation of quartz from iron ores has also become one of the hot research areas.

Currently, there are three main approaches for separation of quartz from iron ores: reverse flotation with anionic collectors [6], reverse flotation with cationic collectors [7], and direct flotation [8]. In the reverse flotation process of hematite, the common anionic collectors are fatty acids. Bai et al.'s study showed that the flotation recovery of hematite by sodium oleate was over 80% at pH 8.2 [9], but sodium oleate exhibited poor solubility and flotation selectivity. The traditional cationic collectors were dominated by amine collectors, and dodecylamine is one of the most representative cationic collectors. Zhang et al.'s research showed that by using starch as a depressant, dodecylamine could float hematite from quartz [10], but dodecylamine also displayed some issues, such as viscous and big foam and weak solubility [11]. The ether amines are more soluble than fatty amines, while their low flotation selectivity and rich foaming property limit their wide application [12]. At present, fatty acids are dominant collectors used in the reverse flotation process of hematite production [13]. To achieve a satisfactory separation efficiency, the flotation process is recommended to be performed above 35 °C, which significantly increases the production costs [14]. Direct flotation is floating out iron oxide minerals from iron ores, thus removing

quartz from iron concentrates [15]. The direct flotation collectors for hematite are anionic surfactants [16], such as fatty acids [17] and petroleum sulfonates [18], which have the advantages of a simple reagent scheme and low cost [19]. While using fatty acid collectors, the floatability of hematite is usually weak, and its separation efficiency from quartz is low [20]. In addition, to increase their dispersity in water, it is necessary to heat the flotation pulp [21]. To solve the negative impact of quartz on the steel metallurgy process, flotation desilication with more efficient collectors is a crucial research hotspot.

To address the above problems, researchers have developed some new collectors for flotation separation of hematite and quartz, such as dodecyl hydroxyethyl dimethyl ammonium bromide [22], poly (N-isopropyl acrylamide) [23], (E)-8,11-dihydroperoxyoctadec-9-enoic acid (EDEA) [24], sodium oleate (NaOL)-dodecylamine acetate (DAA) [25], modified sodium oleate (MSO) [26], mixed cationic C₁₂ amine and anionic sulphate/oleate collectors [27], Curdlan [28], and innovative biosurfactants [29]. Luo et al. first synthesized a novel surfactant, 2-((2-(decyloxy)ethyl)amino)lauric acid (LDEA), substituting 3-(decyloxy)propan-1-amine (DPA) on the α -carbon position of lauric acid, and utilized it as a collector for the flotation of hematite mineral [30]. Luo et al. synthesized a new fatty acid collector, α -bromodecanoic acid, by introducing a strongly electronegative Br atom at the α -carbon position, which could complete floatation separation of hematite from quartz at 16 °C and pH 11.5, but it had large potential hazardous property [31]. Guo et al. designed a novel quaternary ammonium collector, N-(2-hydroxyethyl)-N, N-dimethyl-3-[(1-oxododecyl)amino]-1-propanaminium, which exhibited good water solubility and effectively floated hematite from quartz by using starch as the depressant [32]. Liu et al. synthesized a novel collector, N-(2,3-propanediol)-N-dodecylamine (PDDA), by introducing one propylene glycol group into DDA, which had better solubility and hydrophobicity than DDA [33]. Although these new collectors alleviated the shortcomings of traditional collectors, the problems of high costs, the need to add a depressant, and low-temperature performance are still serious. Therefore, it is very important to develop environmentally friendly, economical, efficient, and temperature-adaptive collectors.

Bionics is a pivotal field to promote the technological innovation and progress [34]. Researchers have crafted innovative materials, including hydrogels and membranes, drawing inspiration from the adhesive properties of marine mussels [35]. From their research, catechol is a unique structural component [36], which could interact with surfaces through hydrogen bonding, coordination bonds, or hydrophobic interactions [36–40]. Especially, catechol exhibits a strong affinity to iron and its oxides. Additionally, catechol compounds possess good solubility and low-temperature dispersity performance [41]. This shows that catechol has a strong affinity for iron minerals and may have better solubility and low-temperature performance than sodium oleate. Therefore, it is interesting to introduce catechol surfactants as flotation collectors for hematite separation and purification.

This paper investigates the performance of 4-tert-butylcatechol (TBC) in flotation separation of hematite from quartz. Afterwards, the flotation mechanism of TBC to hematite is explored via the contact angle, zeta potential, adsorption capacity, Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). This work also provides new research insight on the development of novel collectors through bionics technology.

2. Materials and Experimental Methods

2.1. Materials

The high-purity samples of hematite and quartz were purchased from Ye Mineral Company, Guangzhou, China, and their 38–74 μ m particles were prepared sequentially by crushing, grinding, and sieving. The results of their X-ray diffraction (XRD) and X-ray fluorescence (XRF) are shown in Figure 1 and Table 1, respectively, indicating a high purity.

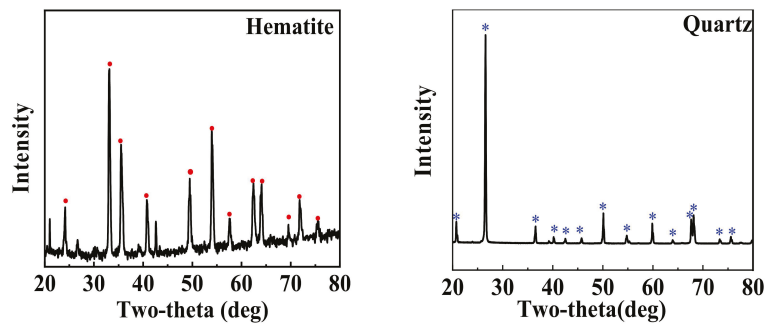


Figure 1. XRD patterns of hematite and quartz (red dot: the peak of hematite crystal, blue *: the peak of quartz crystal).

Table 1. The XRF of hematite and quartz.

Formula (wt/%)	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MgO	P ₂ O ₅	Other
Hematite	99.11	0.78	0.04	0.01	0.01	0.01	0.04
Quartz [42]		99.8					0.20

TBC, hydrochloric acid (HCl), and sodium hydroxide solutions (NaOH) were obtained from Aladdin Reagents Company. Distilled water was used throughout the tests.

2.2. Micro-Flotation Tests

The micro-flotation experiments were performed in a Hallimond tube with 220 mL volume [43], and the operation processes are shown in Figure 2. Each experiment used 2 g samples (the mass ratio of hematite to quartz for their artificial mixture flotation was 1:1), with a particle size ranging from 38 to 74 μm . The pulp pH was regulated using NaOH and HCl solutions [44]. After weighing and analyzing the tailings and concentrates, as listed in Figure 2, the flotation recovery was calculated by Equation (1) (for single mineral) or Equations (2) and (3) (for the mixed minerals) [45]. In Equations (1)–(3), m_1 and m_2 represent the weight of concentrates and tailings, β_1 and β_2 are the hematite content in concentrates and tailings, respectively, and r represents the flotation recovery. The reported results were the average recovery of three independent tests:

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

$$r_{\text{hematite}} = \frac{m_1 \times \beta_1}{m_1 \times \beta_1 + m_2 \times \beta_2} \times 100\% \quad (2)$$

$$r_{\text{quartz}} = \frac{m_1 \times (1 - \beta_1)}{m_1 \times (1 - \beta_1) + m_2 \times (1 - \beta_2)} \times 100\% \quad (3)$$

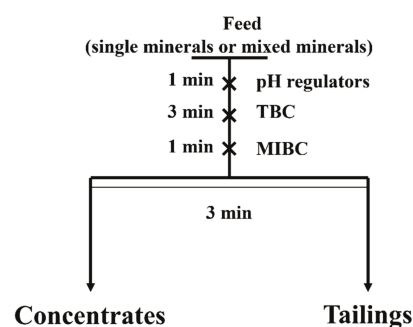


Figure 2. The operation process of flotation.

2.3. Contact Angle (CA) Measurements

The slices of hematite and quartz were polished by SiC sandpaper [46]. After that, they were submerged in 220 mL of 1.0×10^{-5} mol·L⁻¹ TBC solutions for 10 min. Following that, the slices were removed and washed, and their contact angles were determined using the JC2000C contact-angle device (Zhongchen Digital China, Shanghai, China) [47].

2.4. Zeta Potential Experiments

The $-5 \mu\text{m}$ mineral particles were used to measure their zeta potential on a Brookhaven's ZetaPlus analyzer (Brookhaven Instruments, New York, NY, USA). After adding 50 mg samples into 50 mL of 1.0×10^{-2} mol·L⁻¹ KCl electrolyte, NaOH or HCl solutions were added to regulate the suspension pH. Then, 1×10^{-5} mol·L⁻¹ TBC solutions were added into the suspension, which was stirred for an extra 10 min before the zeta potential was measured.

2.5. The Adsorption Capacity Measurement

The spectrophotometry approach was used to determine the adsorption capacity of TBC on the hematite surface with a UV-visible spectrophotometer (Evolution 201, Thermo Fisher Scientific, Waltham, MA, USA) [48]. In each experiment, 0.2 g of mineral samples was placed in a conical flask containing distilled water, and the pH was adjusted. Then, the concentration of TBC was adjusted to 1.1×10^{-4} mol·L⁻¹ (18.26 mg·L⁻¹). After shaking the slurry for 12 h, the TBC concentration in the supernatant was calculated by the measured absorbance. Based on the concentration difference of TBC in solutions before and after adsorption, the adsorption capacity of TBC on hematite surfaces was obtained.

2.6. FTIR Tests

The FTIR spectra of TBC, hematite, and TBC-treated hematite were measured on a Nicolet FTIR-740 spectrometer (Thermo Nicolet Corporation, Madison, WI, USA) [49]. The suspension, which contained 0.5 g of minerals ($-5 \mu\text{m}$) and 50 mL of 1.0×10^{-4} mol·L⁻¹ TBC solutions (pH ~9.0), was stirred at 25 °C for 6 h. The TBC-treated hematite was then obtained by filtrating the suspension and washing the filter cake three times with water. After drying in a vacuum oven, the FTIR spectra were measured through the KBr disk approach.

2.7. XPS Tests

Thermo Fisher Scientific's ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) was used for the XPS experiments. The X-ray source was an Al K α ray with 1486.7 eV photoelectron energy. The vacuum degree of the test chamber was 10^{-9} – 10^{-8} Torr, and the pass energy was set as 20.0 eV. After being corrected with 284.8 eV C 1s binding energy, the XPS curves were fitted and analyzed using Thermo Advantage 5.9 software [50].

3. Results and Discussion

3.1. Micro-Flotation

3.1.1. Single Mineral

Figure 3 shows the effect of pH and the initial TBC concentration on the flotation recovery of hematite and quartz. Figure 3A indicates that the recovery of hematite increased with rising pH and reached 88.47% at pH ~9.0. Then, hematite recovery decreased with the increase in pH. Compared with hematite, the flotation recovery of quartz was below 25% at pH 6.0–11.0. Thus, the flotation separation of hematite from quartz by TBC might be favorable at pH ~9.0. Figure 3B shows that as the initial concentration of TBC increased from 3×10^{-6} to 15×10^{-6} mol·L⁻¹, the recovery of hematite increased significantly from 6.09% to 93.78%, while the recovery of quartz only slightly increased from 11.34% to 29.74%.

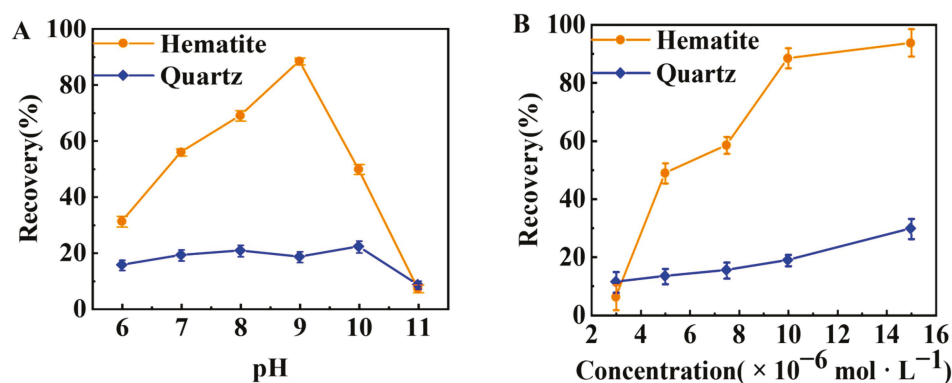


Figure 3. Effect of (A) pH ($1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ TBC) and (B) the initial TBC concentration (pH ~9.0) on the flotation recovery of hematite and quartz.

3.1.2. Artificially Mixed Minerals

The flotation performances of TBC were further investigated by artificially mixed minerals. Figure 4 shows the flotation recovery of hematite and quartz from their artificially mixed minerals as a function of pH and the initial TBC concentration. Figure 4A indicates that with rising pH, the flotation recovery of hematite increased and reached 96.31% at pH 9.0, and then decreased. Meanwhile, the recovery of quartz remained below 22% at pH 6.0–11.0. Figure 4B shows that as the initial TBC concentration increased from 5×10^{-6} to $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, the recovery of hematite increased from 61.52% to 98.31%, while the recovery of quartz only increased from 10.23% to 17.61%. Therefore, TBC was an efficient collector for the flotation separation of hematite from quartz.

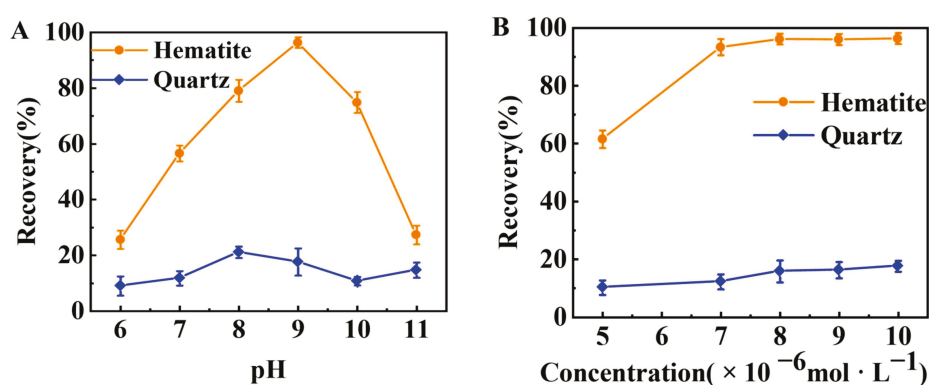


Figure 4. Flotation recovery of hematite and quartz in the artificially mixed minerals as a function of (A) pH ($1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ TBC) and (B) the initial TBC concentration (pH ~9.0).

3.1.3. The Effect of Pulp Temperature

The effect of temperature on the flotation recovery of hematite and quartz from their mixture by TBC was further investigated. Figure 5 shows that as the temperature increased from 5 to 30 °C, the recovery of hematite rose from 42.54% to 96.92%, while the recovery of quartz only increased from 9.78% to 24.74%. At 20 °C, the recoveries of hematite and quartz were 84.31% and 16.22%, respectively. This meant that the favorable temperature for TBC flotation separation of hematite and quartz was above 20 °C. The flotation temperature of sodium oleate is generally higher than 35 °C [14], so TBC has stronger temperature applicability than sodium oleate.

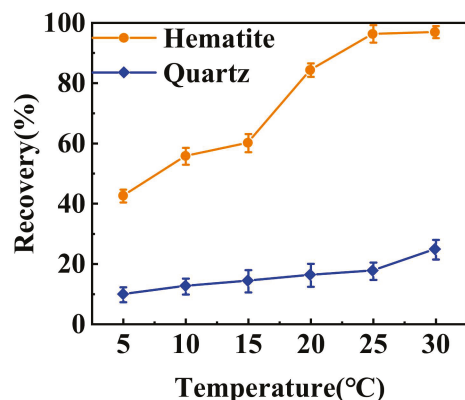


Figure 5. Flotation recovery of hematite and quartz in the artificially mixed minerals function of pulp temperature (pH ~9.0 and 1×10^{-5} mol·L⁻¹ TBC).

3.2. Contact Angle

Figure 6 shows the effect of pH on the contact angle of TBC-treated hematite and TBC-treated quartz. The contact angles of fresh hematite and quartz were 18° and 13°, respectively. As represented in Figure 6A, after being treated with 1×10^{-5} mol·L⁻¹ TBC, the contact angle of hematite increased from 32° to 48° as the pH increased from 6.0 to 9.0, and then decreased rapidly when the pH increased to 11.0. These results were consistent with the effect of pH on the flotation recovery of hematite. Figure 6B shows that after TBC treatment, the contact angle of the hematite surface was significantly greater than that of the quartz surface at pH 7.0–10.0. Therefore, the contact angle results deduced that the hydrophobic effect of TBC on the hematite surface was stronger than that on the quartz surface.

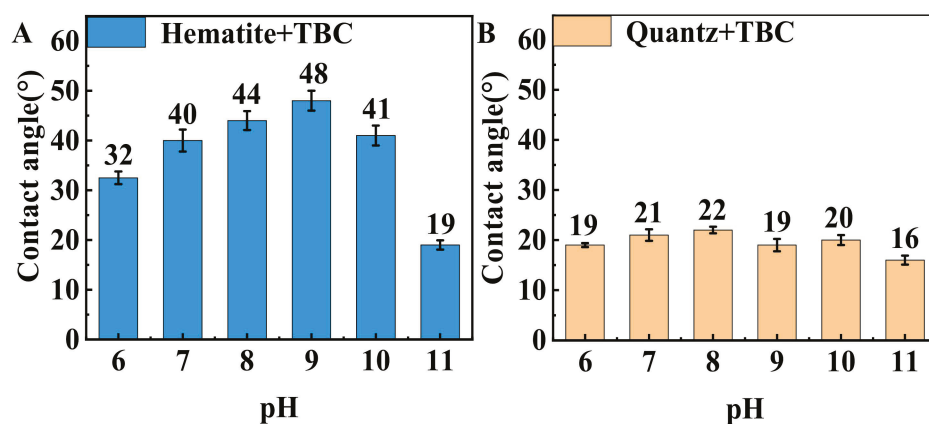


Figure 6. The contact angle of the (A) TBC-treated hematite and (B) TBC-treated quartz as a function of pH (1.0×10^{-5} mol·L⁻¹ TBC).

3.3. Zeta Potential

Figure 7 shows the effect of pH on the zeta potential of quartz and hematite with or without TBC. As shown in Figure 7A, the isoelectric point (IEP) of hematite was observed near pH ~5.0, which was consistent with the reported value [51]. In the presence of TBC, the zeta potential of hematite particles decreased, especially under pH > 6.0, inferring an adsorption of TBC on the surface of hematite.

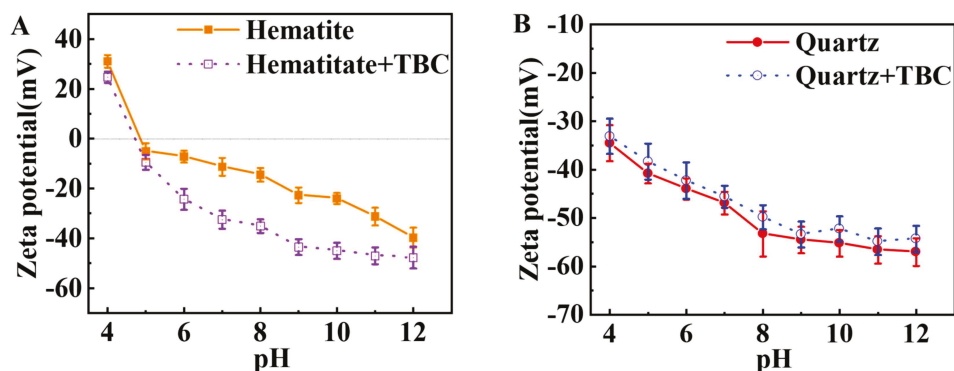


Figure 7. Effect of pH on the zeta potential of (A) quartz and (B) hematite before and after $1 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ TBC treatment.

As shown in Figure 7B, the zeta potential of quartz was negative at pH 4.0–12.0. In the presence of TBC, the zeta potential of quartz particles slightly shifted positively, implying a weak adsorption of TBC on the quartz surface. The zeta potential results deduced the superior adsorption affinity of TBC to hematite rather than quartz under pH > 6.0.

3.4. The Adsorption Capacity of TBC

The adsorption capacity of TBC on the surface of hematite under different pH values is shown in Figure 8, which indicates that as the pH increased from 6.0 to 9.0, the adsorption capacity of TBC on hematite increased from $6.33 \text{ mg}\cdot\text{g}^{-1}$ to $15.24 \text{ mg}\cdot\text{g}^{-1}$; subsequently, with pH increasing to 10.0 and 11.0, the adsorption capacity of TBC decreased to 12.42 and $1.93 \text{ mg}\cdot\text{g}^{-1}$, respectively. The results revealed that the preferable pH value for TBC adsorption onto the hematite surface appeared at 8.0–10.0, being in agreement with the flotation and contact angle findings.

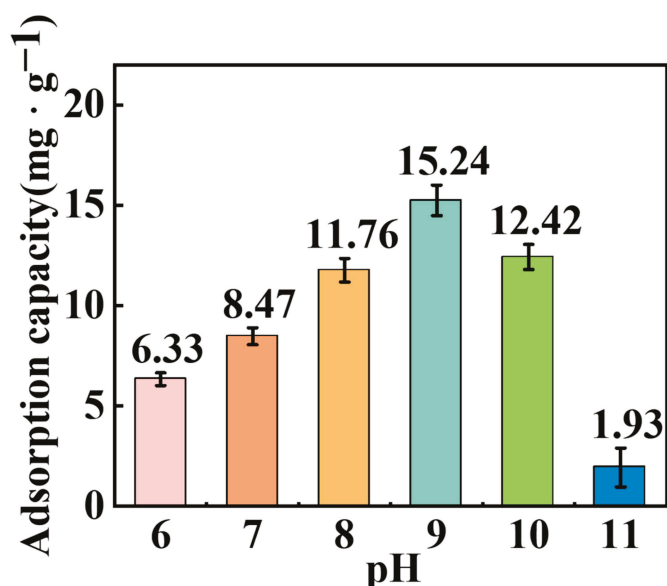


Figure 8. Effect of pH on the adsorption of TBC on the surface of hematite ($1.1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ TBC initial concentration).

3.5. FTIR Analyses

The FTIR spectra of TBC, hematite, and TBC-treated hematite are listed in Figure 9. For TBC, the peaks at 3060 and 2961 cm^{-1} corresponded to the C-H stretching vibrations of the benzene ring and methyl groups [52], respectively. The C=C vibrations of the benzene ring appeared at 1600 and 1521 cm^{-1} , the hydroxyl (-OH) peaks emerged at 3344 , 1367 , and 1119 cm^{-1} [53], and the C-C vibrations of the tert-butyl group appeared at 1276 cm^{-1} .

After the interaction of TBC with hematite, the new peaks at 1478 and 2961 cm^{-1} appeared on the surface of hematite, which were assigned to the C=C vibrations of the benzene ring and the C-H vibrations of the methyl group, respectively. The FTIR spectroscopy results suggested the adsorption of TBC on the hematite surface.

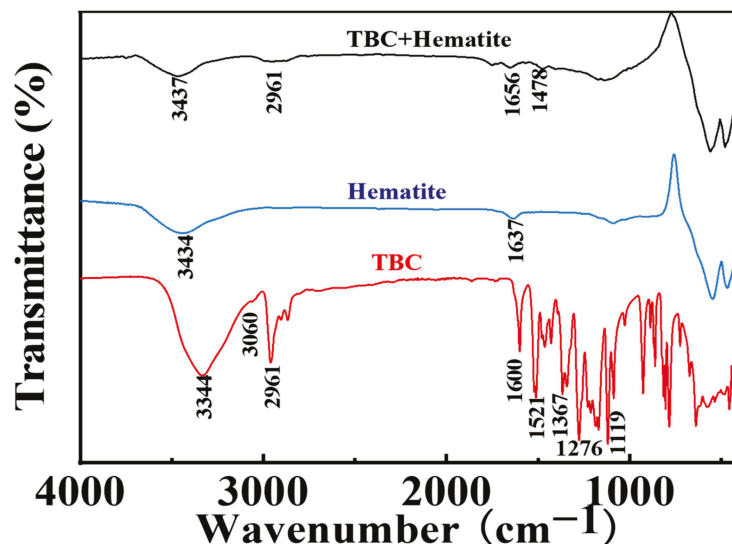


Figure 9. FTIR spectra of TBC and hematite before and after the reaction with TBC.

3.6. XPS Results

The adsorption mechanism of TBC on hematite at pH ~9 was further explored by XPS. Figure 10A,B show the survey XPS spectra and interface element contents of hematite before and after TBC treatment, which demonstrated that after TBC adsorption, the atomic proportion of C in the interface of hematite increased significantly, while that of O and Fe decreased, inferring the cover of TBC on the hematite surface.

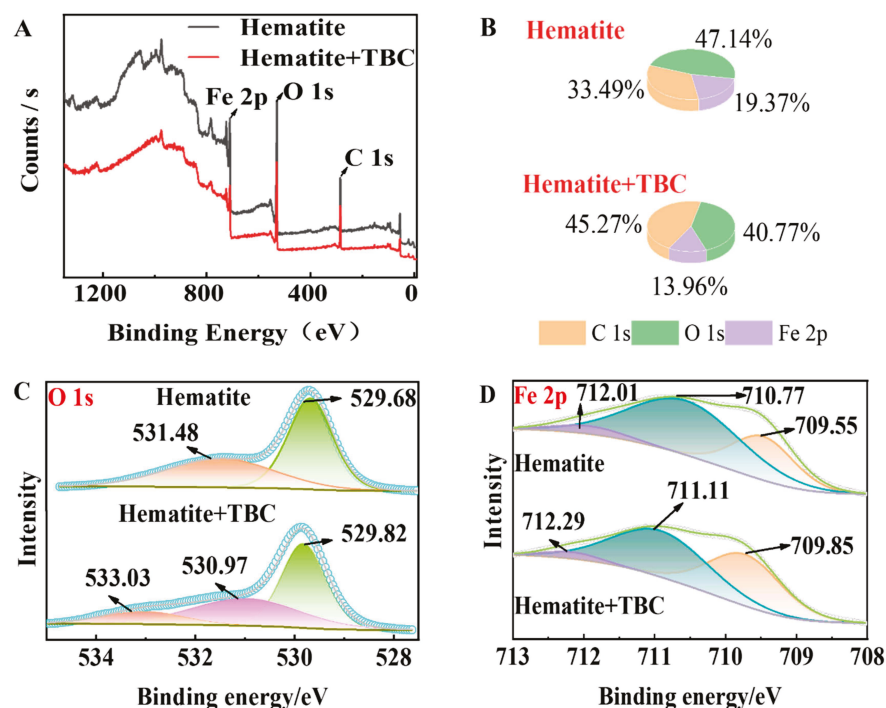


Figure 10. XPS spectrum (A) and atomic concentration (B) of hematite before and after TBC treatment, and XPS high-resolution (C) O1s and (D) Fe 2p_{3/2} spectra of hematite before and after TBC treatment.

The Fe 2p_{3/2} and O1s high-resolution XPS spectra of hematite before and after TBC treatment are shown in Figure 10C,D. Figure 10C indicates that the O1s XPS of the pure hematite were composed of two peaks at 529.68 and 531.48 eV, which were attributed to the lattice and interface O atoms of hematite, respectively [54,55]. After TBC treatment, a new peak at 533.03 eV appeared on the hematite surface, which might be due to the O atoms of TBC chemisorbed on hematite. The XPS peaks of the lattice and interface O atoms for the TBC-modified hematite appeared at 529.82 and 530.97 eV, respectively. The lowered binding energy of interface O atoms implied that some OH species might be removed from the hematite surface.

Figure 10D demonstrates that the Fe 2p_{3/2} XPS spectra of pure hematite were divided into three peaks at ~712.01, 710.77, and 709.55 eV, which were assigned to Fe(III), Fe(III), and Fe(II) adsorption bands, respectively [56–58]. After TBC treatment, the three Fe 2p_{3/2} XPS peaks all shifted to the higher binding energies of ~712.29, 711.11, and 709.85 eV [59], and the proportion of adsorption bands at 709.85 eV increased significantly. These results implied that TBC chemisorbed on the hematite surface, accompanied by the reduction of some Fe(III) into Fe(II).

As a whole, the fine XPS of Fe 2p_{3/2} and O1s suggested that the TBC–Fe complexes were formed on the hematite surface where the O atoms of TBC bonded with the surface Fe atom(s) of hematite.

3.7. Discussion

The binding model of the catechol group of Dopa to the metal material surface involved at least three different forms: molecular adsorption (through H-bond), partially dissociated monodentate adsorption, and fully dissociated bidentate adsorption [60]. Dopa could strongly interact with Fe(III) or Fe(II) via its catechol group to form the stable complexes [61].

The zeta potential results deduced a special affinity of hematite toward TBC, and the adsorption capacity experiments revealed that the preferable pH for hematite adsorption of TBC appeared at 8.0–10.0, being in agreement with the flotation and contact angle findings. In addition, the FTIR spectra suggested the adsorption of TBC on the hematite surface, while the XPS suggested that the TBC–Fe complexes were formed on the hematite surface where TBC's two O atoms bonded with the surface Fe atom(s) of hematite.

The pK_{a1} and pK_{a2} of TBC were 9.5 and 14.0 [62], respectively. Under pH < 8.0, TBC existed in water solutions mainly as its molecular species, at pH 8.0–10.0, TBC existed as its deprotonated form TBC[−], and under pH > 14.5, the completely deprotonated species TBC^{2−} dominated in solutions. The molecular species of TBC might interact with hematite through weak interactions, such as the H-bond, which renders TBC with a weak collecting ability to hematite. The deprotonated form TBC[−] possessed a strong electron-donating ability, which could bond iron atoms on the hematite surface. As a result, TBC[−] improved the hydrophobicity and floatability of hematite under pH 8.0–10.0. Although the completely deprotonated species TBC^{2−} had a stronger electron-donating ability, under pH > 10.0, TBC was easy to auto-oxidize to quinone configuration, which dramatically weakened its affinity to iron atoms. Therefore, TBC did not return good results of flotation, contact angle, adsorption capacity, and zeta potential under pH > 10.0.

Based on the above experimental results and analyses, a possible adsorption model of TBC on the hematite surface at pH ~9.0 was suggested and shown in Figure 11. It demonstrated that TBC's two O atoms bonded with the surface Fe atom(s) of hematite to form the five-membered chelating ring, while the H atom of TBC's hydroxyl formed an H-bond with the O atom of the hematite surface.

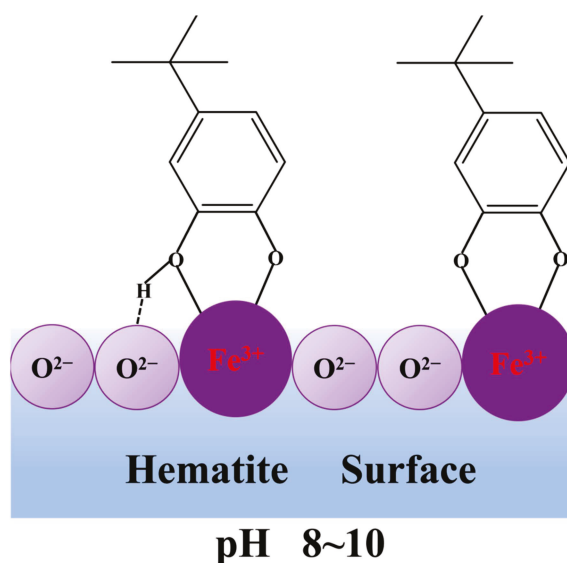


Figure 11. Possible adsorption model of TBC on the hematite surface.

4. Conclusions

Using TBC as a collector, the flotation separation of hematite from quartz was carried out. Based on the experimental findings and discussion, the main conclusions were drawn, as follows:

- (1) At pH 9.0, $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ TBC recovered over 96% hematite and only 17% quartz from the artificial mixture. TBC exhibited an excellent flotation selectivity for separation of hematite from quartz.
- (2) TBC significantly enhanced the hydrophobicity of the hematite surface, while it had little effect on that of quartz, which increased their surface hydrophobicity difference, being a key factor to realize their selective flotation separation.
- (3) At pH 9.0, TBC adsorbed on the Fe-active site on the hematite interface mainly via its deprotonated species TBC^- to form a stable five-membered chelating ring.

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Article

Pyrite–Coal Depressants Interactions During Coal Reverse Flotation

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Abstract: This work investigates coal desulfurization by using reverse flotation. In this method, pyrite (the only source of sulfur in the studied coal) was separated from the meta-bituminous coal by using three different coal depressants (starch, dextrin and humic acid). A novel variable elimination approach was used to determine the contribution of the depressant type and the depressant concentration on the desulfurization performance. The results showed that the pyrite recoveries are influenced by the depressant type while the highest pyrite recovery was achieved in the presence of humic acid. Therefore, humic acid should be used in flotation rougher and scavenger cells in which the aim is to achieve high pyrite recovery. By contrast, the pyrite grades are affected significantly by the depressant concentration. Considering that the aim in flotation cleaner cells is to achieve high pyrite grade, any of the studied coal depressants can be successfully used but at high concentrations. This work demonstrated that the selection of flotation depressants depends on the type of flotation cells used in coal desulfurization.

Keywords: reverse flotation; meta-bituminous coal; desulfurization; depressants; variable elimination approach

1. Introduction

Sulfur is a detrimental impurity when present in coal and is a typical problem in coal deposits in many parts of the world [1,2]. It can be present in coals in inorganic, organic or sulphatic forms [3]. Sulfide minerals such as pyrite contribute significantly to the inorganic Sulfur in many coals. The removal of pyritic minerals from coal leads to increased economic benefits. In addition, the reduction in sulfur content in combustible coal reduces SO₂ emission into the environment, and the subsequent acid rain [4]. Sulfuric acid is produced when pyrite present in tailings is oxidized in the presence of oxygen and water, leading to acid mine drainage which is considered as the main cause for the release of toxic elements from tailings into the environment [5]. Therefore, the desulfurization of coal prior to its combustion has significant economic and environmental implications, as well as the sustainability of coal mining operations.

Reverse flotation is commonly used to reduce either the Sulfur or ash content of coals and other minerals [6,7]. In this process, the gangue minerals containing Sulfur or ash

are floated while the flotation of coal is depressed. The gangue minerals that lead to ash in coal have significantly different flotation properties to those of pyritic minerals (i.e., sulfur-containing minerals). Thus, reverse flotation for ash reduction and Sulfur removal could not be performed in a single process. A number of studies have been conducted to investigate the performance of reverse flotation to lower the ash content of coal [8–11]. However, studies conducted on pyritic minerals flotation for Sulfur reduction in coals are very few [12,13].

Since coal is naturally floatable, depressants play a critical role in rendering the coal hydrophilic and thus enhancing the selectivity of the coal's reverse flotation process. The most commonly used coal depressants are either organic colloids such as dextrin, starch, quaternary amines, tannic acid or humic acid [10,12,14]. Dextrin is derived from starch through heat degradation and thus is a smaller but highly branched molecule as compared with starch molecules which are larger and consist of a water-soluble linear (amylose) and water-insoluble branched (amylopectin) components [15,16]. Coal flotation depression by starch and dextrin occurs through hydrophobic bonding between the non-polar groups of starch/dextrin and the coal surface. Humic acids are macromolecular, negatively charged polyelectrolytes that are composed of carboxylic and phenolic functional groups, which adsorb on coal surfaces and reduce the number of active sites on minerals that can be adsorbed by collectors [17].

Although these depressants were proven to be effective in depressing coal flotation, it is important to note that the gangue floated in these studies were silicates and carbonates (e.g., calcite, dolomite, and silica) with the aim of reducing ash content in coal [18]. Thus, it is important to investigate whether these coal depressants affect the flotation of gangue pyritic minerals from coal. For example, some depressants such as dextrin can also depress pyrite at high concentrations [19,20]. Dextrin was found to be an effective depressant of pyrite above pH 4 even in the presence of an xanthate collector [19]. However, the influence of different depressants that cannot cause harm to the environment (i.e., green chemical compounds) such as dextrin, starch and humic acid on the flotation performance of pyrite from meta-bituminous coal has not been studied. More importantly, the impact of the type of depressant and their concentration have also not been systematically evaluated. It should be noted that considering that dextrin is a derivative of starch, it is possible that starch may possess some pyrite depression behavior.

In the present study, the efficiency of reverse flotation in the separation of pyrite from meta-bituminous coal in the absence and presence of three different depressants (starch, dextrin and humic acid (HA)) was investigated. The flotation kinetics of pyrite from meta-bituminous coal with different depressants at various concentrations were compared. The flotation performance in a microflotation cell was characterized by pyrite recovery and the pyrite grade of the concentrates. The variable elimination approach method, recently developed by Albijanic et al. [21], was used to quantify the influence and systematically analyze both the depressant type and its concentration on the desulfurization of the meta-bituminous coal to suggest the best depressant for different stages of a flotation circuit (i.e., rougher, scavenger and cleaner stage).

2. Materials and Methods

2.1. Materials

The pyrite samples utilized in this study were sourced from Navajun, La Rioja, Spain with a purity >95%. The total Sulfur content in the samples was analyzed by XRD and was 52.4% [22]. The meta-bituminous coal samples were collected from the Shanxi province in China [22]. Pyrite was first dry ground with a ceramic mortar and pestle and then screened

to obtain a $-212 + 150 \mu\text{m}$ size fraction. The coal sample was crushed and screened to obtain a $-0.5 + 0.25 \text{ mm}$ size fraction. The pyrite sample was ground to a lower size distribution than that of the coal sample since pyrite particles are embedded in the raw coal and the size distribution of pyrite is much lower than the coal particles [23]. The moisture content (M_{ad}), the volatile content (V_{ad}), the fixed carbon content (FC_{ad}), the ash content (A_{ad}) and the total Sulfur content (S_{t}) in the coal are shown in Table 1. A detailed mineralogy of the coal used in this study has been published elsewhere [24]. The main minerals in the meta-bituminous coal sample were kaolinite (39.3%), quartz (29.1%), montmorillonite (6.4%) and calcite (4.6%). The total Sulfur content was negligible in the coal samples.

Table 1. Analysis of air-dried meta-bituminous coal [24].

M_{ad} (%)	A_{ad} (%)	V_{ad} (%)	FC_{ad} (%)	S_{t} (%)
1.5	26.9	18.3	53.3	0.39

Potassium amyl xanthate PAX 99% (Chem-Supply, Gillman, Australia) and copper sulfate 99% (Chem-Supply, Australia) were used as pyrite collectors and activators, respectively. Methyl isobutyl carbinol MIBC 99% (Orica, Melbourne, Australia) was used as a frother. Soluble potato starch 99% (Sigma-Aldrich, St. Louis, MI, USA), potato dextrin 99% (Chem-Supply, Australia) and humic acid 99% (Sigma-Aldrich, USA) were used as depressants. Starch and dextrin solutions were made by preparing a paste of 1 g of starch or dextrin with cold water and then adding the paste to 100 mL of boiling water. Double distilled water $18.2 \text{ M}\Omega\cdot\text{cm}$ was used.

2.2. Microflotation Tests

The separation of pyrite from meta-bituminous coal was analyzed through micro-flotation tests. In each flotation test, 1 g of pure pyrite particles were fully mixed with 1 g of coal particles. The 50% pyrite–coal mixture was used to enhance the analysis sensitivity to detect changes in the pyrite removal and to help understand the mechanisms of pyrite depressant interactions. Pyrite and coal were mixed in the flotation cell at a 1% solid concentration, i.e., 1 g of pyrite–coal mixture and 99 g of water. Before the micro-flotation tests, samples were deslimed in an ultrasonic cleaner (Derui, China) to reduce the effect of fine particle entrainments at 40 kHz for 1 min. The deslimed samples were conditioned for 5 min using a magnetic stirring plate with potassium amyl xanthate collector ($1 \times 10^{-4} \text{ mol/L}$), starch, dextrin or humic acid depressant (1 kg/t, 2 kg/t, 3 kg/t or 4 kg/t), CuSO_4 activator (20 g/t) and MIBC frother (2 kg/t). The conditioned pulp was adjusted to pH 6 and was then transferred into a 300 mL flotation column (FLSmidth, Australia), which was used to conduct the micro-flotation experiments [22]. The air flow rate was 0.5 L/min and the revolutions used were 700 rpm. The flotation performance was characterized by the recovery and grade of the pyrite determined by Sulfur analysis using a LECO SC632 Sulfur analyzer. Each experiment was conducted in triplicate and the experimental error was found to be less than 5%. The flotation experiments were conducted until no froth was produced (ca. 4 min). The flotation concentrates were collected after 1, 2 and 4 min.

2.3. Data Analysis—A Variable Elimination Method

The effect of the depressant type and its concentration was analyzed through a variable elimination approach [22]. A regression model was proposed, as in Equation (1)

$$y = f(x, \beta) \quad (1)$$

where $\beta = [\beta_1, \beta_2, \dots, \beta_m]$ and $x = [x_1, x_2, \dots, x_n]$ are the vectors showing regression coefficients and input variables, respectively; while y is a response variable. The following two hypotheses are tested to determine the significance of β_i .

(1) $H_0(\beta_i = 0)$ β_i is not significant,

(2) $H_1(\beta_i \neq 0)$ β_i is significant.

An elimination of β_i from the model shows the significance of β_i on the calculated y . In other words, there are two cases:

Case I: All coefficients are included in the model (see Equation (1)).

Case II: One coefficient is excluded from the model, i.e., one of the coefficients is zero ($\beta_i = 0$), while other coefficients are unchanged (see Equation (1)).

Therefore, the coefficient β_i is significant if the elimination of this coefficient (i.e., $\beta_i = 0$) from the model has a significant influence on the calculated y and thus the hypothesis H_1 is valid. As a result, there is a significant difference between the quality of curve fitting of Case I and Case II.

The quality of curve fitting is determined by calculating and average relative error (δ), which is for Case I:

$$\delta = \frac{1}{n} \sum_{j=1}^n \left| \frac{y_e^j - y_c^j}{y_e^j} \right| \quad (2)$$

where n represents the number of experimental data; y_e^j and y_c^j are the j^{th} experimental and calculated values, respectively. The calculated average relative error $\delta(\beta_i = 0)$ for Case II is:

$$\delta(\beta_i = 0) = \frac{1}{n} \sum_{j=1}^n \left| \frac{y_e^j - (y_c^j)_{\beta_i}}{y_e^j} \right| \quad (3)$$

where $(y_c^j)_{\beta_i}$ is the j^{th} calculated values for y , when the regression coefficient β_i is excluded from the model and other regression coefficients are unchanged. A higher average relative error indicates a significant influence from the input variable x_i associated with that regression coefficient β_i .

3. Results and Discussion

3.1. Desulfurization Process

The desulfurization process of the meta-bituminous coal was studied by determining the removal of pyrite through flotation in the presence of three depressants (starch, dextrin and humic acid (HA)); the only source of Sulfur in the meta-bituminous coal is pyrite. Figure 1 shows the pyrite grade after flotation with starch, dextrin and humic acid. It was shown that the pyrite grade increased with the increase in concentration for all depressants, which suggests that each of them was effective in depressing the floatability of coal particles. This may be due to all depressants adsorbing into pyrite through $-\text{COOH}$ and $-\text{OH}$ interactions with the ferric hydroxide groups of pyrite [25]. Humic acid showed the lowest pyrite grade at concentrations below 3 kg/t, while starch and dextrin showed an almost constant high pyrite grade (>90%) regardless of concentration. This could probably be due to humic acid being more hydrophobic when compared to starch and dextrin, and therefore decreasing humic acid–pyrite adsorption at low concentrations [26].

The classical first-order kinetic model [27] was used to study pyrite recovery ε , see Equation (4).

$$\varepsilon = \varepsilon_{\infty}[1 - \exp(-kt)] \quad (4)$$

where ε_{∞} is the ultimate recovery in %, t is the flotation time in *min*, and k is the flotation rate constant in 1/*min*. The fitting of Equation (4) was carried out by using the least square method and the Solver function in Microsoft Excel. Table 2 shows the results for the ultimate recoveries, the flotation rate constants and the regression coefficient for different concentrations of the three depressants. As seen in Table 2, the classical first-order kinetic model successfully predicted the flotation performance of separation of pyrite from meta-bituminous coal with various types of depressants (R^2 was at least 0.99). The ultimate recoveries and the flotation rate constants decreased with the increase in the depressant concentration. However, the use of humic acid resulted in the highest ultimate recovery independent of concentration (>95%). This might be due to the higher hydrophobic properties of humic acid benzene rings than those of the polysaccharides of starch and dextrin. At higher concentrations starch and dextrin may increase the hydrophilicity of pyrite particles while humic acid keeps the hydrophobicity of pyrite particles.

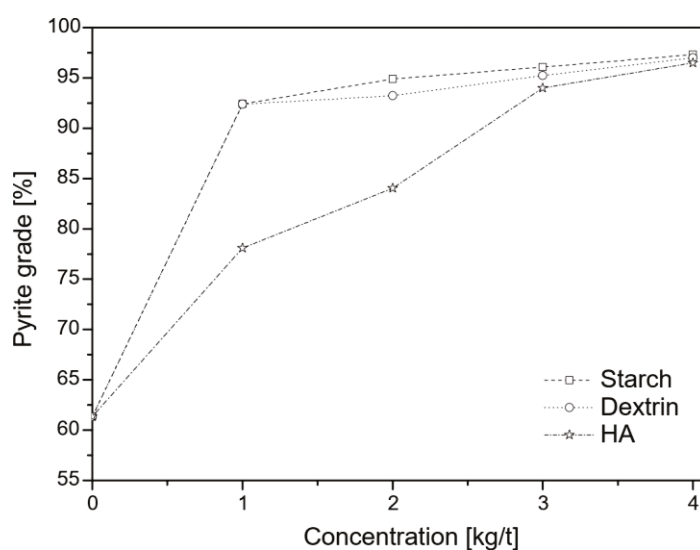


Figure 1. Pyrite grade after meta-bituminous coal reverse flotation at different concentrations of starch, dextrin and humic acid HA.

Table 2. Pyrite flotation performance results in the presence of different depressants at 10^{-4} mol/L PAX solution.

Depressant Types	Concentration (kg/t)	ε_{∞}	k (1/min)	R^2	Coal Recovery
Starch	0	99.38	8.38	1.00	78.69
	1	96.09	5.50	0.99	13.45
	2	95.11	5.44	0.99	7.13
	3	94.96	5.24	0.99	3.29
	4	67.81	4.80	0.99	3.18
Dextrin	0	99.38	8.38	1.00	78.69
	1	97.58	6.14	0.99	4.26
	2	96.25	5.85	0.99	3.32
	3	95.86	5.78	0.99	2.12
	4	76.15	4.12	0.99	1.34
HA	0	99.38	8.38	1.00	78.69
	1	99.27	7.12	0.99	24.24
	2	98.62	7.03	0.99	19.79
	3	97.48	6.98	0.99	5.01
	4	96.18	6.86	0.99	1.26

3.2. Variable Elimination Approach

To better understand the desulfurization process, the variable elimination approach was used. In this method, the correlation was proposed for predicting the flotation recoveries, the pyrite grades and the flotation rate constants:

$$Y = \beta_1(1 + T)^{\beta_2}(1 + C_{DEP})^{\beta_3} \quad (5)$$

where β_1 , β_2 and β_3 are the regression coefficients in the proposed correlation, Y is the corresponding predicted variable (the flotation recovery, the flotation rate and the pyrite grade), and T is the type of the depressant, i.e., for starch ($T = 1$), for dextrin ($T = 2$) and for HA ($T = 3$); C_{DEP} (kg/t) is the depressant concentration. The regression coefficients (β_1 , β_2 , and β_3) were obtained by using the LAB fit software V 7.2.50c [28] in which the Levenberg–Marquardt algorithm was used. Table 3 shows the calculated regression coefficients, their standard errors and t-values for each coefficient. The experimental and predicted variables using Equation (5) are shown in Figure 2.

Table 3. Regression coefficients and model validation.

Predicted Variables Y	β_1 (t Value)	β_2 (t Value)	β_3 (t Value)	δ (%)
ε_{∞}	90.90 ± 8.14 (11.17)	0.11 ± 0.07 (1.44) *	-0.09 ± 0.04 (−2.38)	6.21
k	6.00 ± 0.72 (8.34)	0.28 ± 0.10 (2.81)	-0.26 ± 0.05 (−5.61)	7.97
Pyrite grade	73.66 ± 5.99 (12.30)	-0.08 ± 0.07 (−1.30) *	0.25 ± 0.04 (6.86)	5.40

* Insignificant coefficients (95% confidence).

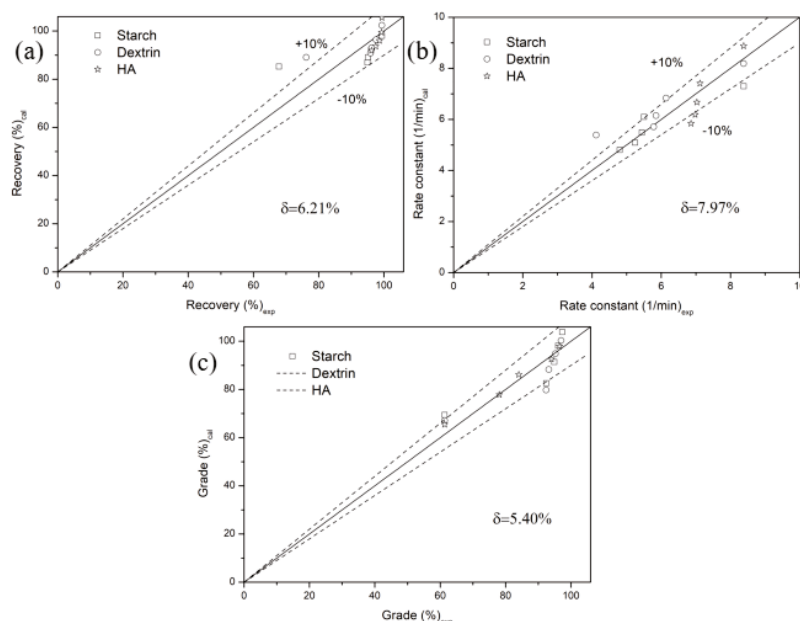


Figure 2. Calculated and experimental values of (a) the ultimate recoveries, (b) the rate constants and (c) the pyrite grades.

A variable elimination approach, described in Section 2.3, was used to quantify the contribution of the depressant type and its concentration on the desulfurization process (the flotation recovery, the flotation rate constant, and the pyrite grade). As seen in Equation

(4), the influence of the depressant type on the desulfurization process determines β_2 while the influence of the depressant concentration on the desulfurization process reveals β_3 . The coefficient β_1 does not represent the effect of either the depressant type or the depressant concentration and thus β_1 is not used in this analysis i.e., β_1 is kept constant. More precisely, for example in the case of the pyrite grades, two cases were considered:

(1) $\beta_1 = 73.66$, $\beta_2 = 0$ and $\beta_3 = 0.25$, i.e., the elimination of β_2 from the model (see Table 3 and Equation (4)) determines whether this coefficient affects significantly the pyrite grade prediction.

(2) $\beta_1 = 73.66$, $\beta_2 = -0.08$ and $\beta_3 = 0$, i.e., the elimination of β_3 from the model (see Table 3 and Equation (4)) determines whether this coefficient affects significantly the pyrite grade prediction.

Figure 3 shows the parity plot diagrams and calculated $\delta(\beta_i = 0)$ for the ultimate recovery, the flotation rate constant and the pyrite grade. Considering that $\delta(\beta_i = 0)$ is always zero, it is not shown in Figure 3. As seen in Figure 3, in the case of the pyrite grade and the flotation rate constant, $\delta(\beta_3 = 0)$ is higher than $\delta(\beta_2 = 0)$ which indicates that the depressant concentration is a more significant variable than the type of depressant. The opposite is true in the case of the ultimate recovery since $\delta(\beta_3 = 0)$ is lower than $\delta(\beta_2 = 0)$. The effect of the type of depressant on pyrite recovery may be due to the differences in the hydrophobicity of depressant, while starch and dextrin contain many hydrophilic functional groups, humic acid contains benzene rings increasing its hydrophobicity. In the case of the effect of depressant concentrations on pyrite grade, it may be due to an optimum concentration, while insufficient depressant might not fully inhibit coal, leading to a lower grade, while excessive depressant can also affect the flotation process, reducing overall efficiency.

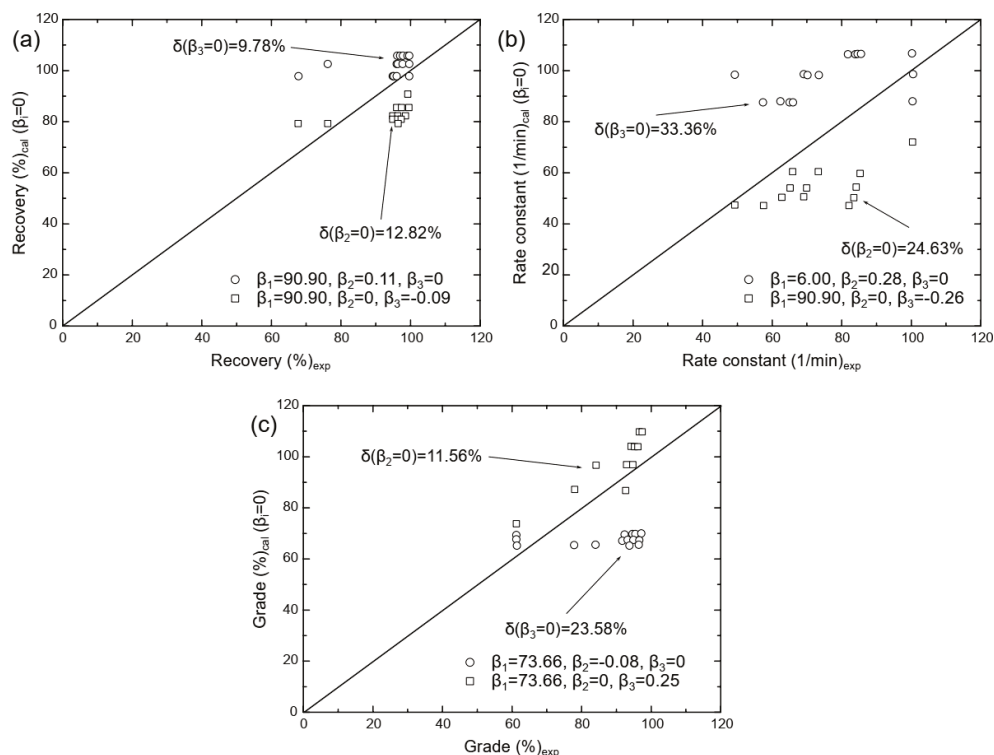


Figure 3. Comparison between experimental and calculated values for (a) ultimate recovery, (b) rate constant and (c) grade (β_2 or β_3 is eliminated from the model (i.e., $\beta_i = 0$), while the values of other regression coefficients are kept constant).

Therefore, it is recommended to use humic acid rather than starch and dextrin in rougher and scavenger coal flotation circuits, as recovery is highly affected by the depressant type, and the aim in these circuits is to achieve the highest possible recovery. As regards the pyrite grade, the depressant concentration influences more pyrite grade rather than the depressant type ($\delta(\beta_3 = 0) > \delta(\beta_2 = 0)$). It means that considering that the aim in coal flotation cleaner cells is to achieve high pyrite grade and not high pyrite recovery, any of the studied coal depressants can be successfully used but at high concentrations.

4. Conclusions

In this paper, a variable elimination approach was used to quantify the contribution of the depressant type (humic acid, starch and dextrin) and the depressant concentration on the desulfurization of meta-bituminous coal. It was found that the pyrite recoveries are significantly more influenced by the depressant type rather than the depressant concentration and thus it is recommended to select humic acid to achieve the highest pyrite recovery. In contrast, the pyrite grades are affected significantly by the depressant concentration and thus any of the studied coal depressants can be successfully used but at high concentrations. The corresponding pyrite recovery and grade using humic acid as a depressant are both over 96% at higher concentrations (4 kg/t). When the depressant concentration is more important than the depressant type, the least expensive depressant should be selected. This paper demonstrated that the variable elimination approach is a reliable method when selecting the reagents for the desulfurization of the meta-bituminous coal, which indicated that the type of depressant is a more significant variable than the depressant concentration and it is recommended to use humic acid rather than starch and dextrin to achieve high mineral recovery. This is very important considering that maximizing flotation plant efficiency and reducing operating costs are essential during the coal desulfurization process. A significant amount of further work concerning the flotation kinetics and corresponding restriction factors is required to investigate the desulfurization process for samples with different mixtures of coal and pyrite.

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Article

Harnessing Mixed Fatty Acid Synergy for Selective Flotation of Apatite from Calcite and Quartz with Sodium Alginate

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Abstract: Maximizing the efficient utilization of critical apatite resources through flotation necessitates the exploration of effective and innovative collectors. This study investigates the potential of a fatty acid mixture (FAM) synthesized from saturated palmitic and stearic acids, monounsaturated oleic and palmitoleic acids, and polyunsaturated linoleic acid. The saponified collector FAM and the depressant sodium alginate (NaAl) achieved a direct flotation of apatite from calcite and quartz (97% apatite, 10% calcite, and 7% quartz). The flotation performance with the tested combination exhibited a highly effective enrichment of apatite, mainly from calcite, which aligns with the surface chemistry assessments. Adsorption tests and zeta potential measurements confirmed the micro-flotation results. They provided compelling evidence of a chemisorption interaction between Ca^{2+} sites on calcite and the carboxyl and hydroxyl groups of NaAl. FTIR analyses suggested a reaction between the apatite surface and the carboxyl groups of saturated and unsaturated acid groups in FAM, even those conditioned with NaAl before, facilitating the complex formation. Remarkably, the synergistic effect of the functional groups demonstrates dual functionality, serving as both a hydrophilic entity for calcite and a hydrophobic entity for apatite flotation. The universal mechanism unveils substantial potential for the extensive application of FAM within apatite flotation.

Keywords: fluorapatite; direct flotation; fatty acids formulation; synergistic effect; adsorption mechanism

1. Introduction

Phosphate ores, which are crucial for producing phosphate fertilizers, are commonly enriched through flotation to maintain food production sustainability [1,2]. As high-grade phosphate reserves continue to decline, there is growing interest in mining and processing low-grade phosphate to meet the rising demand for fertilizers driven by the increasing population [3–6]. The main components of most sedimentary phosphate ores are calcium minerals, namely apatite, carbonates, and silicates. The selective separation of these minerals is challenging due to their similar surface properties [7–9]. Single fatty acids are

the commonly used collectors in calcium mineral flotation. However, their effectiveness and selectivity toward specific minerals depend on numerous factors, such as the length of their hydrocarbon chain, degree of unsaturation, and the polar and nonpolar functional groups they contain [10–16].

Industrial practices and laboratory investigations have shown that a suitable flotation strategy for upgrading a specific phosphate ore may not be so for another. Variations in mineralogical composition and P_2O_5 content insufficiently explain the different flotation responses of phosphate ores from diverse origins. Several research works have outlined the intrinsic characteristics of the minerals that compose the ore and their interactions with the reagents, such as the chemical heterogeneity, surface texture, crystallinity, and degree of dissolution [17].

Substantial effort has been made in recent decades to tackle the complexity of this particular grade using various technologies and methods [18–24]. However, their sensitivity to the operating conditions and their limitations due to industrial constraints render them less efficient and not scalable, leading to the prominence of froth flotation as an effective and economical beneficiation technique for apatite recovery.

In the wake of the absence of universal guidelines for the flotation of low-grade phosphate ores, various strategies can be followed, including direct, reverse, or stepwise flotation, also known as the double float process [25–30]. It is important to note that the choice of flotation strategy depends on the behavior of the phosphate with respect to the reagents used [31,32]. Direct flotation is suitable for phosphate ores with low apatite grade and high gangue mineral content, as it reduces the consumption of collectors. As a result, it has gained significant attention in recent decades.

The mining industry has dedicated significant efforts to developing potent collectors for apatite and depressants for carbonates in direct flotation processes. Several surfactants, such as sodium oleate [33,34], oleic acid [35,36], linoleic acid [37,38], and hydroxamic acid [39,40], have been used in industrial processes. However, limitations persist regarding selectivity, thus hindering their widespread industrial use unless combined with selective depressants. Single fatty acids grapple with affinity issues toward valuable and accessory minerals, imperiling their selectivity. To address these concerns, researchers have focused on creating more robust collectors. One notable approach involves the design of mixed fatty acids, which has proven essential in improving overall flotation performance, addressing selectivity, adsorption compactness, and excessive consumption [41]. Novel surfactants with multifunctional groups demonstrate the industry's commitment to constant improvement and offer promising solutions to existing challenges in phosphate flotation.

The performance of mixed collector systems relies on the properties of the reagents, the interaction between the collector and the particles, as well as the ratio and structure of the reagents [42]. Research on combinations of collectors has shown that their synergistic effects offer benefits such as lower reagent dosage, enhanced grade/recovery, increased coverage of mineral surfaces, improved contact angle, and mitigation of the deleterious effect of Ca^{2+} ions, which cause the collector to precipitate [43–47].

Using mixed collectors in optimal conditions combines the advantages of individual collectors and meets multifaceted requirements [48,49]. For instance, Cao et al. found that a mixture containing 54% oleic acid, 36% linoleic acid, and 10% linolenic acid demonstrated stronger collecting power for apatite than using oleic acid alone. FTIR analyses confirmed improved chemisorption involving the carboxyl groups of each fatty acid and calcium species at the apatite surface [37]. Karlkvist et al. demonstrated the effectiveness of the dicarboxylic collector $C_{12}MalNa_2$ in efficiently floating apatite in the complex apatite/calcite system, despite both minerals having similar types of adsorption sites on their surfaces [50].

Santos et al. discovered that the mixed composition in oil-based Amazonian collectors, mainly composed of oleate and palmitate, affected the critical micelle concentration (CMC), adsorption density, and selective conditions for separating apatite and carbonate minerals [51]. El-Midany and Arafat investigated the reverse apatite flotation using a mixture of oleic acid and sodium dodecyl sulfate at a 1:1 mixing ratio and a pH of 6. A concentrate grade of up to 33% P_2O_5 with a recovery of 85% at a lower collector dosage was achieved [52]. Filippova et al. highlighted the synergistic effect of combining the anionic reagent D2EHPA (di-2-ethylhexylphosphoric acid) with a nonionic reagent, which was particularly effective in shielding the ionic head groups by reducing the electrostatic repulsion and hydrophobic chain interactions [53]. Farid et al. explored a mixture of soybean and sunflower oil as a collector for the reverse flotation of the apatite/calcite system. A product with 29.57% P_2O_5 and a recovery rate of 98.82% at a pH of 4 was obtained [54]. However, very few studies have focused on the direct flotation of apatite using mixed collectors, even though choosing the right collector combination is crucial for improving flotation efficiency and reducing costs.

As part of an ongoing research project focused on developing efficient collectors for phosphate mineral flotation, the present work assesses the synergistic effect of the collector FAM featuring saturated and unsaturated fatty acids in the adsorption and recovery of calcium minerals. Micro-flotation experiments were further consolidated with zeta potential measurements, adsorption tests, and FTIR spectra analyses to scrutinize its performance.

2. Materials and Methods

2.1. Materials

2.1.1. Pure Mineral Specimens

Pure mineral specimens of fluorapatite (98.34%), calcite (99.03%), and quartz (99.28%), based on the mineralogy of the phosphate ore to be beneficiated, were collected from localities in Morocco. XRD characterization (Figure 1) and XRF analysis (Table 1) double-checked the purity of the pebbles. The measurements were conducted using a PANalytical X'PERT³ Powder diffractometer (Malvern PANalytical, Malvern, Worcestershire, UK) and a PANalytical AxiosMAX sequential spectrometer (Malvern PANalytical, Malvern, Worcestershire, UK), respectively. The specimens were hand-sorted, crushed, then ground with an agate mortar to produce two-size fractions. The $[-160 + 125 \mu\text{m}]$ fraction was intended for micro-flotation tests, whereas the sub-40 μm fraction was reserved for zeta potential measurements, adsorption tests, and FTIR analyses.

Table 1. Chemical composition of pure specimens of fluorapatite, calcite, and quartz.

Minerals	Composition, %								
	P_2O_5	CaO	SiO_2	MgO	Fe_2O_3	Al_2O_3	MnO	K_2O	Na_2O
Fluorapatite	41.86	56.70	0.72	0.10	0.01	0.12	0.01	0.04	0.63
Calcite	0.13	99.05	0.41	0.04	0.01	0.25	0.02	0.05	0.05
Quartz	0.01	0.07	99.32	0.02	0.35	0.22	0.02	0.02	0.00

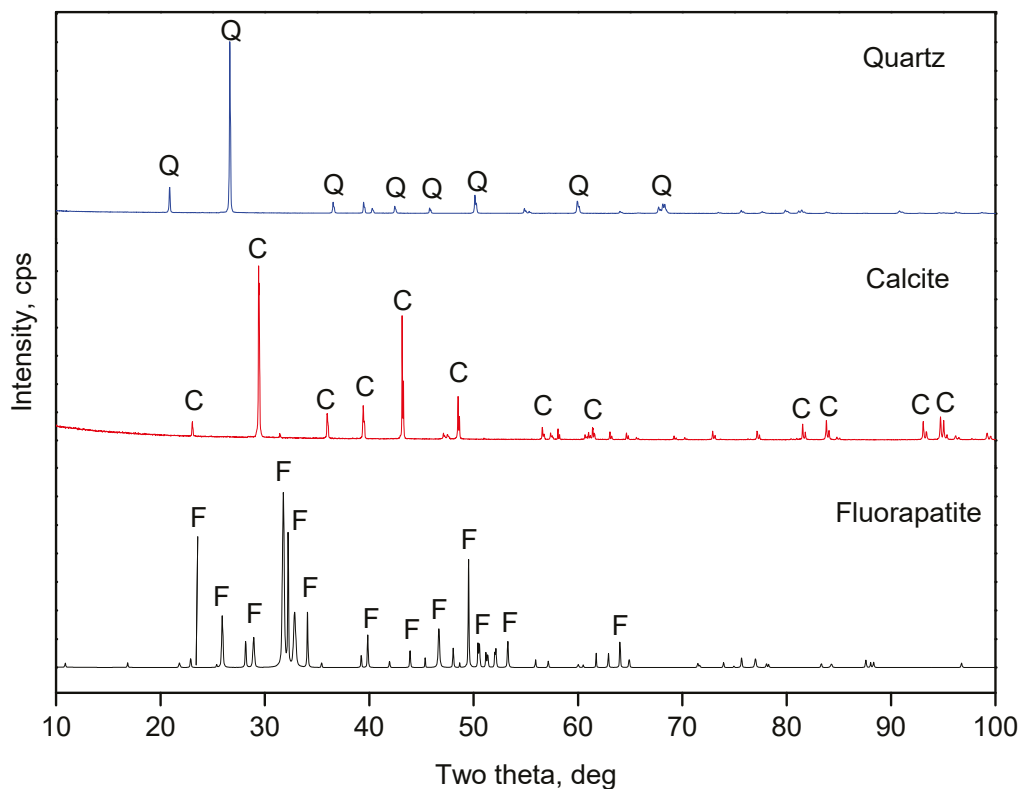


Figure 1. XRD patterns of fluorapatite, calcite, and quartz.

2.1.2. Chemical Reagents

The study used reagents purchased from Sigma Aldrich, except for the fatty acids from VWR Chemicals. Table 2 discloses the details. FAM encompasses the fatty acids in the mixing ratio listed in Table 3. The collector's performance in phosphate ore flotation improves with a predominant concentration of oleic acid over linoleic acid [55].

Table 2. Reagents used in the flotation experiments.

Reagent	Role	Formula	Purity
Sodium alginate (NaAl)	Depressant	(NaC ₆ H ₇ O ₆) _n	Alginate acid sodium salt from brown algae, low viscosity
Methyl isobutyl carbinol (MIBC)	Frother	C ₆ H ₁₄ O	AR grade 98%
Sodium hydroxide	pH controller	NaOH	ACS reagent $\geq 97\%$

Table 3. Composition of FAM.

Fatty Acid	Oleic Acid C18:1	Linoleic Acid C18:2	Palmitic Acid C16:0	Stearic Acid C18:0	Palmitoleic Acid C16:1
Content, %wt.	81	10	4	2	<1

To synthesize FAM, the fatty acids were mixed with 95% ethanol and NaOH in a 250 mL round-bottom flask and agitated for 2 h under reflux heating at a temperature of 65 °C. Afterward, the crude collector was transferred into a beaker containing a saturated sodium chloride solution, resulting in a layer of soap precipitate floating on the surface of the salted water. The product was then vacuum filtered, washed with distilled water, and dried in a vacuum drying oven at 40 °C for 72 h, resulting in the corresponding collector FAM.

2.2. Experimental Methods

2.2.1. Micro-Flotation Tests

Micro-flotation tests were conducted in a 325 mL Hallimond tube fitted with a sintered glass of porosity three and a magnetic stirrer, using 1 g of pure mineral [$-180 + 125 \mu\text{m}$], 100 mL of deionized water, and NaOH to adjust the pH. Deionized water was used to provide a chemically stable and controlled medium, free from interfering ionic species that may affect reagent–mineral interactions. The pulp was conditioned with reagents for 3 min each, poured into the Hallimond tube, and nitrogen flowed at 100 mL/min rate, with the micro-flotation test lasting 1 min. The froth products were collected, filtered, dried, and weighed to calculate the recovery rate. Experiments were carried out in triplicate to ensure accuracy and reliability. The average value was the final result, and the error bars display the standard deviation.

2.2.2. Zeta Potential Measurements

The Zeta potential of pure minerals was measured using a Zetasizer Nano ZS (Malvern PANalytical, Malvern, Worcestershire, UK) at room temperature. In so doing, 0.1 g of the sub-40 μm pure mineral fraction was suspended in 50 mL of a 1.0 mM NaCl background electrolyte. The pulp pH was adjusted using HCl/NaOH solutions and then conditioned with reagents at a specific dosage and conditioning time, according to the micro-flotation procedure. After 30 min of settling, 1 mL of the supernatant was derived for measurement. The reported value was the average of three repetitions, and the error bars displayed the standard deviation.

2.2.3. Adsorption Tests

The adsorption of reagents was quantified via the colorimetric method using HITACHI U-3900H spectrophotometer (Hitachi High-Tech Corporation, Tokyo, Japan). The amount of the residual mixed collector in the supernatant was determined through the Gregory method [56] at a wavelength of 435 nm. On the other hand, the Dubois method [57] was called upon to measure the adsorption of organic depressant NaAl at a wavelength of 490 nm.

To conduct adsorption tests, 0.5 g of a pure mineral fraction with a particle size of less than 40 μm was suspended in 50 mL of reagent solution. After pH adjustment, the mixture was stirred for 5 min at room temperature. The supernatant was obtained through solid–liquid separation via centrifugation at 5000 rpm for 5 min.

The specific surface areas of fluorapatite, calcite, and quartz were $6.75 \text{ m}^2/\text{g}$, $1.97 \text{ m}^2/\text{g}$, and $2.43 \text{ m}^2/\text{g}$, respectively, determined by the BET N₂ adsorption method using 3Flex 3500 Micrometric (Micromeritics Instrument Corporation, Norcross, GA, USA).

2.2.4. FTIR Spectra Analyses

FTIR spectroscopy was performed using IR VERTEX 70 (Bruker Optics GmbH, Bremen, Germany) to study FAM adsorption onto the mineral surfaces. For this purpose, 0.15 g of sub-40 μm pure mineral underwent the same procedure described in the micro-flotation section. The solid fraction was filtered, gently washed with deionized water, and dried at 80 °C for 24 h. An amount of 1 mg of mineral powder was mixed with 99 mg of KBr and pressed into a thin plate for analysis. The samples were analyzed in transmittance mode within the 4000–400 cm^{-1} wavenumber range. For each sample, 32 scans were conducted at a 2 cm^{-1} resolution.

3. Results and Discussion

3.1. Single Mineral Flotation

The floatability of apatite, calcite, and quartz was first assessed through micro-flotation tests in the FAM system without depressants at an alkaline pH. Figure 2 shows that pure mineral recoveries increase with increasing FAM concentration, with the apatite recovery reaching the maximum at a concentration of 80 mg/L. Apatite and calcite follow the same pattern, with a slight difference in favor of apatite. Quartz recovery remains well below that of apatite and calcite. Therefore, FAM alone is insufficiently effective to separate apatite and calcite.

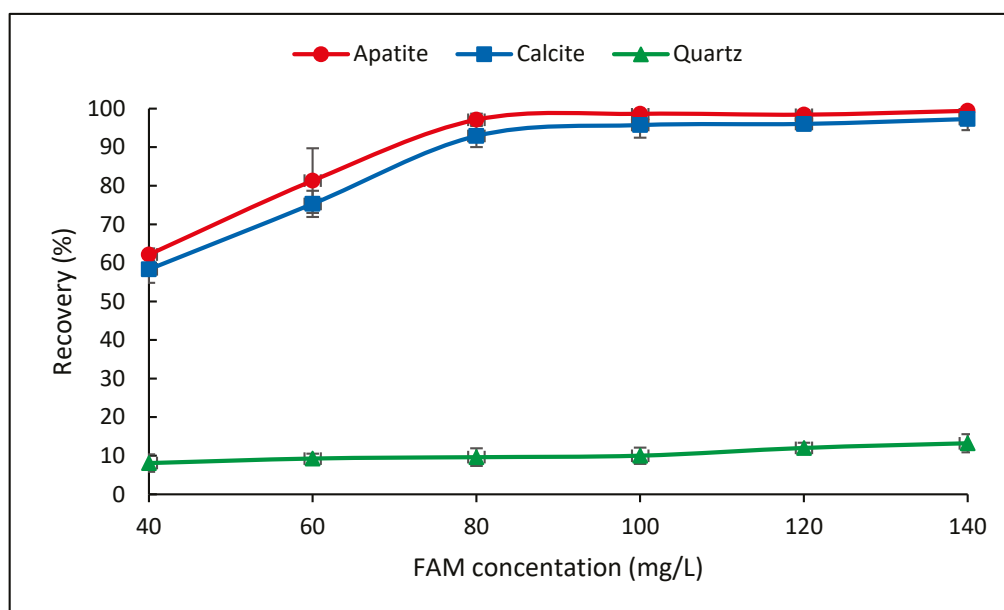


Figure 2. Apatite, calcite, and quartz flotation as a function of FAM concentration.

Figure 3 displays the effect of pH and reagents on apatite, calcite, and quartz floatability. Both apatite and calcite exhibit notable floatability with a recovery of over 80% at an alkaline pH in the absence of NaAl, which is consistent with the results of previous studies [58,59]. However, when conditioned with NaAl before FAM, the apatite and calcite flotation patterns exhibit significant differences. In the presence of NaAl, calcite recovery gradually decreases with increasing pH until it reaches approximately 10% at a pH of 11. Nonetheless, NaAl barely affected the apatite recovery, which remained up 96%. As for quartz, neither FAM nor NaAl affected its floatability. The differences in the flotation performance of pure minerals make NaAl/FAM an effective combination for separating mainly calcite from apatite at a pH of approximately 11.

The effect of NaAl concentration on pure mineral floatability was investigated at a pH of 11 and 80 mg/L FAM. Figure 4 depicts the findings. As the NaAl concentration rises from 0 to 35 mg/L, calcite recovery declines from 90% to 10%, while apatite recovery remains stable at approximately 97%. Meanwhile, quartz recovery slightly dropped from 9% to 7%. An amount of 30 mg/L of NaAl was optimal to achieve the maximum difference in apatite and calcite recovery. Based on flotation recovery rates of pure minerals under different reagent schemes, a pH of 11, NaAl 30 mg/L (equivalent to ~3.0 Kg/t), and FAM 80 mg/L (~8.0 Kg/t) were identified as optimal conditions for single-mineral flotation tests.

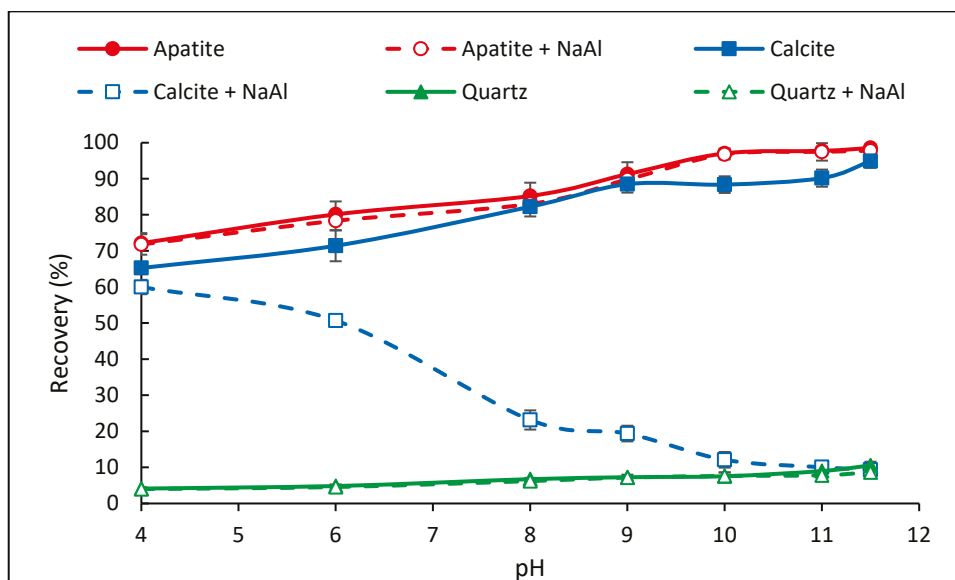


Figure 3. Micro-flotation results as a function of pH with/without NaAl (FAM: 80 mg/L; NaAl: 30 mg/L).

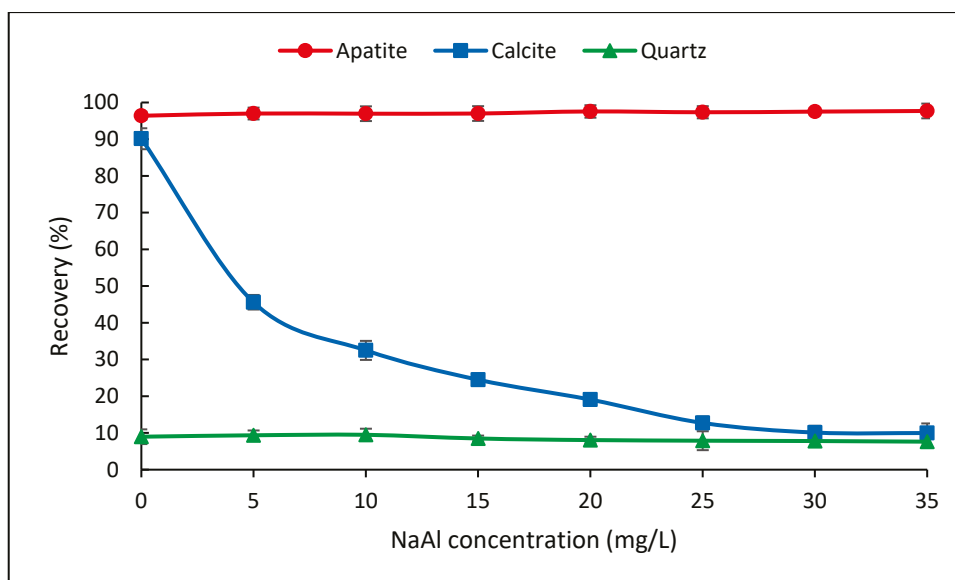


Figure 4. Micro-flotation results as a function of NaAl concentration (FAM: 80 mg/L; pH: 11).

Compared to a previously reported system employing sodium oleate (NaOl) in combination with NaAl as a depressant [58], the current NaAl + FAM scheme demonstrates enhanced reagent efficiency, improved selectivity, and greater cost-effectiveness. Specifically, the required depressant dosage was reduced by approximately 25%, while the recovery of calcite was more effectively suppressed, dropping to around 10%, in contrast to 39% under the NaOl-based formulation. Importantly, apatite recovery remained consistently high at approximately 97%. These results reflect the superior synergistic interaction between NaAl and FAM, and they highlight the potential of this reagent combination as a cost-effective and selective alternative formulation for the flotation of carbonate-rich phosphate ores.

The fundamental mechanism underlying NaAl/FAM flotation selectivity is delved into in the subsequent sections, providing a comprehensive understanding of the surfactants' effectiveness in the complex apatite/calcite/quartz mineral system.

3.2. Adsorption Behavior and Mechanistic Insights

The adsorption performance was investigated at a pH of 11, NaAl 30 mg/L, and FAM 80 mg/L. Figure 5 shows the adsorption characteristics of minerals and reagents. FAM proved a higher affinity toward calcite (2.853 mg/m^2) than apatite (0.522 mg/m^2), whereas the adsorption of FAM on quartz (0.083 mg/m^2) was far lower than on the two minerals. These findings comply with previous studies and micro-flotation results [58,60], which ascribed this adsorption order to the calcium density at the mineral surface (calcite ($8.2 \mu\text{mol}\cdot\text{m}^{-2}$) > apatite ($5.1\text{--}6.6 \mu\text{mol}\cdot\text{m}^{-2}$) as well as the solubility product of minerals: calcite (4.6×10^{-9}) > apatite (6.3×10^{-126}) [24,33,61]. Moreover, the synergistic effect of fatty acids composing FAM on the adsorption enhancement was patent. The quantity of reagents adsorbed onto the minerals' surfaces noticeably increased compared to NaOl [58]. Although conditioned with NaAl, FAM adsorbed onto the apatite surface, which managed to float. The observed phenomenon can be explained by the fact that saturated and unsaturated acids adsorb tightly to apatite due to their compact nature and stable affinity.

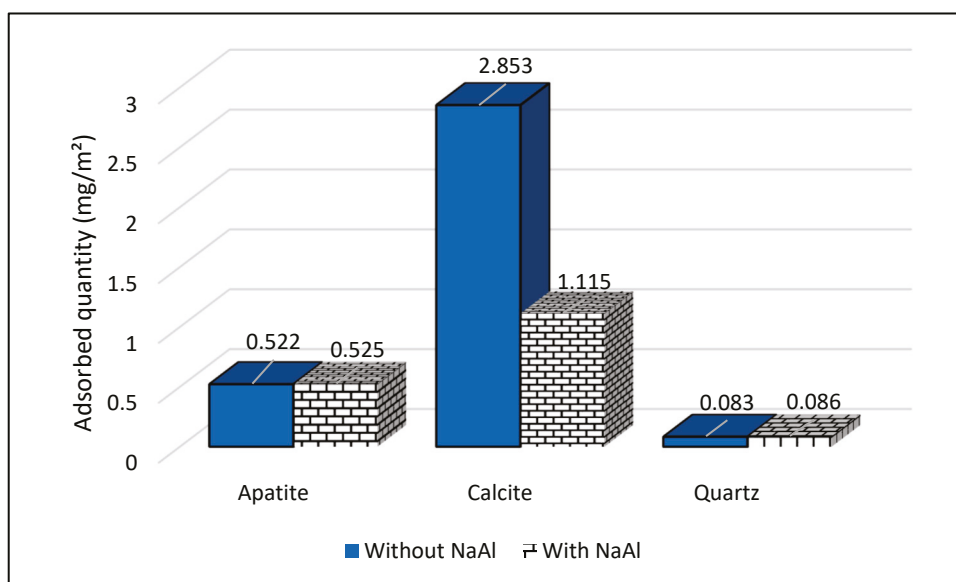


Figure 5. Adsorption of FAM with/without NaAl onto pure minerals.

Furthermore, the NaAl treatment before FAM had minimal effect on the amount of reagents adsorbed onto apatite and quartz. However, FAM adsorption onto the calcite surface decreased significantly from 2.853 mg/m^2 to only 1.115 mg/m^2 . This result further highlights the effectiveness of NaAl as a depressant of calcite, attributed to the chelating mechanism and bulky structure leading to steric hindrance, thus hampering FAM adsorption on Ca^{2+} [58,59,62].

3.3. Zeta Potential and Surface Charge Behavior

To further clarify the adsorption characteristics, the zeta potentials of pure apatite, calcite, and quartz minerals treated with flotation reagents at different pH values were measured. Figure 6 indicates that the isoelectric points (IEPs) for untreated apatite, calcite, and quartz were 3, 3.5, and 3.4, respectively. These findings are consistent with reported values in the previous studies [47,58,63].

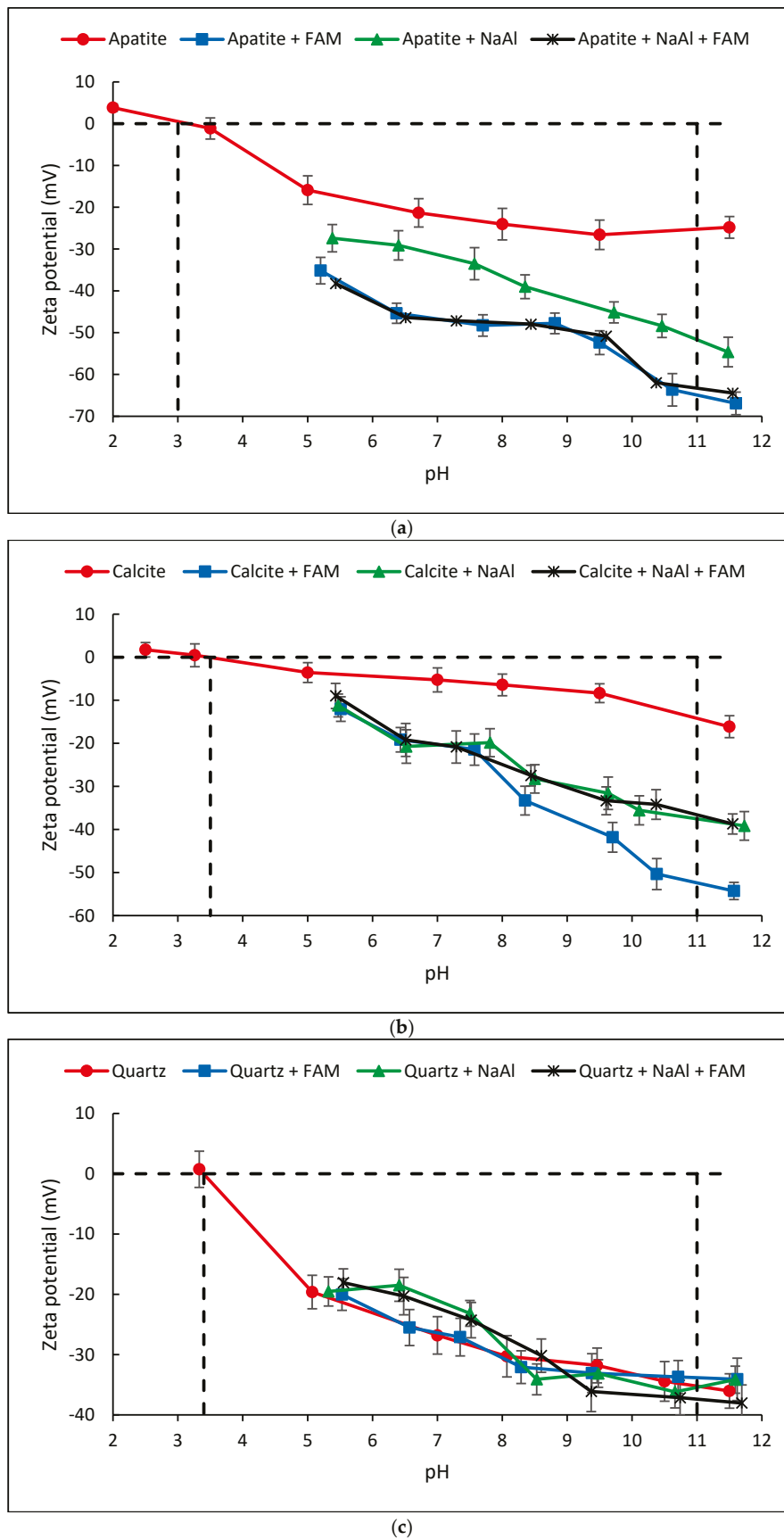


Figure 6. Zeta potential with/without different reagents: (a) apatite, (b) calcite, and (c) quartz.

A significant decrease in the zeta potential of pure minerals with increasing pH over the investigated pH range was apparent.

When exposed to NaAl alone, both apatite and calcite exhibited negative shifts. At a pH of 11, the zeta potential of apatite shifted from -25.12 mV to -52.25 mV, while the zeta potential of calcite dropped from -14.8 mV to -37.16 mV. The degree of change in the zeta potential is quasi-comparable for both minerals, as it is slightly superior for apatite, suggesting that the carboxylate species on NaAl were attracted to and adsorbed onto the Ca^{2+} sites of both minerals.

Similarly, when conditioned with FAM, the intense interaction of the carboxylate and calcium species dissolved from saturated and unsaturated fatty acids of FAM with the calcium sites led to considerable changes in the zeta potentials of apatite and calcite in the negative direction. At a pH of 11, the zeta potentials of apatite (Figure 6a) and calcite (Figure 6b) shifted to -65.03 mV and -52.74 mV, respectively, after treatment with FAM alone. Apatite exhibited a more pronounced negative shift in the zeta potential than calcite.

However, when NaAl and FAM were added, apatite and calcite showed different zeta potential shift trends. Sequentially adding NaAl and FAM to calcite slurry results in similar surface zeta potentials of calcite as adding NaAl alone, indicating that NaAl pre-adsorption on calcite surface hinders subsequent FAM adsorption. In contrast, the zeta potential of apatite further negatively shifted to -62.94 mV upon the sequential addition of NaAl and FAM. These results imply that NaAl exhibits weaker interactions with apatite than calcite, and FAM still can firmly adsorb onto the surface of apatite in the presence of NaAl. The compact and tight adsorption of FAM on the apatite surface can be attributed to a combination of electrostatic shielding between functional groups and the variation in fatty acid chain lengths (C16–C18), which include both saturated and unsaturated components. The presence of heterogeneous chain lengths is known to promote synergistic interactions among the molecules, facilitating closer packing and reducing steric hindrance. As reported in the previous studies [29,51,64,65], this variation enhances the balance between molecular mobility and hydrophobic coverage, thereby increasing the stability and compactness of the adsorption layer. In this context, the synergistic effect of the mixed fatty acids contributes to a more uniform and effective surface coverage, improving the collector's performance.

Concerning quartz (Figure 6c), either untreated or treated with reagents, the zeta potential had barely shifted, inferring that NaAl and FAM had little effect on the quartz surface [47].

Consistent zeta potential measurements with the adsorption tests and micro-flotation results motivated the FTIR spectra analyses.

3.4. FTIR Interpretation of Reagent-Surface Interactions

FTIR spectroscopy was conducted to investigate the functional groups involved in the adsorption of the NaAl and FAM reagent system on the surfaces of apatite, calcite, and quartz. The analysis aimed to elucidate the chemical interactions underlying the selective adsorption behavior observed in micro-flotation tests. Figure 7 presents the FTIR spectra of each mineral before and after conditioning with FAM and the NaAl + FAM combination.

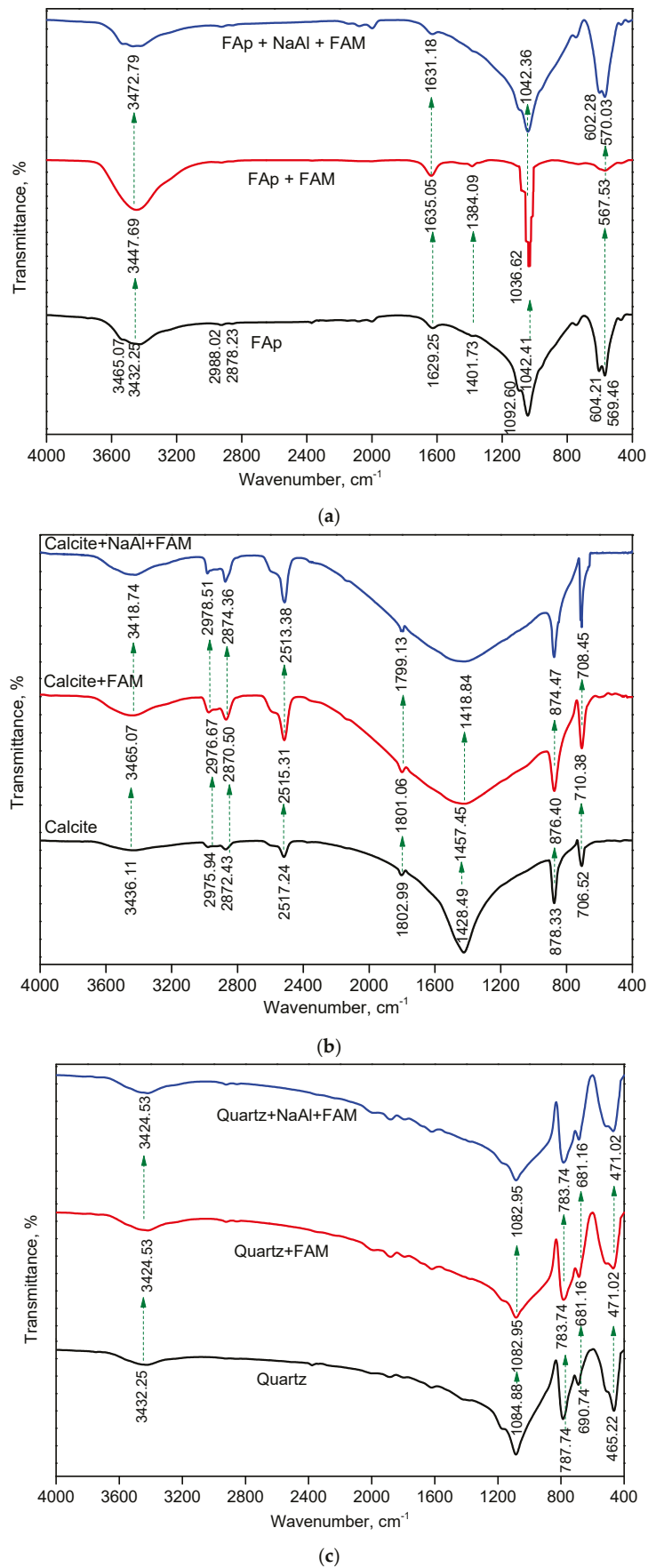


Figure 7. FTIR spectra of (a) fluorapatite, (b) calcite, and (c) quartz nonconditioned/conditioned with FAM and NaAl + FAM.

For apatite (Figure 7a), the spectral region between 3600 and 2700 cm^{-1} , associated with methyl and methylene stretching vibrations of the hydrocarbon chains, displayed distinct peaks at 2988.02 cm^{-1} and 2878.23 cm^{-1} , corresponding to the asymmetric stretching of CH_3 and symmetric stretching of CH_2 , respectively [66–68]. In the region between 1750 and 1400 cm^{-1} , attributed to the carboxylate group, several meaningful shifts were observed. The band at 1629.25 cm^{-1} shifted to 1635.05 cm^{-1} after FAM conditioning and shifted slightly back to 1631.18 cm^{-1} following NaAl + FAM treatment, indicating changes in the asymmetric stretching vibration of the $\nu_{as}(\text{COO}^-)$ group. Similarly, the peak at 1401.73 cm^{-1} , associated with $=\text{C}-\text{H}$ (cis) bending, shifted to 1384.09 cm^{-1} after FAM adsorption [69]. The following pronounced shift was also observed in the phosphate region: the P–O asymmetric stretching peak initially at 1042.41 cm^{-1} moved to 1036.62 cm^{-1} after FAM treatment and nearly returned to 1042.36 cm^{-1} after NaAl + FAM conditioning. Minor changes in the P–O bending vibration were also noted, with a shift from 569.46 cm^{-1} to 567.53 cm^{-1} with FAM and to 570.03 cm^{-1} with NaAl + FAM. These spectral variations suggest strong interactions between FAM and phosphate groups, while the minimal differences following NaAl + FAM treatment indicate that sodium alginate does not impede the adsorption of FAM onto apatite surfaces. These observations align well with the adsorption data.

For calcite (Figure 7b), characteristic carbonate bands appeared at 1802.99 cm^{-1} and 1428.49 cm^{-1} due to the stretching vibrations of the CO_3^{2-} group and at 878.33 cm^{-1} and 706.52 cm^{-1} due to its deformation vibrations [70]. After FAM treatment, CH_2 stretching bands at 2976.67 cm^{-1} and 2870.50 cm^{-1} became apparent, indicative of the hydrocarbon tail of the collector. The asymmetric $-\text{COO}-$ band at 1428.49 cm^{-1} broadened and shifted to 1457.45 cm^{-1} , confirming the chemisorption of FAM functional groups on the calcite surface. Upon NaAl + FAM conditioning, the carbonate stretching band at 1802.99 cm^{-1} shifted to 1799.13 cm^{-1} , while the 1428.49 cm^{-1} band moved to 1418.84 cm^{-1} and broadened significantly, reflecting further adsorption of NaAl. These changes suggest a competitive interaction, whereby NaAl adsorbs preferentially or additionally on the calcite surface, reducing FAM coverage. This is consistent with the reduced floatability of calcite observed in flotation experiments.

In the case of quartz (Figure 7c), characteristic silicate vibrations were observed at 465.22 cm^{-1} (Si–O–Si stretching), 690.74 cm^{-1} (symmetric Si–O bending), 787.74 cm^{-1} (Si–O symmetric stretching), and 1084.88 cm^{-1} (Si–O stretching). After treatment with FAM and NaAl + FAM, these bands exhibited only minor shifts to 471.02, 681.16, 783.74, and 1082.95 cm^{-1} , respectively, indicating negligible interactions between the reagents and the quartz surface [58]. The weak response of quartz to the reagent system further supports its passive behavior in the flotation process.

Overall, the FTIR spectral shifts observed for apatite and calcite, contrasted with the limited spectral changes for quartz, reinforce the selectivity of the NaAl + FAM reagent system. These findings, when considered alongside micro-flotation, zeta potential, and adsorption study results, provide consistent evidence of the mineral-specific interactions governing the adsorption mechanisms and flotation behavior.

4. Conclusions

This study demonstrates the potential of a novel reagent scheme based on a mixed fatty acid collector (FAM) combined with sodium alginate (NaAl) as a selective depressant for the efficient separation of apatite from calcite and quartz. The synergistic interaction of the fatty acid mixture, mainly composed of oleic acid and minor proportions of linoleic, palmitic, stearic, and palmitoleic acids, was systematically investigated through micro-flotation

experiments, adsorption studies, zeta potential measurements, and FTIR spectroscopy. The principal findings are as follows:

Micro-flotation experiments confirmed that the NaAl + FAM combination successfully achieved the direct flotation of apatite from calcite and quartz, with a 97% apatite recovery, a 10% calcite recovery, and a 7% quartz recovery at an optimal alkaline pH of 11.

- Adsorption tests indicated that NaAl efficiently depresses calcite and quartz without interfering with FAM adsorption on apatite surfaces, ensuring mineral-specific separation.
- Zeta potential measurements revealed a shift toward more negative values after conditioning with NaAl/FAM. The overlapping trends between (i) NaAl and NaAl + FAM curves for calcite and (ii) FAM and NaAl + FAM curves for apatite highlighted distinct adsorption behaviors, supporting the system's selectivity.
- FTIR spectral analysis identified characteristic functional groups involved in collector and depressant interactions, further validating the proposed adsorption mechanism and surface affinities.
- The NaAl + FAM system demonstrated a high flotation selectivity with minimal depressant consumption, achieving effective calcite depression while maintaining high apatite recovery and minimal quartz flotation. This underlines the system's technical efficiency and economic advantage in processing carbonate-rich phosphate ores.

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Article

Effect of Gas Holdup on the Performance of Column Flotation of a Low-Grade Apatite Ore

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Abstract: As a consequence of the gradual exhaustion of apatite ore reserves, intensive comminution has been implemented in mineral processing operations to enhance phosphorus liberation. Consequently, improving the flotation efficiency of fine particles has remained a persistent challenge within the phosphate industry. The performance of flotation columns is strongly affected by the interaction between gas (bubble) and particle. The present research was designed to evaluate how certain process variables and chemical dosages influence gas holdup and its correlation with the column flotation performance of fine particles derived from a low-grade apatite ore. Column flotation experiments were conducted employing a factorial experimental approach to evaluate the effects of air flow rate, surfactant concentration, collector dosage, and depressant dosage on gas holdup, P_2O_5 grade, and recovery. The results made it possible to identify the levels of gas holdup that lead to appropriate values of P_2O_5 grade and recovery simultaneously, and their relation with the operating variables and reagent dosage. Gas holdup values higher than 23.5% led to the desired values of P_2O_5 grade (>30%) and recovery (>60%) simultaneously. Statistical models were developed with high correlation coefficients ($R^2 > 0.98$) to predict P_2O_5 grade and recovery as functions of the operating variables. This research provides a comprehensive framework of the gas holdup effect on column flotation systems, offering significant potential for improving the economic viability of low-grade phosphate ore processing.

Keywords: flotation; gas holdup; apatite; low-grade ore; column flotation

1. Introduction

The majority of igneous phosphate ores exhibit diminished P_2O_5 content and require enrichment procedures to generate commercially viable products [1]. Froth flotation is the most important stage within the mineral beneficiation industry's concentration workflow. Inefficient performance in flotation results in substantial revenue losses and the unnecessary depletion of mineral reserves [2]. Phosphate flotation outcomes are deemed economically feasible when the concentrate achieves a P_2O_5 grade exceeding 30% while simultaneously maintaining phosphorus recovery rates above 60% [3].

Flotation constitutes a complex separation technique involving multiple constituents, phases, and heterogeneous systems wherein suspended solid particles in aqueous medium interact with air bubbles, creating an air–pulp dispersion [4]. Throughout this enrichment operation, chemical reagents are introduced to selectively alter the surface characteristics of target minerals, rendering the valuable mineral hydrophobic and consequently amenable to flotation, while simultaneously making gangue minerals hydrophilic and therefore

non-floatable [5]. During the flotation procedure, valuable particles are captured by air bubbles within the liquid phase and transported toward the pulp–froth interface, whereas hydrophilic particles remain suspended in the pulp and are discharged as tailings [6].

Overall, froth flotation effectiveness depends upon three primary sub-processes: collision, adhesion, and detachment [7]. The probability of particle–bubble contact, the adherence of particles to bubbles subsequent to collision, and the persistence of this attachment throughout the pulp phase are mechanisms strongly dependent on particle size and bubble diameter, which, in turn, are directly influenced by the gas holdup. Thus, the operating variables that change the gas holdup also influence the flotation performance [8]. Therefore, understanding the relationship between gas holdup and bubble–particle interaction and the forms to enhance it is extremely important for enhancing mineral flotation processes [9].

Column flotation has been effectively employed in apatite beneficiation owing to its superior performance compared to traditional cells, generating foam with enhanced flow properties [10]. Gangue entrainment within the froth is minimized while bubble residence time in the pulp is extended, leading to improved selectivity [11].

Processing fine particles of low-grade apatite ore through flotation remains problematic for phosphate companies, chiefly because of the limited probability of collisions between particles and air bubbles, which reduces attachment potential and subsequently lowers flotation effectiveness [12]. Thus, the focus in the fine particle’s flotation is the improvement in the conditions that lead to more favorable bubble–particle contact [13].

Bubble–particle contact is influenced by particle and bubble sizes. The distribution of bubble sizes is affected by gas holdup. Gas holdup is defined as the volumetric fraction of gas (air bubbles) present in the gas–liquid–solid mixture within the flotation column, typically expressed as a percentage. This parameter can be managed via air flow rate and the incorporation of surfactants, in addition to the concentration of flotation chemicals, such as collectors and depressants [14]. Surfactants within the flotation operation are predominantly employed to boost the likelihood of collisions between particles and air bubbles through the creation of fine bubbles and the provision of foam stability [15]. The introduction of surfactants minimizes bubble coalescence and drives bubbles from the slurry region toward the foam layer, owing to the extended residence duration of air bubbles. As a result, the likelihood of bubble–particle collision may be improved [16].

The present research was designed to evaluate how certain process variables and chemical dosages influence gas holdup and its correlation with the efficiency of column flotation for fine particles derived from a low-grade apatite ore.

This research encompasses a comprehensive investigation of gas holdup’s effect on column flotation systems, specifically targeting low-grade apatite ore processing. The scope includes (a) a systematic evaluation of operating variables on gas holdup and flotation performance; (b) the development of predictive statistical models; and (c) implications for industrial applications.

2. Materials and Methods

2.1. Characterization of Phosphate Ore

The sample utilized in this investigation consisted of a low-grade apatite ore obtained from the Mosaic Fertilizantes, situated in Araxá, Minas Gerais State, Brazil. The country rock formations primarily comprise carbonatites and glimmerites [17].

Chemical composition analysis was conducted using X-ray fluorescence spectrometry with a Bruker spectrometer (S8 Tiger model). The samples’ particle size distribution (PSD) was determined through a laser diffraction methodology employing a Malvern Mastersizer 2000.

Mineralogical identification of the feed material was accomplished by combining X-ray diffraction with scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). X-ray diffraction analysis was performed using a Rigaku Geigerflex semi-automatic diffractometer. Microstructural investigations were also conducted with SEM/EDS techniques. These measurements were executed using a JSM-5410 SEM microscope and a Noran TN-M3055 EDS spectrometer (JEOL, Peabody, MA, USA).

2.2. Reagents and Ore Conditioning

The conditioning protocol was implemented based on previous investigations [17,18], wherein a fatty acid soap derived from crude rice oil at a concentration of 2.5 wt% oil served as the collector, while gelatinized cornstarch at 3.0 wt% concentration functioned as the depressant. A 10% NaOH solution was employed to adjust the pulp pH to approximately pH 11, and Genagen[®] surfactant from Clariant was incorporated into the process as a frother.

The Genagen[®] surfactant plays a crucial role in the flotation process as a frother, acting primarily to control bubble size distribution and foam stability. This non-ionic surfactant belongs to the family of alcohol ethoxylates and functions by reducing surface tension at the gas–liquid interface, thereby preventing bubble coalescence and promoting the formation of smaller, more stable bubbles. The mechanism of action involves the adsorption of surfactant molecules at the bubble surface, creating a protective layer that inhibits bubble merging. This results in increased gas holdup due to the reduced rise velocity of smaller bubbles, which enhances their residence time in the flotation column. The interaction between Genagen[®] and other flotation reagents is particularly important, as the surfactant can form mixed adsorption layers with the collector molecules at the mineral surface, potentially enhancing the hydrophobicity of apatite particles while maintaining selectivity against gangue minerals.

2.3. Experimental Apparatus and Experimental Measurements

Flotation experiments were carried out in a batch flotation column made of polymethyl methacrylate (PMMA) with a height of 1.50 m and a 40 mm inner diameter, as illustrated in Figure 1. The pulp was fed into the top of the column and air was fed and distributed by a sparger (a porous conical device made of sintered bronze) at the bottom of the column. The column functioned using bottom product recirculation, while froth wash water was introduced at the top. Air and wash water flow rates were quantified using rotameters.

The technique used to obtain the air holdup was the same as that developed by Finch and Dobby [19]. In this approach, the air holdup was calculated from the pressure differential between two points within the column. The pressure differential in the column was measured by employing two pressure transmitters (model VTP-1000, Vectus, Noida, India). The signals were relayed to a data acquisition board (National Instruments, NI USB-6211, NI Austin, TX, USA) and subsequently analyzed and processed using data acquisition software. Equation (1) [19] was applied to determine gas holdup from the pressure drop information. The solid density was determined using a helium pycnometer (AccuPyc 1340, Micromeritics Instrument Corporation, Norcross, GA, USA) with an accuracy of $\pm 0.02\%$.

$$\varepsilon_g = 1 - \frac{\Delta P}{\rho_{SL} L g} \quad (1)$$

$$\rho_{SL} = \rho_W \times (1 - C_s) + \rho_S \times C_s \quad (2)$$

where

C_s is the solid concentration by volume;
 ε_g is the gas holdup, defined as the volumetric fraction occupied by air in the mixture present in the flotation column (dimensionless);
 ΔP is the pressure drop (Pa);
 ρ_{SL} is the suspension density (kg/m^3);
 ρ_W is the water density (kg/m^3);
 ρ_S is the solid density (kg/m^3);
 L is the distance between the pressure measurement points (m);
 g represents the acceleration due to gravity = $9.81 \text{ m}/\text{s}^2$.

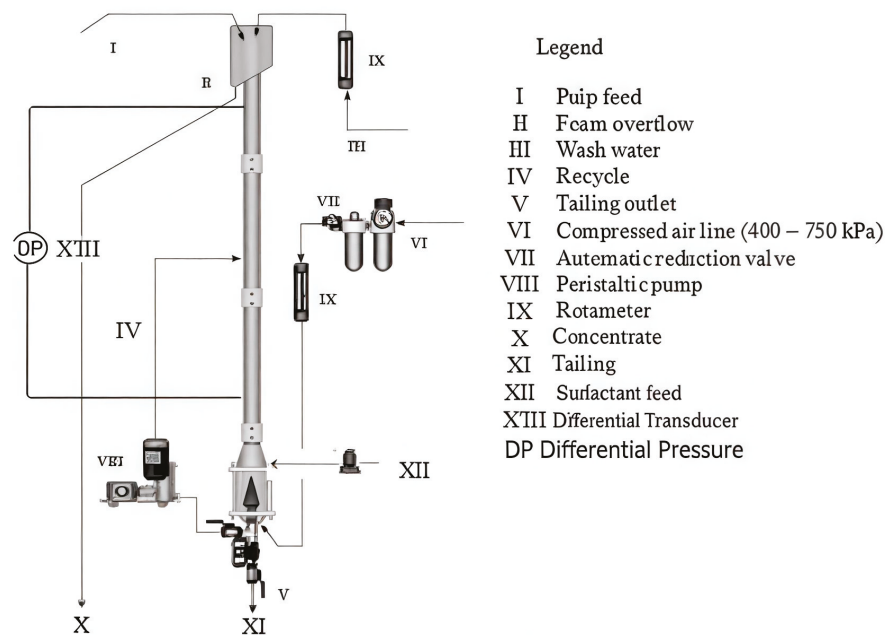


Figure 1. Schematic diagram of the experimental apparatus.

The flotation column operated with a circulating load (0.50 L/min) that suspended the feed particles and guaranteed their transit through the collection zone. The pulp underwent pre-conditioning and was then diluted to supply the batch flotation column from the top (14% solid content in the feed), after air flow rate regulation and pulp recirculation system connection. Wash water (0.15 L/min) was initiated and the floatable material was gathered until the foam layer was exhausted. The surfactant flow rate was maintained at 0.05 L/min. The air supply was provided by an oil-free compressor equipped with a pressure regulator and moisture trap to maintain consistent air quality. The air flow rate was continuously monitored using a rotameter with $\pm 2\%$ accuracy. Additionally, all experiments were conducted under controlled temperature conditions ($25 \pm 2 \text{ }^\circ\text{C}$) to minimize density variations that could affect flow measurements.

During each flotation experiment, both flotation and non-flotation products were removed from the equipment and oven-dried at $110 \pm 0.5 \text{ }^\circ\text{C}$ for 24 h, weighed, and analyzed for chemical composition. The chemical composition of the flotation products was determined by X-ray fluorescence spectrometry using a Bruker spectrometer (S8 Tiger, Bruker, Karlsruhe, Germany).

A set of experiments was proposed using a factorial experimental design to evaluate the effects of operating variables on flotation performance. The investigated variables were air flow rate, surfactant concentration, and collector and depressant dosages. The full set of

experimental results was evaluated comprehensively using multiple regression analysis, determining the impact of the independent variables on P_2O_5 grade and recovery.

3. Results

3.1. Results of the Phosphate Ore Characterization

The results of the chemical composition of the feed sample are shown in Table 1. The ore presents a low P_2O_5 grade of 19.73%, which is typical of low-grade phosphate ores that require concentration processes to achieve commercial grades. The highest proportion of gangue minerals associated with apatite are silicate and iron minerals, representing significant challenges for selective flotation. Studies on igneous phosphate ores consistently report silicates and iron oxides as the primary gangue minerals causing flotation difficulties. The complex intergrowths between apatite and these gangue minerals require fine grinding, which further complicates the separation process [1].

Table 1. Chemical composition of the feed sample.

Component	(%)
CaO	26.82
P_2O_5	19.73
Fe_2O_3	23.94
SiO_2	12.13
TiO_2	8.98
BaO	2.93
Al_2O_3	1.39
SO_3	0.98
MgO	0.78
SrO	0.77
MnO	0.50
ZrO_2	0.48
Nb_2O_5	0.36

The particle size distribution (PSD) of the feed sample used in this study, which was obtained using laser diffraction, was fitted to the main statistical models for estimating the PSD. The Rosin–Rammler–Bennett (RRB) model (Equation (3)) best fitted the experimental data ($R^2 = 0.998$): the fitted parameters were $d_{63.2} = 87.6 \mu m$ and $n = 1.83$. The parameter $d_{63.2}$ represents the particle size at which 63.2% of the particles are finer.

$$X = 1 - e^{\left[-\left(\frac{d_p}{87.6} \right)^{1.83} \right]} \quad (3)$$

where d_p is the particle diameter, and X is the cumulative fraction.

The characterization revealed that most particles in the fine fraction have diameters varying between 20 and 140 μm , with a Sauter mean diameter of 50.86 μm . This particle size range is particularly challenging for flotation due to the reduced probability of bubble–particle collision and the increased influence of hydrodynamic forces that can cause particle detachment from bubbles [18].

3.2. Gas Holdup Measurements and Validation

Before conducting the flotation experiments, the pressure sensor system was validated by comparing the gas holdup measurements obtained through pressure difference with those obtained using the phase difference technique, which is considered the most accurate

method for gas holdup determination [20]. The validation experiments showed that the pressure sensor measurements were reliable, with a mean relative deviation of less than 6.8% compared to the phase difference technique. For high gas velocities, the gas holdup obtained by the pressure difference method was slightly lower than that obtained by the phase difference method, which can be attributed to the turbulence of the air–water system at high air velocities, promoting large oscillations in the gas–liquid height.

3.3. Effect of Surfactant and Collector on Gas Holdup

The influence of surfactant addition on gas holdup was evaluated in air–water systems under identical operating conditions, i.e., a surfactant dosage of 15 ppm (Figure 2). A significant increase in gas holdup was observed with surfactant addition, which can be attributed to the surfactant's action in reducing bubble coalescence phenomena. The presence of surfactant in the system reduces bubble size and consequently increases gas holdup due to the lower rise velocity of smaller bubbles, which increases their residence time in the column.

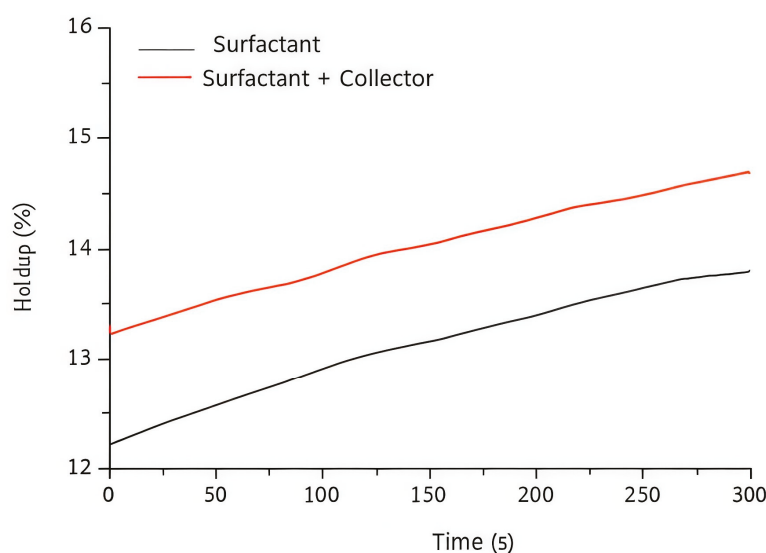


Figure 2. Variation in air holdup with the addition of surfactant and surfactant and collector.

The addition of collector (at 10 ppm) to the surfactant solution caused a further elevation in gas holdup values in the air–water system. According to Dukhin et al. [21], this occurs due to a force known as Gibbs elasticity, where reagent molecules slide along the bubble surface to the bottom of the bubble as water flows over the surface, creating a surface tension gradient that retards bubble rise velocity.

3.4. Effect of Particle Presence on Gas Holdup

As depicted in Figure 3, the presence of mineral particles significantly affected gas holdup values compared to the air–water system, at the same conditions. Under the conditions studied, gas holdup increased 2–3 times in the presence of mineral particles compared to the situation without particles. This difference was more pronounced at lower air velocities, where gas holdup was approximately three times higher at a superficial gas velocity of 0.53 cm/s, while at velocities of 1.06 and 1.60 cm/s, gas holdup was about two times higher.

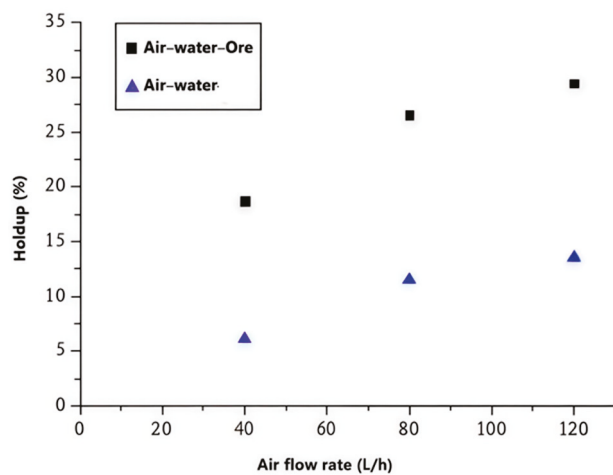


Figure 3. Air holdup with and without the presence of ore.

This increase in gas holdup due to particle presence can be explained by two main mechanisms: (1) bubble loading, where particle presence reduces the rise velocity of bubble–particle aggregates, and (2) reduced bubble coalescence due to particles acting as a barrier between bubble interfaces [22]. Vazirizadeh et al. [23] identified that in the presence of surfactants, talc mineral increased gas holdup due to the loading phenomenon, which reduces the velocity of bubble–mineral aggregates. The study by Perez-Garibay [24] demonstrated that silica particles functioned as a compact layer around bubbles, preventing interactions between gas–liquid interfaces and, therefore, bubble coalescence.

3.5. Results of the Flotation Tests

The flotation results and corresponding operating conditions are shown in Table 2. The independent variables investigated were air flow rate (Q_{air}), concentration of the surfactant ($C_{\text{surf.}}$), collector dosage ($D_{\text{col.}}$), and depressant dosage ($D_{\text{dep.}}$). The experiments were designed to evaluate the effects of these variables on flotation performance.

Table 2. Results and operating conditions of the flotation tests.

Tests	Q_{air} (L/h)	$C_{\text{surf.}}$ (ppm)	$D_{\text{col.}}$ (g/t)	$D_{\text{dep.}}$ (g/t)	Gas holdup (%)	P_2O_5 Grade (%)	P_2O_5 Recovery (%)
1	80.0	7.0	110.0	200.0	21.3	35.6	39.0
2	80.0	15.0	110.0	200.0	19.0	36.6	41.4
3	80.0	15.0	240.0	200.0	20.9	36.7	33.6
4	140.0	15.0	240.0	200.0	26.7	34.7	53.7
5	80.0	7.0	110.0	700.0	19.3	35.9	34.6
6	140.0	15.0	110.0	700.0	26.0	35.7	48.5
7	80.0	7.0	240.0	700.0	22.9	36.7	46.4
8	140.0	7.0	240.0	700.0	25.5	33.7	63.5
9	80.0	15.0	240.0	700.0	19.8	36.7	35.2
10	159.9	11.0	175.0	450.0	25.8	34.2	65.5
11	110.0	17.7	175.0	450.0	22.7	35.2	51.0
12	110.0	11.0	175.0	33.9	23.3	34.9	62.5
13	110.0	11.0	175.0	866.1	25.2	34.7	53.7
14	110.0	11.0	175.0	450.0	23.3	35.6	44.0
15	110.0	11.0	175.0	450.0	23.5	35.4	41.0

The results in Table 2 show that the air flow rate was the operating variable that had the highest effect on air holdup; thus, the conditions that led to the highest values of gas holdup also led to an increase in bubble size diameters [25].

Figures 4 and 5, respectively, show the relation between the P_2O_5 grade and recovery with the air holdup. Despite the data fluctuation due to the influence of the operating variables, there is a clear effect of decrease in P_2O_5 grade and increase in P_2O_5 recovery with increasing gas holdup.

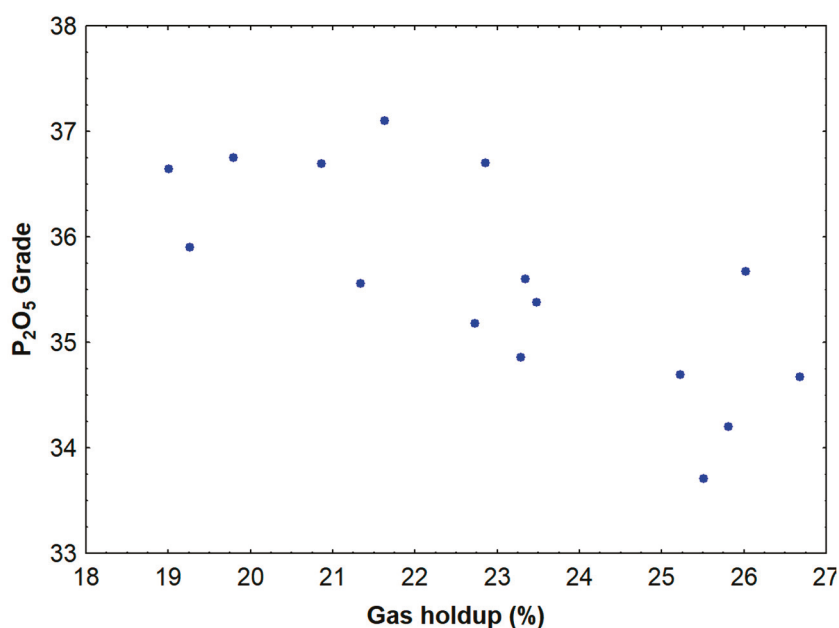


Figure 4. Relationship between P_2O_5 grade and gas holdup.

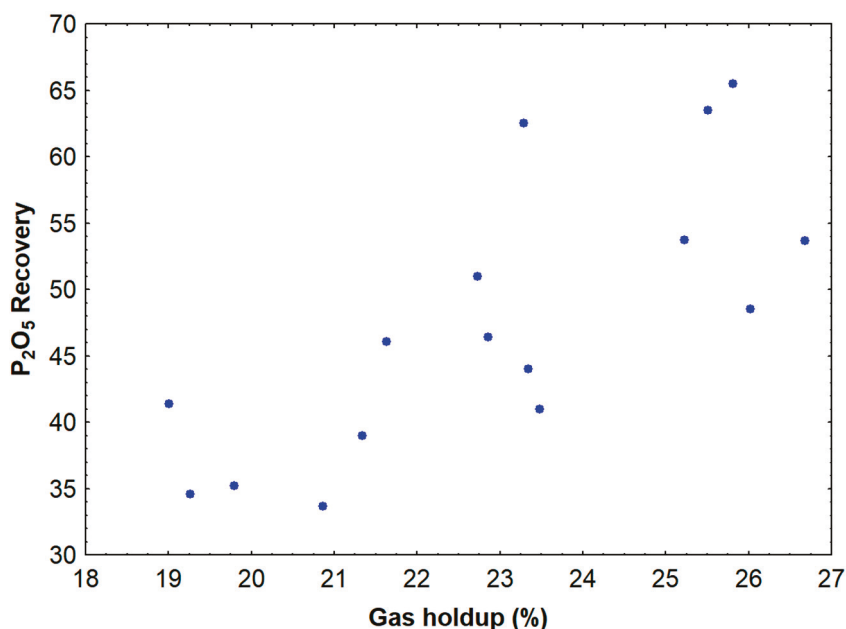


Figure 5. Relationship between P_2O_5 recovery and gas holdup.

Considering the minimum values of P_2O_5 grade and phosphorus recovery that make the process economically attractive (30% and 60%, respectively), it is possible to determine that despite the decrease in P_2O_5 grade at high gas holdup values, the desired values

of P_2O_5 grade and recovery were achieved simultaneously only under conditions with gas holdup values higher than 23.5%. However, some tests under these conditions did not reach the desired recovery, indicating that additional control of reagent dosages was required to simultaneously meet both criteria.

Figures 4 and 5 illustrate the inverse relationship between grade and recovery with variations in gas holdup, confirming the classical trade-off observed in flotation systems [26]. This fundamental relationship is crucial for flotation optimization, necessitating a careful balance to achieve economically viable results.

Under the operating conditions employed in this study, the P_2O_5 grade was favored (Figure 4). This is because all obtained grades were economically attractive, exceeding 30%. This favorable outcome is attributed to the high probability of collision and adhesion, which promotes true flotation. True flotation is characterized as a selective process where hydrophobic particles (valuable minerals) primarily adhere to the bubble surface.

The reduced P_2O_5 recovery achieved when apatite flotation was conducted under low gas holdup conditions and, consequently, with extremely small bubbles occurred because these bubbles exhibit diminished ascent velocity, generating insufficient drag force and therefore some of the formed aggregates are carried to the column bottom with the tailings [25]. This phenomenon represents a complex balance between competing mechanisms: while lower bubble rise velocity indeed increases bubble–particle collision probability through extended residence time, and reduced drag force decreases detachment probability by minimizing hydrodynamic shear forces, the critical limiting factor becomes the insufficient net buoyancy force. For fine particles in the size range studied, the buoyancy force generated by very small bubbles is insufficient to overcome the combined effects of particle weight and downward liquid flow, resulting in aggregate settling despite successful collision and attachment events. This clarifies why the application of microbubbles or nanobubbles is not always the optimal solution in fine particle flotation since the improvement in grade results in substantial recovery losses [25].

3.6. Statistical Analysis and Modeling

The experimental data were analyzed using multiple regression analysis to quantify the effects of the independent variables on the responses [27]. A significance level of 5% was adopted for the regression analysis of the parameters. The four independent variables appear in the equations, either as individual terms or with quadratic terms and interactions. The prediction equations for the two responses are described in Equations (4) and (5), for P_2O_5 grade (G) with $R^2 = 0.987$ and recovery (R) with $R^2 = 0.988$, respectively. In these equations, the variables are expressed in coded form (dimensionless), and Table 3 shows the coding equations. Coded units allow comparison of coefficient magnitudes on a common scale to determine which factor has the largest impact on the response [28].

$$G = 35.58 + \underline{x}'b_1 + \underline{x}'B_1\underline{x} \quad (4)$$

$$b_1 = \begin{bmatrix} -0.94 \\ 0.44 \\ 0 \\ 0 \end{bmatrix}; B_1 = \begin{bmatrix} 0 & 0.11 & -0.14 & 0 \\ 0.11 & -0.42 & -0.10 & 0 \\ -0.14 & -0.10 & 0.60 & 0 \\ 0 & 0 & 0 & -0.29 \end{bmatrix}; \underline{x} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix}$$

$$R = 42.47 + \underline{x}'b_2 + \underline{x}'B_2\underline{x} \quad (5)$$

$$b_2 = \begin{bmatrix} 9.30 \\ -4.42 \\ 0 \\ -3.01 \end{bmatrix}; B_2 = \begin{bmatrix} 2.74 & -1.40 & -1.98 & -1.50 \\ -1.40 & 5.75 & 0 & 0 \\ 1.98 & 0 & -7.63 & 0 \\ -1.50 & 0 & 0 & 5.67 \end{bmatrix}; \underline{x} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix}$$

Table 3. Coded equations.

Independent Variable	Coding Equations
Q_{air}	$x_1 = \frac{Q_{air} - 110}{30}$
C_{surf}	$x_2 = \frac{C_{surf} - 11}{4}$
D_{col}	$x_3 = \frac{D_{col} - 175}{65}$
D_{dep}	$x_4 = \frac{D_{dep} - 450}{250}$

The statistical analysis shows the contradictory effect of air flow rate on grade (negative effect) and recovery (positive effect), as can be seen in the signals of the parameters associated with x_1 . The apatite recovery increases with increasing bubble size, because the small bubbles have insufficient buoyancy force to carry particle–bubble aggregates to the froth phase. It is known that, in the flotation process, high solid recovery is obtained at higher superficial gas velocity. This can be explained by the increase in entrainment, i.e., the transport of particles from the pulp phase to the foam phase through liquid present between the rising bubbles. However, in conditions with large bubbles and small particles, many gangue particles are also entrained, which decreases the flotation selectivity and, hence, the P_2O_5 grade [20].

Collector and surfactant concentrations exhibited nonlinear relationships with P_2O_5 grade (see Equation (3)), indicating that excessive collector addition may diminish selectivity. This behavior can be attributed to the indiscriminate adsorption of collector on gangue minerals at elevated dosages, resulting in enhanced gangue flotation and decreased concentrate grade [29].

The correlation between depressant dosage and P_2O_5 recovery was negative, which is expected as depressants are designed to reduce the flotation of gangue minerals. However, excessive depressant addition can also depress valuable minerals, leading to reduced recovery.

These empirical models (Equations (4) and (5)) can be utilized for process optimization and predicting flotation performance under various operating conditions. The judicious selection of operating conditions can lead to significant improvements in flotation performance, where even modest gains can yield substantial economic benefits for large-scale operations. Optimizing these conditions offers a low-cost approach to achieving such improvements, as it primarily requires adjusting existing equipment rather than capital investment in new technology [30].

The results obtained in this study reveal several important mechanisms that explain the observed performance improvements in the column flotation of low-grade apatite ore. The significant increase in gas holdup observed with the addition of Genagen[®] surfactant can be attributed to its specific molecular structure and interfacial properties. As a non-ionic alcohol ethoxylate, Genagen[®] reduces the surface tension at the gas–liquid interface through the formation of oriented molecular layers. The hydrophobic alkyl chains of the surfactant molecules align toward the gas phase while the hydrophilic ethoxylate groups

remain in the aqueous phase, creating a stabilizing barrier that prevents bubble coalescence. This mechanism is particularly important in the context of fine particle flotation, where the traditional challenges of low collision probability and weak attachment forces must be overcome [31].

Genagen[®] demonstrates exceptional ability to produce and maintain smaller, more uniform bubbles compared to conventional frothers like MIBC or pine oil. This is particularly crucial for fine particle flotation where optimal bubble–particle size ratios are essential for effective collision and attachment. The alcohol ethoxylate structure of Genagen[®] provides better surface activity and reduced bubble coalescence compared to conventional frothers, resulting in more stable bubble size distributions [13].

The synergistic effect observed when both surfactant and collector are present in the system represents a complex interfacial phenomenon. The fatty acid soap collector, derived from crude rice oil, contains long-chain carboxylate groups that can interact with both the mineral surface and the surfactant molecules. At the apatite surface, the collector molecules chemisorb through coordination bonds between the carboxylate groups and calcium ions, creating a hydrophobic layer. Simultaneously, the presence of Genagen[®] in the bulk solution modifies the local environment around the bubbles, potentially enhancing the stability of the collector layer and promoting more effective bubble–particle attachment [31].

4. Discussion

4.1. Particle Loading Effects and Bubble Dynamics

The dramatic increase in gas holdup observed in the presence of mineral particles (2–3 times higher than in air–water systems) can be explained through two complementary mechanisms that operate simultaneously in the flotation system. The first mechanism, known as bubble loading, occurs when particles attach to bubble surfaces, effectively increasing the density of the bubble–particle aggregates and reducing their rise velocity. This phenomenon is particularly pronounced with fine particles, where the surface area to volume ratio is high, allowing for multiple particle attachments per bubble.

The second mechanism involves the disruption of bubble coalescence by the presence of solid particles at the gas–liquid interface. Fine mineral particles can act as physical barriers between approaching bubbles, preventing the drainage of the thin liquid film that separates them. This stabilization effect is enhanced by the presence of surfactant molecules, which can form mixed adsorption layers with the particles at the bubble interface. The combination of these effects results in a more stable foam structure with smaller average bubble size and higher gas holdup.

4.2. Trade-Off Between Grade and Recovery

The inverse relationship between P_2O_5 grade and recovery observed with increasing gas holdup reflects fundamental principles of flotation selectivity and entrainment. At low gas holdup conditions, the system operates with smaller bubbles that provide high selectivity due to their lower carrying capacity and reduced entrainment of gangue particles. However, these conditions also result in lower recovery because the small bubbles have insufficient buoyancy force to carry particle–bubble aggregates to the froth phase, particularly when dealing with fine particles that may have weak attachment forces.

As gas holdup increases, larger bubbles are formed, which possess greater buoyancy and can more effectively transport attached particles to the froth phase. This explains the observed increase in recovery with higher gas holdup values. However, larger bubbles also have a greater tendency to entrain gangue particles through hydrodynamic forces, leading to the observed decrease in grade. The entrainment mechanism becomes

particularly significant when the bubble size approaches or exceeds the particle size, as the hydrodynamic forces around rising bubbles can capture particles regardless of their surface hydrophobicity.

4.3. Role of Reagent Interactions in Performance Optimization

The complex interactions between the flotation reagents used in this study contribute significantly to the observed performance improvements. The gelatinized cornstarch depressant functions through a different mechanism than the collector and frother, acting primarily to increase the hydrophilicity of gangue minerals through hydrogen bonding and physical adsorption. The starch molecules form a protective hydrophilic layer on silicate and iron oxide surfaces, preventing collector adsorption and maintaining these minerals in the pulp phase.

The interaction between the cornstarch depressant and the Genagen[®] frother is particularly important for maintaining selectivity at higher gas holdup conditions. The presence of starch in the system can influence bubble surface properties by competing with the surfactant for adsorption sites. However, the non-ionic nature of Genagen[®] reduces this competition compared to ionic surfactants, allowing for more stable foam formation while maintaining the depressant action on gangue minerals.

The best reagent dosages identified in this study (fatty acid soap collector at 175 g/t, gelatinized cornstarch depressant at 450 g/t, and Genagen[®] surfactant at 11 ppm), associated with an air flow rate of 159.9 L/h, represent a carefully balanced system where each reagent performs its intended function without interfering with the others. The relatively low surfactant concentration required demonstrates the efficiency of Genagen[®] in modifying bubble characteristics, while the higher depressant dosage ensures adequate gangue suppression even under the enhanced flotation conditions created by optimal gas holdup.

4.4. Mechanistic Understanding of the Results

The appropriate results reported in this study can be attributed to the synergistic effects of the optimized reagent system and controlled gas holdup conditions. The combination of Genagen[®] frother with the fatty acid soap collector creates an interfacial environment that enhances both collision probability and attachment strength between bubbles and apatite particles.

The mechanism behind this enhancement involves the formation of mixed adsorption layers at the bubble–particle interface. The collector molecules provide the primary hydrophobic interaction with the apatite surface, while the surfactant molecules stabilize the bubble structure and modify the local hydrodynamic environment. This combination results in stronger and more stable bubble–particle aggregates that are less susceptible to detachment during transport to the froth phase.

Furthermore, the controlled gas holdup conditions ensure that the bubble size distribution remains within the optimal range for fine particle flotation. The balance between collision probability (favored by smaller bubbles) and transport efficiency (favored by larger bubbles) is achieved through careful control of the gas holdup, which, in turn, is influenced by the air flow rate and surfactant concentration.

4.5. Implications for Industrial Applications

The results of this study have significant implications for the industrial processing of low-grade phosphate ores. The ability to achieve economically attractive results (P_2O_5 grade > 30% and recovery > 60%) through gas holdup optimization represents a cost-effective approach to improving flotation performance. Unlike capital-intensive

solutions such as equipment replacement or circuit redesign, gas holdup optimization can be implemented through relatively simple adjustments to operating conditions and reagent dosages.

When compared to conventional flotation cells operating under similar conditions [32,33], the optimized column flotation process demonstrated superior performance metrics. The enhanced performance can be attributed to the controlled gas holdup environment and the inherent design limitations of the conventional cells [34].

The statistical models developed in this study (Equations (4) and (5)) provide valuable tools for process control and optimization in industrial settings. These models can be used to predict flotation performance under various operating conditions, allowing operators to make informed decisions about process adjustments. The high correlation coefficients ($R^2 > 0.98$) indicate that the models accurately capture the relationships between operating variables and flotation responses, making them suitable for implementation in process control systems.

The conditions currently used in processing plants for low-grade phosphate ores vary significantly depending on ore characteristics, plant design, and operational constraints. Considering the variability in industrial conditions and the limitations of conventional flotation technology, this research was specifically designed to evaluate how process variables and chemical dosages influence gas holdup and its correlation with column flotation performance. The systematic approach allows for the development of appropriate conditions that can be adapted to different industrial scenarios.

5. Conclusions

This study successfully investigated the influence of gas holdup on column flotation performance for fine particles of low-grade apatite ore, quantifying the effects of operating variables and reagent dosages on P_2O_5 grade and recovery. Gas holdup values greater than 23.5% were identified as the critical threshold for simultaneously achieving the desired P_2O_5 grade ($>30\%$) and recovery ($>60\%$), providing a clear operational target for industrial implementation. Surfactant addition substantially enhanced gas holdup by reducing bubble coalescence, with mineral particles increasing gas holdup by 2–3 times compared to air–water systems. The best performance was achieved with fatty acid soap collector at 175 g/t, gelatinized cornstarch depressant at 450 g/t, Genagen[®] surfactant at 11 ppm, and an air flow rate of 159.9 L/h. These conditions demonstrated the importance of balanced reagent interactions, with excessive collector or surfactant dosages reducing selectivity through non-selective gangue flotation. Empirical models with high correlation coefficients ($R^2 > 0.98$) were developed to predict flotation performance under various operating conditions, offering a low-cost optimization strategy through equipment adjustment rather than capital investment. The comprehensive understanding of gas holdup mechanisms and reagent synergistic effects provides a foundation for optimizing flotation circuits processing low-grade phosphate ores, with future research focusing on scaling up these findings to industrial conditions and investigating their applicability to other mineral systems.

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Article

The Effect of Particle Size and Dodecylamine Concentration on the Flotation of Lepidolite in Alkaline Medium

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Abstract: Currently, lepidolite is considered an important natural alternative for obtaining lithium, given the difficulty in processing other species containing this metal. However, its mechanical preparation and beneficiation present considerable challenges and play a critical role in its efficient separation by flotation. This study explores the effect of particle size and dodecylamine concentration during flotation in a laboratory Denver cell. The results indicate that particle size significantly affects the finding in which the optimum was $-90 + 75 \mu\text{m}$, with a separation efficiency of 94%, and with only $2.067 \times 10^{-5} \text{ M}$ of dodecylamine (DDA) (5 g/t) at pH 11.0. The hydrophobicity of lepidolite was generated by the effect of the chemisorption of the cationic collector and the FTIR results indicate detection of the characteristic bands of the adsorption of DDA to the surface of lepidolite.

Keywords: lepidolite; FTIR; hydrophobic; dodecylamine; particle size

1. Introduction

Lithium (Li) is an essential metal for humans. It is widely used in all electronic devices that use Li^+ ion batteries, and its demand is expected to continue increasing [1,2]. Currently, brines are the largest source of lithium extraction. A large percentage is found in countries such as Chile, Argentina, Australia, Canada, China, and Zimbabwe, which lead the extraction of lithium from these non-renewable sources. Therefore, obtaining this element and its compounds, such as LiCO_3 , is assured [3]. However, it is necessary to consider that lithium production in 2024 increased by 18% and that this trend will continue in the following years [4,5], so alternative solid natural resources, such as the crystalline minerals described in the literature, must be sought and processed [6].

One of these lithium minerals is lepidolite, with the chemical formula $\text{K}(\text{Li},\text{Al})_3(\text{Al},\text{Si})_4\text{O}_{10}(\text{OH},\text{F})_2$ and with a specific gravity of 2.9. This is a mica mineral, where the elemental Li content is variable; it ranges from 1.39% to 3.58% (from 3.0 to 7.7%

as Li_2O), has a hardness between 2 and 3 on the Mohs scale, and is much lower than other species such as spodumene, petalite, amblygonite, and eucryptite, which have a hardness of around 6.0. The gangue minerals that accompany lepidolite are mainly calcite, muscovite, feldspars, and quartz, which need to be separated by the most commonly used method for mineral concentration [6,7].

Flotation is the most widely used beneficiation process for concentrating lithium minerals contained in pegmatites; it is especially applicable to minerals of complex chemical nature or low grade. Furthermore, it should be noted that the difference in specific gravity between valuable species and gangue is too limited to require gravimetric separation [6,8]. For this reason, direct or reverse flotation has been used to concentrate lithium species. In the latter, sterile solid phases emerge in the froth generated during the flotation process using cationic collectors, while the minerals of interest remain in solution and represent the tailings [9,10].

It has been reported that the use of mixtures of anionic and cationic collectors, such as sodium oleate (NaOL) and dodecyl ammonium chloride (DTAC), at a respective molar ratio of 9:1, generates high selectivity for lithium ore flotation with respect to feldspars, indicating that NaOL adsorbs on the lithium-containing solid more than on the feldspar, while DTAC enhances this adsorption phenomenon [11].

The importance of lithium as a rare and precious metal has been previously described and is the result of its outstanding physical and chemical properties. It plays an essential role in various industries such as nuclear energy, pharmaceuticals, and lithium batteries [1,11]. This consideration has allowed the synthesis and testing of new collectors, such as hexyloxypropylamine (HPA) and N-dodecyliminodiacetic acid (DIDA). The authors indicate that a respective 1:3 molar mixture of HPA:DIDA produces a concentrate with 85.71% lithium mineral. It is indicated that HPA adsorbs to the surface through hydrogen bonds, while DIDA adsorbs by chemisorption [10].

Typical collectors used in lepidolite flotation described in the literature are, for example, stearyl trimethyl ammonium chloride (STAC), Aeromine 3000C, and Armeen 12D, generally employed at pH 3 and with dosages of 200, 350, and 500 g/t, respectively. The best selectivity of these collectors is achieved at acidic pH and with high collector ratios [12–14].

Lepidolite flotation is carried out at pH 2 using a STAC cation collector because the mineral surface exhibits stronger electrostatic interactions. Zeta potential analysis has determined that the point of zero charge, or isoelectric point, for lepidolite minerals is found at pH 2.5; that is, lepidolite particles below pH 2 exhibit a positive zeta potential, while at pH values above the isoelectric point, the lepidolite zeta potential increases to a negative value [12,13].

The highest lepidolite separation efficiency with the STAC collector is reported at 76.3%, while the Armeen 12D has limited potential due to its low water solubility. However, with a collector dosage of 500 g/t, lepidolite recovery is 91.51%; the concentrate has a lithium content of 1.96% [15]. The use of cationic collector mixtures in the flotation of the lepidolite contained in gravity concentration waste allows for a lithium mineral recovery of 70.37% and a concentrate grade of 4.12% lithium when compared with 40% recovery and a grade of 3.5% when using only an amine-type collector [16]. The lepidolite surface is depressed by the dosage of sodium sulfide Na_2S and starch, while sodium silicate and lithium sulfate can be used as surface activators [17].

The lepidolite surface is depressed by the dosage of sodium sulfide Na_2S and starch, while sodium silicate and lithium sulfate can be used as surface activators [17]. It has been previously established that lepidolite can be floated using cationic amine collectors. However, other parameters are required to obtain good flotation properties of lepidolite,

such as those investigated in this research, such as particle size, collecting agent dosage, and particle size, among others. As a first step, flotation with single-phase minerals was carried out to determine their behavior in the presence of different collector dosages and particle sizes at alkaline pH 11.

It has previously been reported that efficient lepidolite flotation is also related to pulp density and grinding fineness. Therefore, to improve metallurgical results, lepidolite flotation should be performed with a low pulp density. Furthermore, decreasing particle size improves recovery. Primary amines, such as dodecylamine (DDA or DA), are used for lepidolite flotation. Using amine-based collectors, lepidolite exhibits good flotation properties over a wide pH range, from 2 to 11. Flotation of lepidolite with dodecylamine at pH 3 requires high DDA concentrations, for example, 350 g/t [18].

Once a collector that acts efficiently in flotation is identified, it leads to the optimization of the lithium mineral separation process, as in the work where fatty acid (FA) was used as a collector. Lithium recovery improves by conditioning a high-density pulp (high percentage of solids, 60%), pH, residence time, and collector dosage. In this way, it has been found that the use of 625 g/t of FA at an initial pH of 8.25 helps to obtain a concentrate with 90% recovery and >5.5% Li₂O grade [19].

Notwithstanding the relevant findings reported previously, most of the research on lithium mineral beneficiation has focused on the spodumene species contained in pegmatites and, though scarcely, on the solid crystalline phase of lepidolite [9,19], using expensive collectors not available on a large scale. In addition, factors such as particle size, pH, and collector concentration must be taken into account. Therefore, this research paper addresses the effect of dodecylamine collector dosage at very low concentrations, as well as the role of particle size in the flotation separation of lepidolite mineral at alkaline pH. The solids obtained in the concentrate were characterized by FTIR. These are novel topics that have not been addressed by other researchers.

2. Materials and Methods

2.1. Mineral, Reagents and Equipment

A lepidolite-type lithium mineral composed of a single piece of approximately 100 g with a physical appearance consisting of a majority purple phase was obtained from the state of Sonora, México. The crystalline solid was dry ground in a manufacture Lavallab Laval, Quebec Canada automatic agate mortar, model Pulverisette 2. All of the pulverized mineral was separated by particle size by wet sieving, using water and a series of Tyler brand sieves, using particle sizes of 37, 45, 53, 75 and 90 microns (µm).

The mineral's elemental chemical composition was analyzed using laser-induced breakdown spectroscopy (LIBS) on a Keyence EA 300 VHX series instrument (KEYENCE CORPORATION OF AMERICA, Itasca, IL 60143, USA). Table 1 shows the average of 16 LIBS measurements.

Table 1. Elemental chemical analysis (%) of lepidolite mineral.

Mineral	Elemental Composition (%)					
	O	Si	F	Al	K	Li
Lepidolite	54.5	16.0	9.8	9.8	8.3	1.6

For lepidolite mineral flotation tests, pine oil C₁₉H₁₇OH and 98% dodecylamine (DDA) C₁₂H₂₇N with low water solubility (0.018 g/L) were used as frother and cationic collector,

respectively. A 2 M sodium hydroxide solution was used to regulate the alkaline pH of the pulp. Deionized water was used in all tests.

Prior to flotation tests, the mineral particles were analyzed using the instrumental technique of X-ray diffraction in INEL brand Equinox 2000 equipment, using an operating current and a voltage of 20 mA and 30 kV, respectively, from 5° to 90° with a step speed of 0.02 and a cobalt radiation source with a wavelength of 1.789010 Å and an analysis time of 15 min. The determination of the phases was carried out with the Match 2.1 software and a PDF2 database.

The morphology, particle size, and semiquantitative chemical composition of the lepidolite mineral solids were identified using a Thermo Scientific Phenom scanning particle XTC scanning electron microscope equipped with a silicon drift detector (SDD) used for the chemical determination of the elements comprising the sample. It should be noted that this technique does not allow the detection of Li and that the equipment is located at Gerdau Corsa S.A. in Sahagún, Hgo., México. The pulverized mineral was analyzed by scanning electron microscopy (SEM) to identify the morphology of the lepidolite particles and their semi-quantitative chemical composition.

The infrared spectra were recorded in a Perkin Elmer Spectrum GX spectrometer (Revvity Inc. Waltham, MA, USA), (400–4000 cm^{-1} ; 2 cm^{-1} resolution). Samples of 0.01 g were mixed with 0.1 g of binder (infrared grade KBr), compressed into pellets (hydraulic press), and immediately analyzed. The spectral band identification was carried out by comparison with a spectral database and with absorption bands reported in the literature.

During the flotation pulp conditioning stage, the pH and oxidation reduction potential (ORP) (mV) are monitored at each chemical modification using a Thermo Scientific Orion 3 Star potentiometer. To the measured value, +242 mV are added to present the data in reference to the standard hydrogen electrode (SHE) [20].

The weighing of all substances and the concentrate-receiving containers were carried out on an Ohaus precision analytical balance; calibrated micropipettes were used to measure volumes. Lepidolite flotation tests were performed on a laboratory flotation machine and a 1 L Denver brand stainless steel sub-aerated cell equipped with a revolutions per minute (RPM) meter. The equipment was operated at 1200 RPM. Air was introduced into the cell through a suction valve, driven by the movement of the impeller, located at the bottom of the cell along with the diffuser.

2.2. Experimental Procedure

Each lepidolite flotation test began with the conditioning stage, in which 1 L of distilled water and 4 g of mineral of $-90 + 75 \mu\text{m}$, $-53 + 45 \mu\text{m}$, and $-37 \mu\text{m}$ were added to the cell in individual tests, evaluating $\text{C}_{12}\text{H}_{27}\text{N}$ concentrations of 2.697, 5.395, and 8.092×10^{-5} M. Once the collector is in the flotation pulp, the pH is adjusted to 11.0 with 2 M sodium hydroxide, and, finally, the frother is added— 2.29×10^{-4} M of pine oil—to give stability to the bubbles formed.

During conditioning and with each change in pulp chemistry, the pH and redox potential (mV) were measured and recorded, allowing a conditioning time of 5 min for each change. Once the conditioning stage was completed, the flotation test began, aerating the cell at the predetermined times of 0.5, 1, 2, 4, 6, 8, and 10 min. At each flotation stage, the foam generated in the cell was poured off using a rubber accessory, and the concentrate was received in a pre-weighed inert plastic tray; this was undertaken for each planned flotation time.

The water was allowed to evaporate from the wet concentrate at room temperature. The plastic container containing the floated mineral was then reweighed, and the exact

amount of concentrated mineral in grams under each flotation test condition was obtained by calculating the difference in weight. These were converted to a percentage using Equation (1).

$$\% \text{ Flotation Recovery} = \frac{CH_M - CH_v}{C} \times 100 \quad (1)$$

where CH_M is the weight of the tray or container containing the concentrated mineral at each preset flotation time. In total there were 7 time periods used to obtain the concentrate (0.5, 1, 2, 4, 6, 8, and 10 min). CH_v is the weight of the empty container without mineral, which was measured in order to obtain the precise weight of the floated mineral, discarding the mineral losses that could occur if it were removed from the tray. C is the mineral head used—in this case 4 g per test—and 100 expresses the percentage of the floated mineral. In this way, the flotation results are graphed for each time period. The reason for using this small sample size is to evaluate the collector's adsorption on a lepidolite sample with a single, predominantly crystalline phase using FTIR. This would not be possible if a mixture of minerals, as commonly found in nature, were used.

Each test was performed in duplicate, yielding similar results. Therefore, the average of the two tests was used to generate the corresponding graphs and perform the FTIR surface analysis. Error bars are also included for each of the flotation recovery graph points. The redox potential, and pH were graphed to show the behavior of each variable during conditioning and at the end of the flotation test. The potentiometer was calibrated before each test session. The powders obtained in the concentrate were characterized by Fourier transform infrared spectroscopy to determine the surface state of the particles obtained in the concentrate.

3. Results and Discussion

3.1. Mineral Characterization

Lepidolite mineral particles of $\sim 37 \mu\text{m}$ were characterized by X-ray diffraction, with this fraction being representative of the entire sample. Figure 1 shows the obtained spectrum; the characteristic peaks of this lithium phase are observed, identified the species with the International Centre for Diffraction Data (ICDD) database. The solid corresponds to lepidolite with a monoclinic crystal structure. X-ray diffraction (XRD) analysis shows that lepidolite is the only major crystalline phase. The characteristic peaks of the lithium phyllosilicate mineral correspond to the lepidolite components with the following formula: $\text{K}(\text{Li},\text{Al})_3(\text{Al},\text{Si})_3\text{O}_3(\text{OH},\text{F})_2$.

It should be noted that SEM does not detect lithium, though the contents of the associated elements can be determined. Figure 2 shows an SEM micrograph, representing a general view of the lepidolite particles, which have a flaky, scaly morphology [6]. This micrograph shows particles of around 45 microns, the largest in size; in addition, they have microparticles of lithium mineral adhered to them due to electrostatic attractions. It is even observed that the micrometric particles tend to separate into thin sheets of lepidolite and tend to orient themselves preferentially.

This predominant arrangement is with the narrowest surface facing upward, with even the smallest particles, less than 45 microns, exhibiting this behavior. This mica-like morphology is indicative and is a principal characteristic of the lithium mineral (lepidolite). The mineral particles shown in the scanning electron microscopy micrograph in Figure 2 have an irregular, smooth-edged morphology. They exhibit perfect cleavage, elastic toughness, and belong to a variety of the mica family [18].

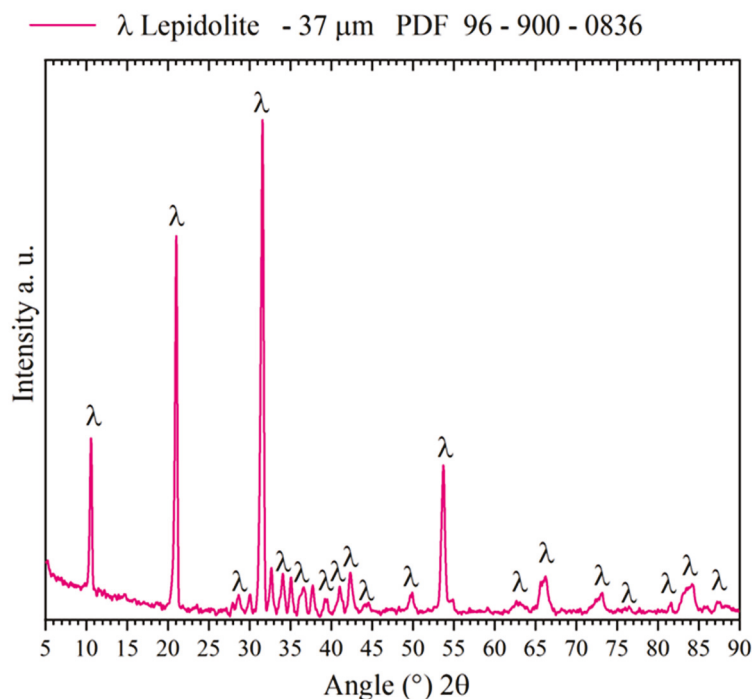


Figure 1. X-ray diffraction spectrum of the lepidolite mineral –37 μm .

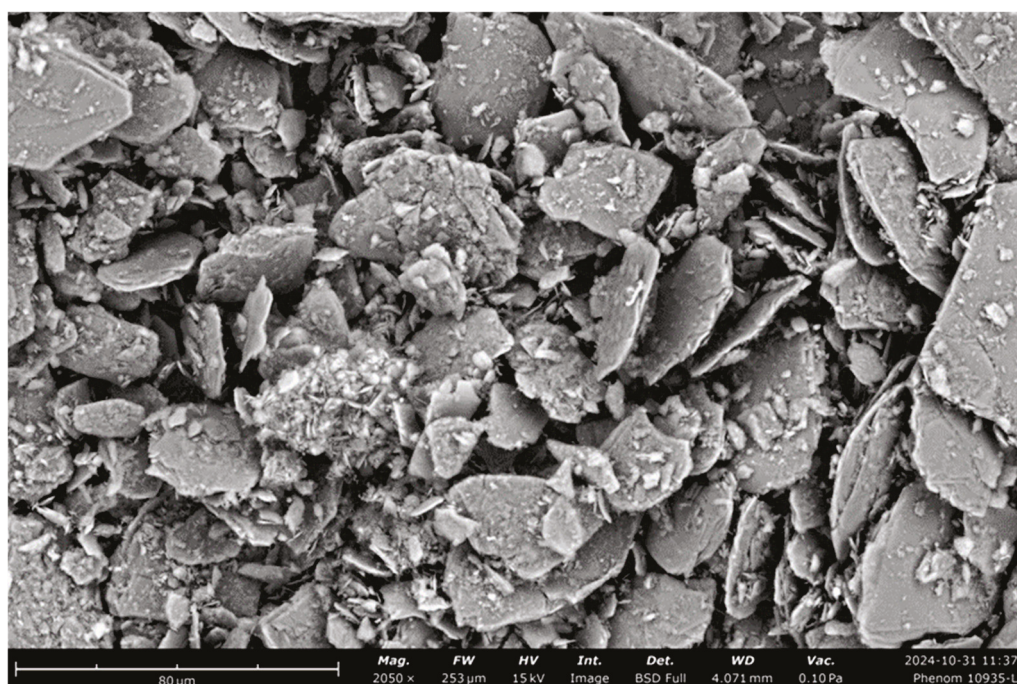


Figure 2. SEM micrograph of the lepidolite mineral at 2050 $\times$, with backscattered electrons.

Figure 3A shows the EDS spectrum, Figure (B) shows the SEM micrograph of the analyzed area, and Figure 3C shows the semi-quantitative chemical analysis; the latter shows the presence of the characteristic elements of lepidolite, such as oxygen with 45.2%. It is worth mentioning that silicon (19.8%), aluminum (12.3%), potassium (10.2%), and calcium (0.4%) in the crystalline structure of lepidolite are forming oxides, such as SiO_2 , Al_2O_3 , K_2O , and CaO , respectively.

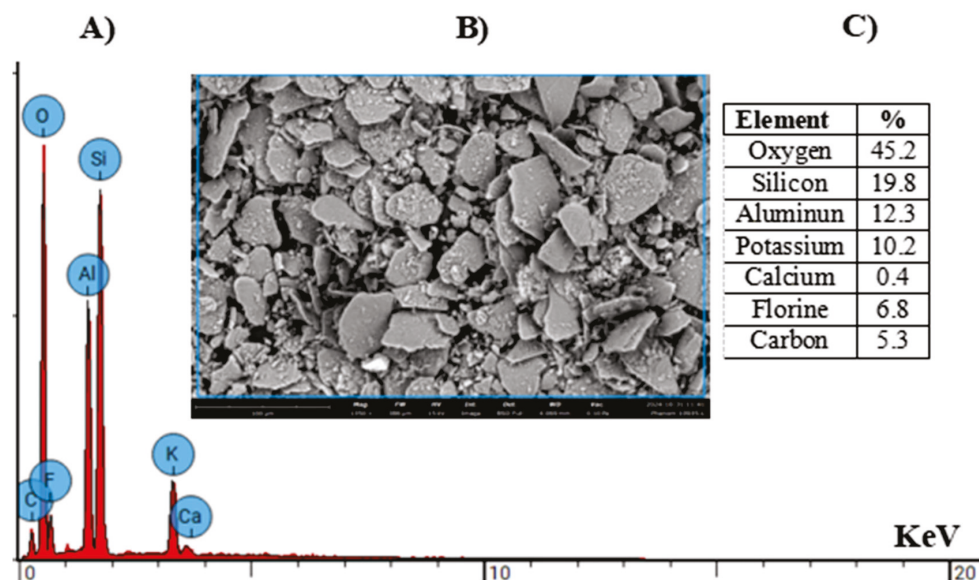


Figure 3. (A) EDS spectrum, (B) SEM micrograph, and (C) semi-quantitative chemical analysis of the lepidolite mineral.

The results, with regard to fluorine, correspond to those reported in the literature, indicating a proportion of 6.8% [18,21]. It is expected that the chemical compositions of the LIBS technique do not correspond to those of EDS because calcium and lithium are not considered in both.

Figure 4 shows the infrared (IR) spectrum of lepidolite particles with a particle size of $-37\ \mu\text{m}$. It is worth mentioning that this is a fresh surface without any treatment; the IR absorption bands presented are at $1630\ \text{cm}^{-1}$, which corresponds with the asymmetric vibration of the O–H bonds of the OH^- ion that are the result of the absorption of water molecules on the surface of the lepidolite particles.

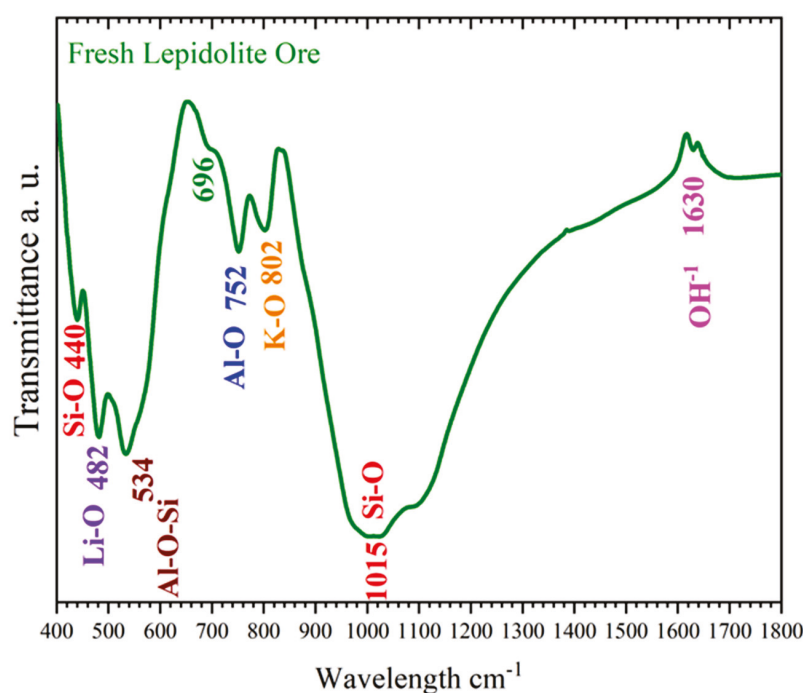


Figure 4. FTIR infrared spectrum of untreated lepidolite particles $-37\ \mu\text{m}$.

The signals at 440 cm^{-1} and 1015 cm^{-1} correspond to the Si–O bonds in silica. The lithium bonding band forming Li–O is assigned to the peak at 482 cm^{-1} . The values of 534 cm^{-1} and 752 cm^{-1} are assigned to the Al–O and Al–O–Si bonds, respectively and the signal at 802 cm^{-1} is attributed to K–O bonds, which is consistent with findings in previous research [22–26].

3.2. Lepidolite Flotation with DDA: Effect of Particle Size

Figure 5 illustrates the relationship between lepidolite recovery and dodecylamine cation concentration ($\text{C}_{12}\text{H}_{25}\text{NH}_3^+$), evaluating molarities of 2.697 , 5.395 , and $8.092 \times 10^{-5}\text{ M}$ for a particle size of $-37\text{ }\mu\text{m}$, a pH of 11.0, and a pulp potential of around $+35\text{ mV}$, which is a slightly oxidizing value that is close to reducing potentials, i.e., less than zero or negative.

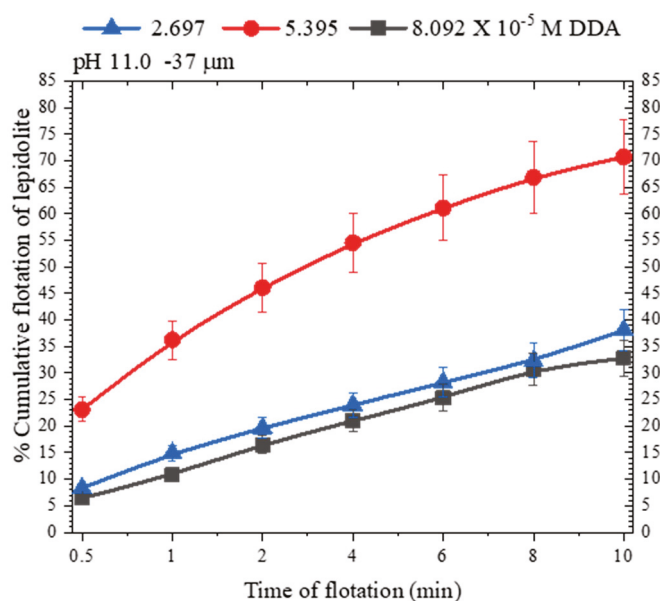


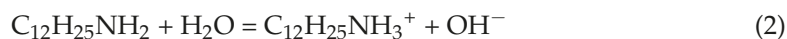
Figure 5. % Cumulative flotation of lepidolite as a function of time for particles $-37\text{ }\mu\text{m}$ pH 11.0.

The flotation of lepidolite particles at $-37\text{ }\mu\text{m}$ improves with collector concentration and processing time; for example, when using $5.395 \times 10^{-5}\text{ M}$ (10 g/t of $\text{C}_{12}\text{H}_{25}\text{NH}_3^+$), the maximum cumulative recovery % in 10 min of experimentation was 70.69%.

This relatively low separation efficiency is attributed to the partial hydrophobicity generated by the electrostatic interaction and hydrogen bonds described above [13,18]. This partial hydrophobicity exists between the mineral surface and the $\text{C}_{12}\text{H}_{25}\text{NH}_3^+$ ion and is promoted by the morphology of the lepidolite-flake-like particles, which, despite their small size, maintain their micaceous exfoliation, which makes the interaction between the collector and the mineral surfaces difficult. This dual adsorption mechanism allows for the selective separation of lithium minerals present in alkaline or acid flotation pulp; dodecylamine is preferentially adsorbed on lepidolite. It has been reported in the literature that alkaline conditions favor the recovery of larger particles [1,6,13].

Increasing the dodecylamine concentration to $8.092 \times 10^{-5}\text{ M}$ (15 g/t $\text{C}_{12}\text{H}_{25}\text{NH}_3^+$) leads to a decrease in lithium mineral recovery, as shown in Figure 5. Experimentally, it we find that the thickness of the froth bed on the surface of the flotation cell increases, that the bubble–particle aggregate that accumulates in the froth delays its exit, and that the effect of the movement of the pulp around the froth bed causes the release of the collected particles that are returned to the pulp. Additionally, we find the influence of a more hydrated froth, containing a lower proportion of particles. These observations agree with the findings of other investigations [1,18,21].

It is noted that the dissolution reaction of dodecylamine in water increases the pH of the pulp by forming OH^- ions, which is a result of the decomposition of an amino group, as indicated by reaction 1. For this reason, the flotation pH selected to carry out the flotation in this experiment was 11.0. However, it has been described in the literature that dodecylamine has the power to collect lepidolite in both alkaline and acidic media [1,6,8]. It is worth mentioning that DDA has limited solubility in water [27].



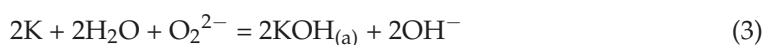
For example, lepidolite flotation at acid pH (3.0) with a combination of the Gemini surfactant hexanediyl- α,ω -bis (Dimethyldodecylammonium bromide) (HBDB) and dodecylamine is reported in the literature, with the authors reporting optimum concentrations of 150 g/ton and 300 g/ton, respectively [28]. In contrast, in the present work, particles of $-37 \mu\text{m}$, pH 11.0 and $5.395 \times 10^{-5} \text{ M}$ (10 g/t) are used, that is, very dilute concentrations of DDA and a lepidolite flotation of 70% is obtained, as observed in Figure 5.

Due to the physicochemical characteristics of the lepidolite mineral, its surface is hydrophilic in nature; thus, its floatability is limited. Further separation of this phase will occur by inverting its surface conditions to a hydrophobic surface, as described in the literature [21]. Laboratory tests showed that the separation of a single phase of lepidolite mineral depends not only on the pH and concentration of the collector but also on the particle size.

For this reason, the effect of lepidolite particle size was evaluated. Figure 6 shows the curves of % cumulative flotation as a function of processing time for particles $-53 + 45 \mu\text{m}$. For example, using 2.697 and $5.395 \times 10^{-5} \text{ M}$ of DDA, proportions of 59.8 and 54.5%, respectively, are achieved. This slightly larger particle size allows for higher recoveries compared with lepidolite solids of $-37 \mu\text{m}$, with these efficiencies obtained after 10 min of flotation. This occurs due to the weak adsorption of DDA to lepidolite micas, associated with the scarcity of active sites that facilitate this physicochemical phenomenon, as previously described [21,23].

With the increase of the DDA concentration in the flotation pulp to $8.092 \times 10^{-5} \text{ M}$ (15 g/t), a pH 11, and with particles $-53 + 45 \mu\text{m}$, the recovery is significant, though it barely exceeds 71%. With regard to this, we have previous findings reported in the literature that the surface of lepidolite in alkaline pulps >10 has a more negative zeta potential, meaning that the increase of electrostatic interactions and hydrogen bonds between the cationic collector and the aluminosilicate structure of the lithium mineral would be expected [13,23]; however, for this particle size, the laminar morphology causes the interactions to remain in low proportion and the hydrophobicity is limited meaning that the recovery, in turn, remains at this average.

During the conditioning stage of the lepidolite flotation test with DDA, the pH and the oxidation-reduction potential (ORP) mV are monitored and referred to as the standard hydrogen electrode (SHE), which is obtained by adding +242 mV to the measured value [29]. Figure 7 shows the obtained behavior. It is observed that the addition of the mineral to the aqueous medium increases the pH. This is due to previous findings related to the oxidation of the potassium (K) contained in the surface of the lepidolite to potassium ion K^+ , forming aqueous potassium hydroxide KOH, as shown in reaction 2. This leaves the mineral surface with a negative character, where O_2^{2-} is the dissolved oxygen in the flotation pulp.



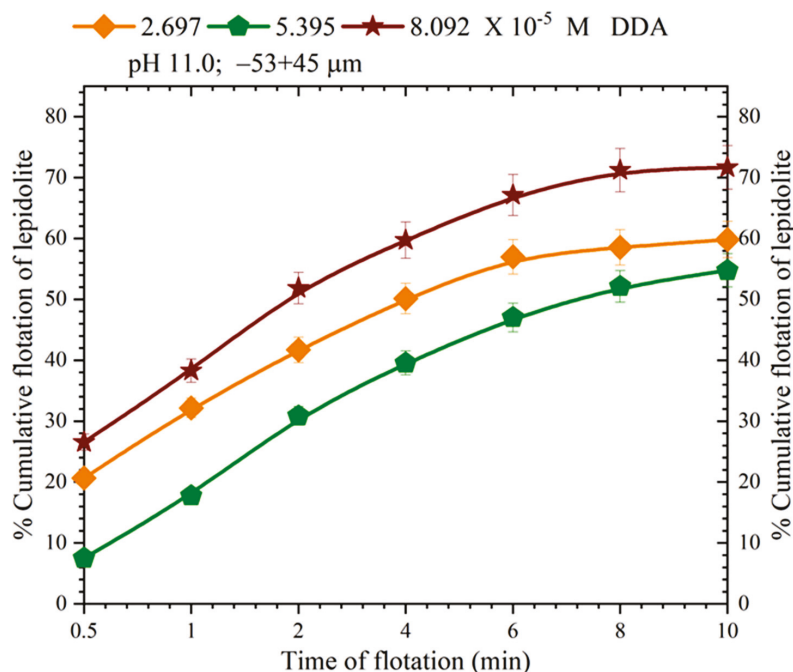


Figure 6. % Cumulative flotation of lepidolite as a function of time for particles $-53 + 45 \mu\text{m}$ and pH 11.0.

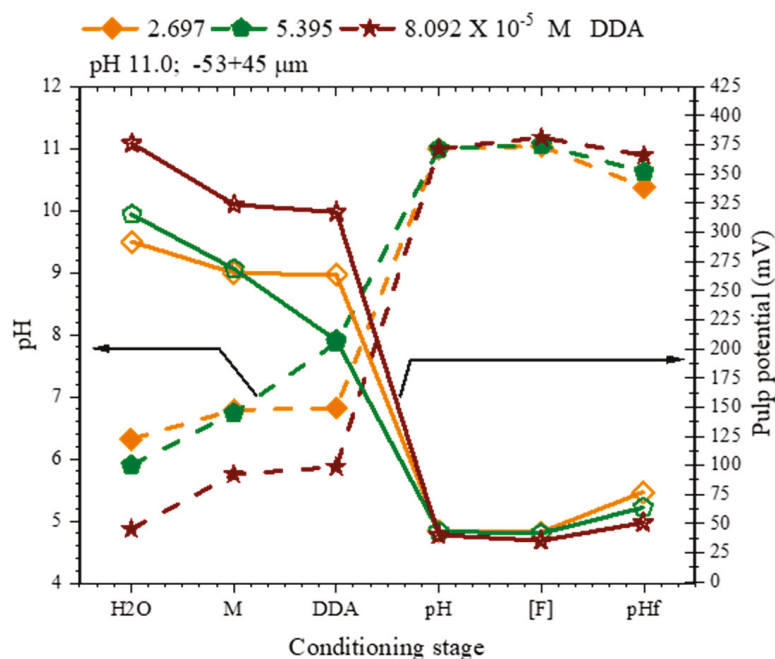


Figure 7. Behavior of pH and pulp potential (PP) Eh (mV) during conditioning, initial pH 11.0, $-53 + 45 \mu\text{m}$. [F] represents the frother agent.

Along with this, the active sites on the surface of the lithium mineral, such as silicon (Si) and oxygen (O), interact with hydroxyl groups formed in reaction 2, binding to the surface, and this contributes to the negative character measured by the zeta potential at alkaline pH, as described by previous authors [13,23].

From Figure 7 it can be observed that, after the addition of the mineral to the pulp and after five minutes of conditioning, the pH increases; subsequently, the pulp is brought to the flotation pH (11.0) with 2 M sodium hydroxide solution. The pulp potential (PP) at the beginning of the test is slightly oxidizing in nature, with a value of +35 mV and

with a greater tendency to reduce. At the end of the flotation experiment, the PP has a slight increase. Flotation of lepidolite with dodecylamine at an alkaline pH is carried out at potentials with minimal oxidizing conditions.

It is worth mentioning that, in all of the flotation tests carried out, a similar behavior of the pH and the pulp potential is maintained under conditions of particle size $-37\ \mu\text{m}$ and $-53 + 45\ \mu\text{m}$, with $8.092 \times 10^{-5}\ \text{M}$ of DDA, a pH 11.0, and a slightly oxidizing potential. The adsorption of DDA remains weak due to the effect of morphology and size, where the bubble–particle aggregate formed in the foam bed breaks before leaving the cell and the collected particles return to the pulp. As a result, the recovery does not increase from approximately 70%.

Figure 8 shows the results obtained in the flotation of lepidolite particles $-90 + 75\ \mu\text{m}$ at pH 11.0 and testing concentrations of 2.697, 5.395, and $8.092 \times 10^{-5}\ \text{M}$ of DDA (5, 10, and 15 g/t, respectively). A clear difference is observed when floating smaller particle sizes, where, for coarser particles, flotation is greatly favored. The morphology of the particles and their type of fracture, in the form of mica, positively influence the success of flotation for this particle size, even when the pulp is only present with 5 g/t of DDA, and, in the first 30 s of start-up, it is concentrated around 75%. The wide difference in reagent consumption of 5 g/t compared with that reported in the literature, where high collector concentrations are required, represents an important advantage at the industrial level of the process due to the high costs of flotation reagents.

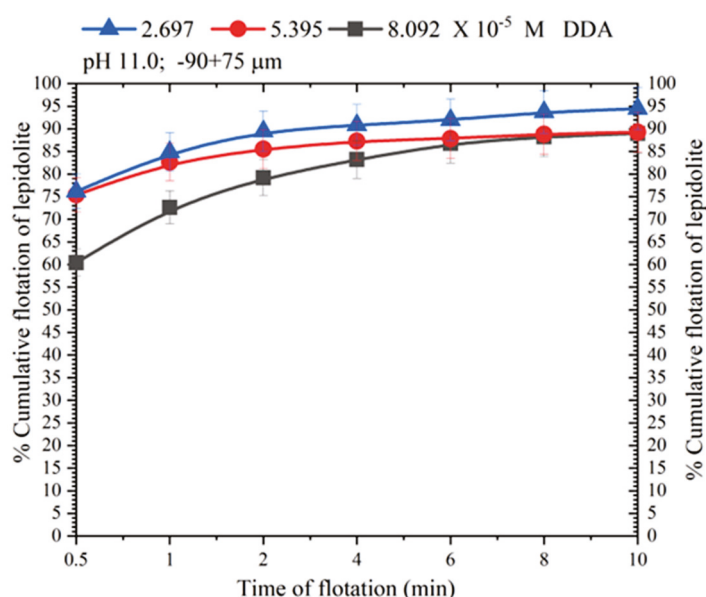


Figure 8. % Cumulative flotation of lepidolite as a function of time for particles $-90 + 75\ \mu\text{m}$, pH 11.0.

The cationic DDA collector adsorbed to the mineral surface reverses the properties from hydrophilic to hydrophobic, and the particles adhere to the bubbles, concentrating them relative to their aqueous medium. These results indicate the positive influence of performing flotation with particles larger than $75\ \mu\text{m}$, and are consistent with the findings of previous research, which indicates that larger lepidolite grains are easier to concentrate [9,13,27].

These characteristics highlight the importance of establishing specific procedures for each mineral and particle size, ensuring efficient and consistent separation of the desired species. Therefore, the degree of liberation of minerals is a factor. Proper enrichment cannot be achieved for ore that is not crushed/ground to the liberated size. In addition, it must

be considered that the grinding must be undertaken dry, using hammer mills. Production of lithium-bearing mineral concentrates such as lepidolite are closely related, firstly, to particle size, followed by collector concentration and flotation time.

Figure 9 shows the IR spectrum of untreated lepidolite particles of $-53 + 45 \mu\text{m}$ as well as of the solids obtained in the presence of $8.092 \times 10^{-5} \text{ M}$ DDA, $2.29 \times 10^{-4} \text{ M}$ pine oil frother agent, and spectrum pure reagent grade 99% Li_2CO_3 . This last spectrum serves as a reference for the signals detected in the IR spectra of lepidolite concentrated by flotation.

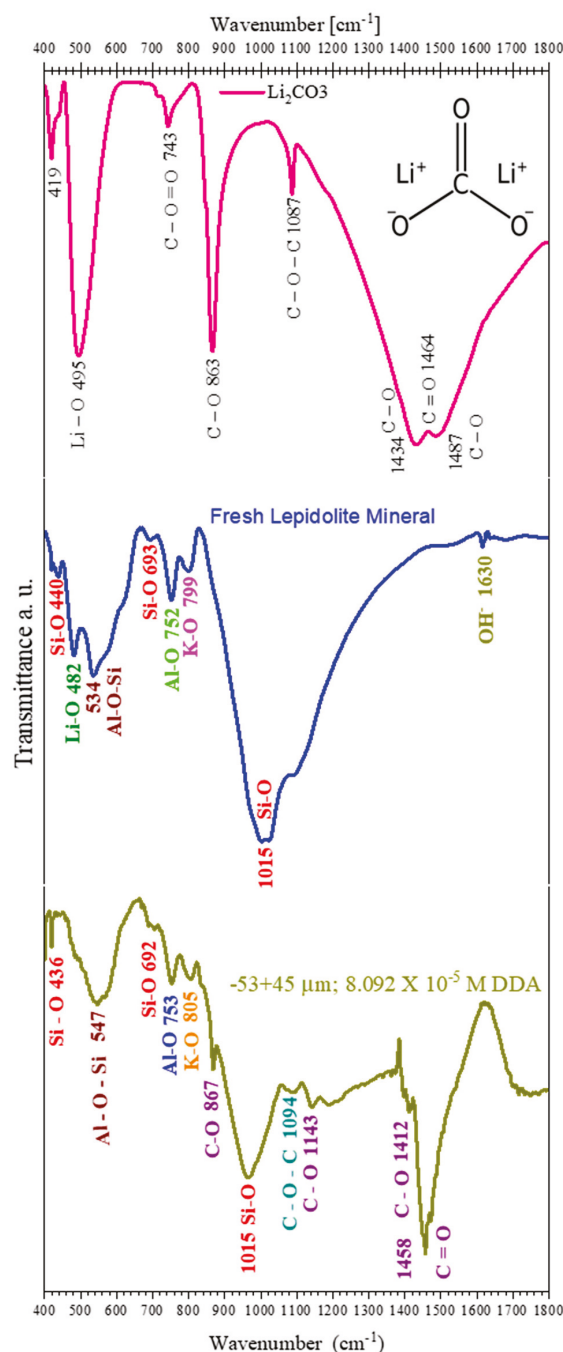


Figure 9. FTIR spectra of untreated lepidolite and $-53 + 45 \mu\text{m}$ particles concentrated with $8.092 \times 10^{-5} \text{ M}$ DDA (15 g/t) and Li_2CO_3 .

The IR spectrum of untreated lepidolite shows at 1015 cm^{-1} , 440 cm^{-1} , and at a lower intensity at 696 cm^{-1} , with the peaks corresponding to the asymmetric stretching vibration

of the Si–O tetrahedron. Meanwhile, the signal at 752 cm^{-1} is associated with the vibration of the Al–O bond corresponding to the octahedron of the lepidolite crystal structure. The bonding band at 534 cm^{-1} corresponds to the asymmetric vibration of Al–O–Si, as reported in the literature [30–32]. This spectrum also presents the characteristic peaks of the K–O and Li–O bonds at the vibration positions of 802 cm^{-1} and 482 cm^{-1} , respectively. It is worth mentioning that only in fresh untreated lepidolite was water adsorption of the O–H bonds of OH^- detected with the bending vibration at 1630 cm^{-1} . To analyze the behavior of the Li–O bond of lepidolite in the presence of DDA during flotation tests, the IR spectrum of reagent grade 99% Li_2CO_3 was obtained.

Figure 9 shows the characteristic peaks of lithium carbonate. Here, the band at 863 cm^{-1} of the C–O bond bending vibrations can be observed, as well as at 1464 cm^{-1} and with an adsorption shoulder at 1487 cm^{-1} , corresponding to the C–O asymmetric stretching vibrations. The band at 1087 cm^{-1} indicates the symmetric stretching vibration, while the band at 1434 cm^{-1} is assigned to the C–O asymmetric stretching, as described in the literature [30–32].

The previously described absorption bands in the IR spectrum of Li_2CO_3 correspond to internal vibrations of the isolated anion. The double degeneracy of the normal modes ν_3 (asymmetric stretching vibrations) and ν_4 (in-plane bending vibrations) is eliminated due to the decrease in the symmetry of lithium carbonate in the crystal lattice relative to the symmetry of the ideal CO_3^{2-} anion, as previously described [30]. The double band corresponding to the asymmetric stretching vibrations ν_3 is observed at 1434 and 1464 cm^{-1} . A band at 743 cm^{-1} can also be observed from the in-plane bending vibrations. In addition, the stretching vibration ν_1 is activated, giving rise to a small band at 1087 cm^{-1} . The bending vibration ν_2 gives a sharp band at 863 cm^{-1} . The bands observed in the IR spectra at 495 cm^{-1} and 419 cm^{-1} can be attributed to vibrations of the Li_2CO_3 quasicrystal reported in the literature [30].

After conditioning and flotation of the $-90 + 75\text{ }\mu\text{m}$ lepidolite particles and after drying the sample at room temperature, the powders were analyzed via FTIR, with the aim of detecting the characteristic adsorption bands of the collector; however, none of the floated products with the three different DDA concentrations for this particle size presented the characteristic peaks of dodecylamine-type collector adsorption, instead presenting only the peaks corresponding to lepidolite, indicating that the adsorption of DDA on the mineral surface was minimal. A similar situation has been reported previously [21,23].

Only in the IR spectra of the $-53 + 45\text{ }\mu\text{m}$ and $-37\text{ }\mu\text{m}$ lepidolite particles, concentrated by flotation, was DDA collector absorption detected. Figure 9 shows the IR of lepidolite particles #325 floated in the presence of $8.092 \times 10^{-5}\text{ M}$ (15 g/t) DDA. The characteristic bonding bands of lepidolite are observed in the IR spectrum at 419 cm^{-1} , 692 cm^{-1} , and 1015 cm^{-1} , corresponding to the Si–O tetrahedral bond vibration bands described in the literature [31,32]. Furthermore, the vibrations of the K–O bonds at 805 cm^{-1} of the Al–O bond are presented. Previously, it has been mentioned that the collector adsorption occurs primarily on the Al/Si–O sites of the lepidolite surface, making it hydrophobic [31–33], a condition favored by the pH modifier (NaOH), which is 11.0. It is worth mentioning that the addition of a frother agent after the addition of DDA was intended to stabilize the bubbles at the water–air interface and facilitate the transport of the particles to the concentrate.

It can be seen from Figure 9 that the band assigned to the Li–O bond vibration in this spectrum was not detected due to collector adsorption. As a first approach, the mechanism by which the Li–O bond signal does not appear in the IR spectrum of floated lepidolite in the presence of $8.092 \times 10^{-5}\text{ M}$ of DDA is the result of the collector preferentially adsorbing to the lithium of the Li–O bond, forming an adsorption layer on the rare metal. This

covalent bond is covered and not detected during the FTIR analysis, something which may also explain the reduction and elaboration of the oxide in such a way that the molecular vibrations are not detected in IR. This disappearance of the Li–O bond is attributed to the interaction of DDA with lithium due to electrostatic attractions. Similar behavior has been previously reported in the literature [31,32].

The intensity of the signal associated with the Al–O–Si bond, located at 547 cm^{-1} , diminishes. On the other hand, in the IR spectrum of lepidolite floated in the presence of $8.092 \times 10^{-5}\text{ M}$ DDA, the Al–O–Si bond is detected at 534 cm^{-1} , so the mechanism for the reduced intensity of the Al–O–Si bond is not linked to the competitive effect of DDA adsorption sites (Al/Si–O). The cationic amines, such as the dodecylamine (DDA), are then introduced to selectively adsorb onto the negatively charged lepidolite and form a negative zeta potential, as described in the literature. The mechanism is carried out by electrostatic interactions and hydrogen bonds, improving its hydrophobicity [23,29].

The faint bands at 867 cm^{-1} , 1143 cm^{-1} , and 1412 cm^{-1} represent the C–O bonds; on the other hand, the signals at 1093 cm^{-1} and 1458 cm^{-1} represent C–O–C and C=O, respectively. This indicates the adsorption of DDA to the mineral surface. These adsorption bands have been described previously [30,32]. In summary, the FTIR results show that the surface hydrophobicity generated by DDA adsorption to lepidolite particles alone does not guarantee mineral flotation; furthermore, it requires an optimal particle size to ensure maximum lithium mineral recovery.

4. Conclusions

This study investigated the activation mechanism of DDA in lepidolite flotation, analyzing the impact of cationic collector concentration and particle size at pH 11.0 on separation performance using flotation tests in a laboratory Denver cell. The characterization by EDXS, XRD, SEM, FTIR confirm that the mineral used for the study of the effect of particle size and dodecylamine concentration in the flotation of lepidolite in an alkaline medium corresponds to a lithium species of a single crystalline majority phase of lepidolite determined by XRD, with a lithium percentage of 1.6%. The characteristic elements contained in this species detected by LIBS are O, Si, F, Al and K, with percentages of 54.5, 16.0, 9.8, 9.8 and 8.3 respectively. The morphology of this mineral consists of fine particles, with a morphology of flakes or narrow-edged micas and a large surface area typical of a lepidolite mineral. FTIR analysis of the fresh untreated mineral presents the characteristic positions of bonds present in lepidolite minerals, such as Li–O, Al–O, Al–O–Si, K–O and Si–O, at 482 cm^{-1} , 752 cm^{-1} , 534 cm^{-1} , 802 cm^{-1} and 440 cm^{-1} , 1015 cm^{-1} respectively.

Particle size is a key factor for the success of lepidolite flotation. The best efficiencies are obtained when using sections of $-90 + 75\text{ }\mu\text{m}$ and, for all used concentrations of DDA— 2.697 , 5.395 and $8.092 \times 10^{-5}\text{ M}$ of dodecylamine (DDA)—the flotation recovery of lepidolite is greater than 90%, with the separation reaching 75% even after only 30 s of flotation. Particle sizes of $-53 + 45\text{ }\mu\text{m}$ and $-37\text{ }\mu\text{m}$ negatively affect the flotation process and the recovery decreases to values of around 31%.

FTIR analysis of the mineral floated in the presence of DDA generated superficial changes in the mineral due to the presence of C–O and C=O bonds located at the vibrational positions of 867 cm^{-1} , 1093 cm^{-1} , 1143 cm^{-1} and 1458 cm^{-1} , respectively, indicating the chemical adsorption and oxidation of the carbon bonds of the DDA, which changes the properties of lepidolite from hydrophilic to hydrophobic and makes its flotation possible. Regarding the Li–O bond, it does not appear in the floated mineral due to the effect of the electrostatic attraction between lithium and the dodecylamine collector, these being the main resulting mechanisms during the flotation of lepidolite with DDA.

The low consumption of collector reagent and the use of coarse grinding necessary to achieve the highest flotation efficiencies found in this research work contribute to the current state of knowledge on the separation of this phase and bring about a reduction in costs in reagent consumption and over-grinding at the industrial scale.

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Article

Effect of Frother Type on Surface Properties and Flotation Performance of Galena: A Comparative Study of EH, PPG250, and MIBC

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Abstract: The selection of suitable frothers in flotation processes plays a crucial role in controlling bubble formation, foam stability, and ultimately mineral recovery. Therefore, understanding the interfacial behavior of frothers is important to optimize flotation efficiency, especially for valuable sulfide minerals such as galena (PbS). In this study, the interfacial behavior and flotation performance of different frothers in PbS flotation were investigated with a particular focus on surface tension, bubble coalescence, foam stability, and flotation recovery. A high-purity crystalline PbS sample ($\approx 96.65\%$ PbS) obtained from Trabzon, Türkiye, was subjected to systematic experimental analyses including surface tension measurements, critical coalescence concentration (CCC) determination, dynamic foam stability (DFS) tests using the DFA100 analyzer, and micro-flotation experiments. 2-ethylhexanol (EH), polypropylene glycol 250 (PPG250), and methyl isobutyl carbinol (MIBC) were used as frothers, while potassium ethyl xanthate (PEX) was employed as a collector. The results revealed that EH had the highest surface activity (42.67 mN/m at 1000 ppm), and the lowest CCC value (~ 2 ppm) compared to PPG250 (~ 3 ppm) and MIBC (~ 8 ppm). According to the micro-flotation results, the flotation recovery gradually increased with increasing frother dosage; the highest recoveries were obtained with PPG250 (99.45%), EH (98.31%), and MIBC (95.17%). PPG250 and EH achieved higher flotation performance at lower dosages compared to MIBC. These findings highlight the critical role of molecular structure and interfacial properties in the effective selection of frothers for galena flotation.

Keywords: galena; flotation; surface tension; critical coalescence concentration; dynamic foam stability; frother selection; reagent optimization

1. Introduction

Flotation is a widely used separation method in mineral processing, particularly for the beneficiation of sulphide ores, and it also finds applications in sectors such as wastewater treatment and paper recycling [1–3]. The process relies on the attachment of hydrophobic particles to air bubbles, while hydrophilic particles remain in the liquid phase, making bubble formation and stability essential for efficiency [4–6]. In this context, froth flotation has become the most common method for concentrating sulphide ores [7], with its performance strongly influenced by the properties of reagents, especially frothers, which reduce surface tension, prevent bubble coalescence, and stabilize the froth phase [6,8,9].

Frothers also control bubble size and rise velocity, thereby playing a critical role in flotation kinetics and froth transport [10–13].

As the frother concentration increases in a flotation cell, the bubble size decreases. This is attributed to the reduction in interfacial tension and the stabilization of liquid films formed between colliding bubbles, preventing them from coalescing [13]. However, froth stability is an important parameter in terms of flotation performance. Studies have shown that even a slight decrease in froth stability can lead to a significant decrease in valuable mineral recovery [14,15].

Frothers are generally classified according to their chemical structures or functional properties [16]. However, frother selection is not limited to promoting foam formation alone; it also significantly affects flotation selectivity and recovery. Indeed, literature indicates that increasing frother dosage beyond a certain threshold can negatively impact flotation performance by reducing selectivity and delaying three-phase contact, thus reducing the probability of bubble–particle attachment [12,17–19]. This is especially critical where excessive frother–collector combinations can result in recovery of gangue materials instead of the target mineral, ultimately decreasing overall recovery [19–21]. In industrial flotation, a variety of frother types are employed beyond the commonly used alcohols. These include cyclic alcohols such as α -terpineol, phenolic mixtures like cresylic acid, alkoxy paraffins with high selectivity, and polyglycol-based frothers whose properties can be tailored by molecular weight. In some cases, dual-function surfactants are applied, while natural reagents like pine oil and emerging biosurfactants such as rhamnolipids represent cost-effective or environmentally friendly alternatives [16].

Various methods are available in the literature to determine the bubble coalescence. For example, Kracht and Finch [22] used ultrasound to determine bubble coalescence. Moreover, in another study, the effect of salts on bubble coalescence was investigated with the help of light intensities [23]. In another study, a McGill bubble size analyzer unit was used to determine the bubble coalescence in terms of Sauter mean diameter (d_{32}) for commercial and analytical chemicals [24]. Gungoren et al. [25] used a modified bubble–particle attachment timer unit to measure the CCC of MIBC in the presence of NaCl and CaCl_2 salts. And, recently, we modified the method used in the literature [23] and built up a unique setup to determine the CCC values for the frothers using a bubble column based on light adsorption [26].

In this context, comparative investigation of the interfacial behavior and flotation effects of frothers with different chemical structures is of great importance for process optimization. While previous studies have investigated the effects of frothers on bubble size [27,28], foam stability [29,30], or flotation efficiency [31,32], comparative studies that evaluate these interfacial properties together with flotation outcomes remain limited. In particular, most investigations have focused on single aspects of frother performance, often employing different mineral systems, experimental conditions, or measurement techniques, which makes direct comparison difficult. As a result, there is limited understanding of how structurally different frothers simultaneously influence surface tension reduction, suppression of bubble coalescence, stabilization of froth, and mineral recovery when evaluated under identical conditions. Addressing this gap requires a systematic experimental design that combines surface chemistry measurements with flotation testing. Therefore, the present study provides an integrated evaluation of three widely used frothers, namely 2-ethylhexanol (EH), polypropylene glycol 250 (PPG250), and methyl isobutyl carbinol (MIBC), by combining surface tension measurements, determination of the CCC, DFS tests, and micro-flotation experiments on a high-purity galena sample. In this way, the study not only compares the interfacial behavior and flotation performance of these structurally

different frothers within a single experimental framework but also helps to provide a clearer understanding of frother selection strategies in galena flotation. In the present study, three different types of frothers were evaluated in galena flotation, focusing on their effects on surface tension, bubble coalescence, froth stability, and mineral recovery. In the present study, three different types of frothers were evaluated in galena flotation, focusing on their effects on surface tension, bubble coalescence, froth stability, and mineral recovery.

2. Materials and Methods

2.1. Materials

The galena (PbS) sample used in the experimental studies was obtained in crystalline form from a mine located in Trabzon, Türkiye. The purity of the sample, determined by chemical analysis using atomic absorption spectrophotometry, revealed a lead content of 83.7%. Based on this result, the mineralogical composition of the sample was calculated to contain approximately 96.65% PbS. The crystalline sample was first ground in an agate mortar and then classified using 74 μm and 38 μm laboratory sieves (Retsch, Haan, Germany). To prevent oxidation, the classified sample was placed in a sealed sample bag filled with N_2 gas and stored in a desiccator. Potassium amyl xanthate (PAX, >90%, Green Chemical, Kocaeli, Türkiye) and potassium ethyl xanthate (PEX, >90%, Green Chemical, Kocaeli, Türkiye), which are commonly used collectors in galena flotation, were used in surface tension experiments to demonstrate their surface activity [33–35]. However, PEX was used as the collector only in the micro-flotation experiments. Polypropylene glycol 250 (PPG250) ($\geq 98\%$), methyl isobutyl carbinol (MIBC) ($\geq 99\%$), and 2-ethylhexanol (EH) ($\geq 99\%$) were used as frothers, while analytical grade hydrochloric acid (HCl, 37%) and sodium hydroxide (NaOH, $\geq 98\%$) were employed for pH adjustments.

2.2. Methods

2.2.1. Surface Tension Measurements

The surface tension measurements were carried out using a Krüss K6 Force Tensiometer (Krüss, Hamburg, Germany) based on the Du Noüy Ring Method. Solutions prepared at various concentrations were transferred into a 50 mL cylindrical container. A platinum-iridium ring was carefully immersed just below the air-liquid interface and then slowly withdrawn using the tensiometer's dynamometer. The measurement was recorded at the point where the liquid film detached from the ring. Before each measurement, the platinum-iridium ring was cleaned with analytical grade ethanol and flame-washed for 1 min to ensure complete removal of residues. All measurements were performed at room temperature ($23 \pm 1^\circ\text{C}$). Each experiment was conducted in triplicate to ensure reproducibility.

2.2.2. Bubble Coalescence Measurements

The critical coalescence measurements were conducted using the method proposed by Guven et al. [26], which is widely used in the literature [36,37]. In this method, a micro-flotation cell with a total volume of 155 cm^3 (30×220 mm) and frit pore sizes ranging from 10 to 16 μm was utilized. Nitrogen gas was introduced into the cell at a controlled flow rate of 50 cm^3/min . The experimental setup included a cold light source (Soif Optical Instrument Co., Shanghai, China), a light intensity detector (Thorlabs, Newton, NJ, USA), and a computer equipped with Optical Power Monitor software (Version 6.1) for data acquisition and analysis. The experimental setup operates on the principle that light emitted from the source passes through the solution within the micro-flotation cell, during which a portion of the light is absorbed by the solution before reaching the detector. The intensity of the transmitted light is then measured. The light beam was directed approximately

10 cm above the frit, which corresponds to the midpoint of the solution column. All measurements were repeated three times, and the average values were reported.

2.2.3. Dynamic Foam Stability Measurements

In this study, foam stability measurements were carried out using the KRÜSS Dynamic Foam Analyzer DFA100 (KRÜSS GmbH, Hamburg, Germany). This instrument is designed to measure foam formation and the stability of the generated foam in liquid systems. The device consists of a measuring cell, optical sensors that monitor the foam height, and a computer system for data acquisition and analysis. In the experiments conducted with the DFA100, the maximum foam height was used to determine the dynamic foam stability (DFS) of the frothers using Equation (1):

$$\Sigma = \frac{v_f}{Q} = \frac{H_{max} \cdot A}{Q} \quad (1)$$

Σ represents the dynamic foam stability (min), V_f is the foam volume (cm³), Q is the gas flow rate (cm³/min), H_{max} is the maximum foam height (cm), and A denotes the cross-sectional area of the column (cm²).

In the experiments, 50 mL of the prepared solution was transferred to a tempered glass column with an inner diameter of 40 mm and a height of 250 mm, and the system was started. Air was introduced at a flow rate of 0.2 L/min to generate foam and dispersed through a porous filter plate with pore sizes ranging from 12 to 25 µm. The foam generation phase was set to 60 s, and the foam height was recorded continuously during this time. After the 60 s foam formation period, the system automatically switched to the decay phase, where foam collapse was monitored for another 40 s. After all measurements, the data were processed using the integrated software. All experiments were conducted at room temperature (23 ± 1 °C). Each test was performed in three repetitions, and the average values were reported.

2.2.4. Micro-Flotation Experiments

Micro-flotation experiments were carried out using a 155 mL volume column with a ceramic frit with pore sizes ranging from 10 to 16 µm. In these experiments, a purified galena sample with a particle size range of −74 + 38 µm was used.

The flotation experiments were carried out at a 1% solids concentration (w/w) by adding an appropriate amount of galena sample to water. The suspension pH was adjusted to 9.00 ± 0.1 using NaOH and conditioned using a magnetic stirrer at 600 rpm for 1 min. This pH value was chosen because it represents an optimum condition for both xanthate–galena interactions and effective action of frothers [38,39]. Then, the desired amount of PEX was added, and the suspension was conditioned for 3 min. Finally, the frother was added and mixed for another 1 min. At the end of the conditioning period, the suspension was transferred to the flotation cell, and air was supplied at a flow rate of 50 cm³/min for 1 min to ensure mineral flotation. Each flotation test took approximately 6 min in total.

In the flotation experiments, the frother dosage was selected within the range of 1–1000 ppm. This range enabled observation of flotation behavior from insufficient frother levels to very high concentrations, helping to evaluate the performance of each frother under both typical and extreme conditions. It is known from the literature that frothers may be insufficient to significantly reduce bubble coalescence at very low concentrations (1 ppm), leading to larger bubble size, low flotation recovery, and poor froth stability [26,40,41]. Furthermore, at higher concentrations (100 ppm), frothers can cause excessive froth stability, leading to entrainment of gangue particles and reduced selectivity. On the other hand, extending the range to 1000 ppm provides a safety margin for determining potential overdose effects.

The choice of operating variables and their levels was based on optimum values reported in the literature for galena micro-flotation studies [35,42–45]. After flotation, the float and sink products were collected separately and subjected to gravimetric analysis, and the flotation recovery was calculated using Equation (2):

$$\frac{m_{ft}}{m_{fd}} \times 100 \quad (2)$$

where m_{ft} denotes the mass of the floated product, while m_{fd} represents the mass of feed. All flotation experiments were performed in triplicate to ensure statistical reliability.

3. Results and Discussion

3.1. Effect of Reagent Type on Surface Tension

The surface tension experiments were carried out for the reagents as a function of concentration from 1 to 1000 ppm (Figure 1). As seen in Figure 1, the results revealed distinct trends depending on the functional group of each reagent.

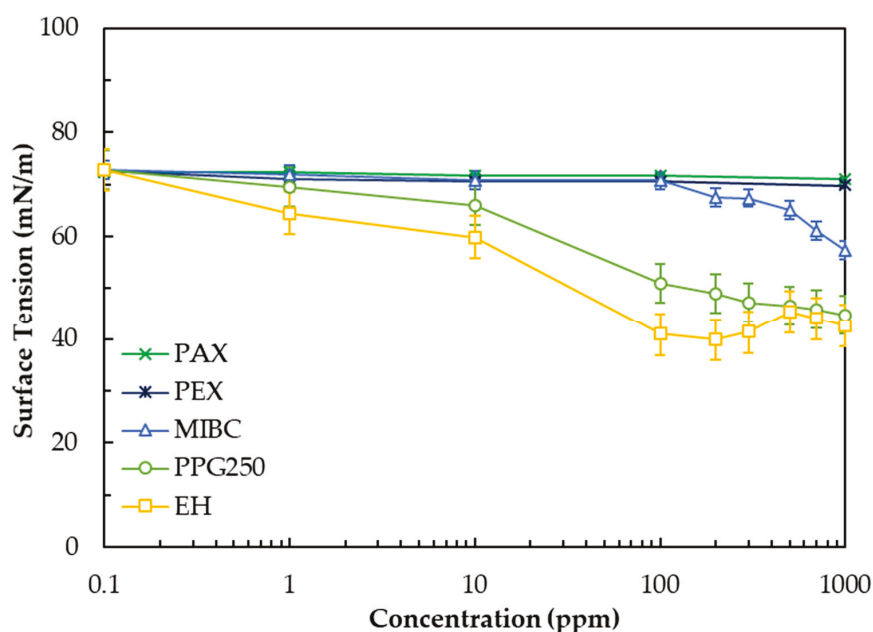


Figure 1. Surface tension of the reagents as a function of concentration.

Among the reagents tested, EH showed the most significant decrease in surface tension. The surface tension, which started from 64.8 mN/m at 1 ppm, decreased sharply to 59.83 mN/m at 10 ppm and reached 42.67 mN/m at 1000 ppm. This rapid decrease suggests that EH has a high affinity for the air–water interface, likely due to its short-chain, branched alcohol structure. Such compounds are known to adsorb rapidly and intensively at the interface, effectively reducing surface tension and increasing foamability in flotation systems [46,47].

Similarly, PPG250 gradually decreased surface tension as its concentration increased, and the values decreased from 69.4 mN/m at 1 ppm to 44.87 mN/m at 1000 ppm. Its amphiphilic and flexible polymeric chain enables the formation of stable interfacial films that delay bubble coalescence. Various studies [6,48] reported that PPG-type frothers provide moderate foam stability and a stable drainage performance. Furthermore, the study by Finch and Zhang [49] showed that the hydrophilic–lipophilic balance (HLB) and the H-ratio are the main factors affecting the CCC, and PPG frothers occupy an intermediate position on the HLB–CCC curve.

MIBC, on the other hand, showed a more moderate and delayed effect. The surface tension remained relatively unchanged up to 100 ppm (70.7 mN/m), while it gradually decreased at higher concentrations, reaching 57.4 mN/m at 1000 ppm. Using molecular dynamics simulations, Alvarado et al. [50] showed that MIBC molecules tend to adsorb less densely and more irregularly at the air–water interface compared to short-chain alcohols [46], leading to a slower and less efficient surface tension reduction. However, this feature can be useful in controlling froth height and mobility in industrial flotation applications.

In contrast, the xanthate collectors PAX and PEX showed minimal effect on surface tension, with values remaining almost unchanged across the entire concentration range. This is consistent with the known behavior of xanthates, which prefer to adsorb onto mineral surfaces rather than accumulate at the air–water interface. Several studies [51–53] have confirmed that xanthates show poor surface activity in aqueous systems and that their main role in flotation is due to chemical interactions with sulfide mineral surfaces rather than surfactant-like behavior [54]. As seen in Figure 1, no significant change was observed in the surface tension of PAX/PEX even at higher concentrations, indicating that the selectivity of PAX/PEX towards the mineral/water interface is quite low. Furthermore, as is known from the literature, there are a few carbon atoms in the hydrocarbon chain structure of xanthate molecules to reduce the surface tension [54].

3.2. Determination of CCC Values of Different Types of Frothers

Figure 2 shows the percentage of bubble coalescence as a function of frother concentration. Using the conventional 50% coalescence threshold to define the CCC [26], EH again emerged as the most efficient frother, with a CCC of approximately 2 ppm, followed by PPG250 (~3 ppm) and MIBC (~8 ppm).

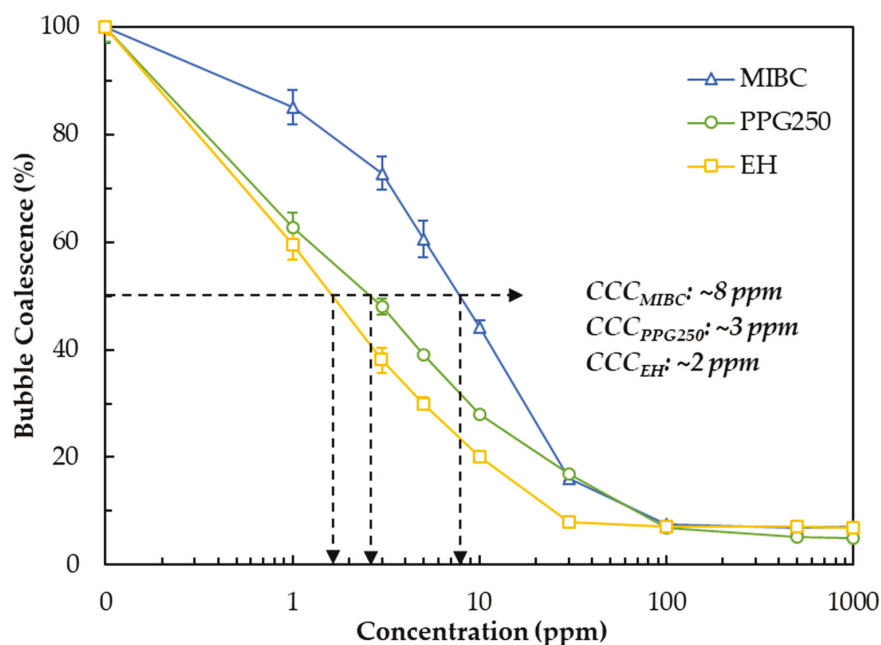


Figure 2. CCC values of frothers.

These CCC trends parallel the surface tension results, indicating that frothers that reduce surface tension also tend to suppress coalescence more effectively. This correlation has been confirmed in previous studies showing that high surface activity promotes rapid formation of stable interfacial films, thereby enhancing bubble-to-bubble repulsion and preventing film rupture [49,55].

The CCC values of polyglycol ether frothers have been reported in the literature to range from 6.0 to 6.6 ppm [8,18,56–58], based on bubble size-concentration measurements using image analysis techniques. In the present study, however, the CCC value of PPG250 was determined as 3 ppm using the light scattering method, indicating that the measurement technique can influence the reported values. PPG-based frothers are well known to generate persistent foams owing to their ability to form sterically stabilized interfacial films that effectively resist drainage and coalescence [18].

Although MIBC is one of the most widely used frothers in flotation due to its moderate selectivity and cost-effectiveness, it exhibits a relatively high CCC, typically reported in the range of 6–10 ppm [26,56]. A higher CCC indicates that higher dosages of MIBC are needed to achieve froth stability similar to more surface-active frothers such as short-chain alcohols or PPG-based polyglycol ethers, which generally have lower CCC values [8,18]. This requirement arises from the fact that frothers with lower CCCs are more efficient in suppressing bubble coalescence at lower concentrations by forming stable interfacial films.

3.3. Dynamic Foam Stability Measurements

Figure 3 illustrates the evolution of foam height over time for various frothers and highlights the performance of the commonly used medium-strength aliphatic alcohol MIBC. The results show that increasing the MIBC concentration leads to a gradual increase in foam height, and maximum foam stability is observed at 1000 ppm. This trend is consistent with the findings of Alsafasfeh et al. [59], who reported that both foam height and dynamic froth stability increased with MIBC dosage in flotation systems. Furthermore, the foam decay curve for MIBC indicates a controlled and continuous drainage pattern, suggesting the formation of moderately stable, yet permeable interfacial films. This observation agrees with the work of Wang et al. [60], who showed that MIBC-stabilized foams exhibited relatively rapid drainage and shorter foam half-lives compared to those formed by more surface-active frothers, such as polypropylene glycols.

In the case of EH, at 1 ppm, the foam height stabilized around 4–5 mm, while 10 ppm and 100 ppm yielded higher and more stable foam layers (~8–10 mm). Further increases up to 1000 ppm resulted in only a marginal additional increase (~11–12 mm). This plateau behaviour is consistent with surface tension measurements reported by Yuan and Herold [61], who found that EH rapidly decreases surface tension to below 45 mN m^{-1} at sub-ppm levels, approaching a solubility-limited plateau near 800–900 ppm.

In the case of PPG250, the foam height was significantly dependent on the concentration, and particularly pronounced effects were observed at 100 and 1000 ppm. These observations are in agreement with previous studies showing that increasing the frother concentration leads to increased foam height and dynamic stability [21,62]. Only a thin and unstable foam layer was observed at the lowest concentration of 1 ppm, while moderate improvements in foam stability occurred at 10 ppm. The most significant foaming behavior was noted at 1000 ppm, where a thick and persistent foam layer developed, consistent with the findings that polyglycol-type frothers promote the formation of smaller and more stable bubbles, thereby strengthening the foam structure as the concentration increases [11,21]. In this study, it was found that at higher concentrations, a residual foam layer of approximately 8 mm thick remained throughout the decaying phase. This type of persistent foam is mechanistically attributed to the suppression of bubble coalescence and the stabilization of the air-water interface through surface tension gradients; this is often described in terms of Gibbs or Marangoni effects [11,63]. However, the prolonged presence of this residual foam layer can lead to operational difficulties as it can inhibit the efficient transport and removal of froth from the flotation cell, a factor that plays a critical role in overall flotation

performance [64,65]. This issue has also been highlighted in recent studies, where excessive froth stability resulting from high frother dosages has been identified as a practical concern in industrial flotation systems [16].

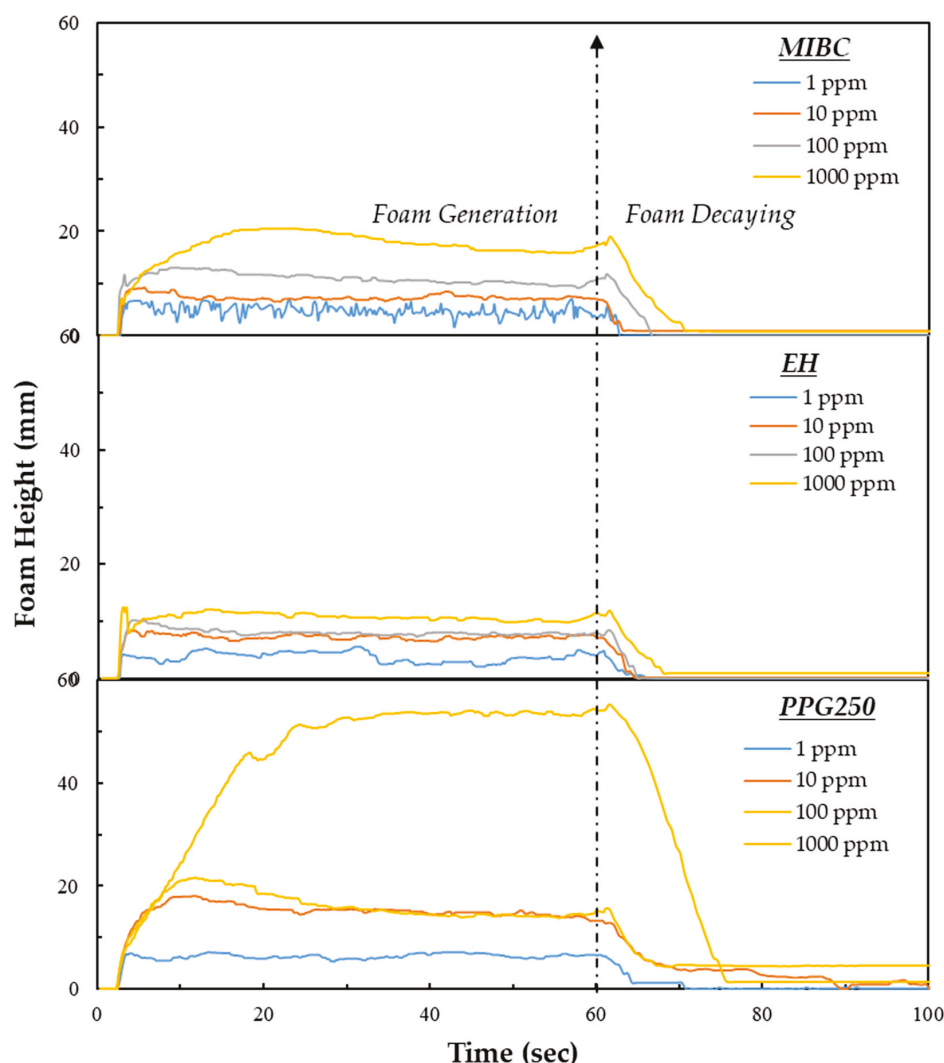


Figure 3. Foam generation/decaying behaviour of different frothers against concentration.

Figure 4 demonstrates a significant concentration-dependent trend in the dynamic foam stability (DFS) of the frothers. While all frothers increased foam life by increasing the concentration from 1 to 1000 ppm, the degree of this improvement varied significantly. Among these, PPG250, a polypropylene glycol-based frother, exhibited the most pronounced and nonlinear increase in DFS, increasing from approximately 25 s at 1 ppm to approximately 65 s at 10 ppm, and exceeding 190 s at 1000 ppm. This trend agrees with previous findings showing that medium-molecular-weight PPGs form sterically stabilized interfacial films that effectively inhibit bubble coalescence when they exceed their CCC (3 ppm) [6,48]. In contrast, MIBC showed a more gradual, almost linear increase in DFS, from approximately 22 to 75 s, reflecting its higher CCC (typically 6–10 ppm) and the lower surface elasticity of its aliphatic films. Similar moderate trends for MIBC were reported by Melo and Laskowski [8] and Finch and Zhang [49]. The lowest foam stability was observed for EH, a branched short-chain alcohol, whose DFS only increased from ~18 to ~50 s. This observation supports previous studies suggesting that EH forms loosely packed films resulting in thin lamellae prone to rapid drainage, despite rapid interface adsorp-

tion [47]. Taken together, the overall order of foam stability, PPG250 > MIBC > EH, coincides with well-known relationships between frother molecular structure, hydrophilic–lipophilic balance, and foam persistence reported in flotation literature [49,66].

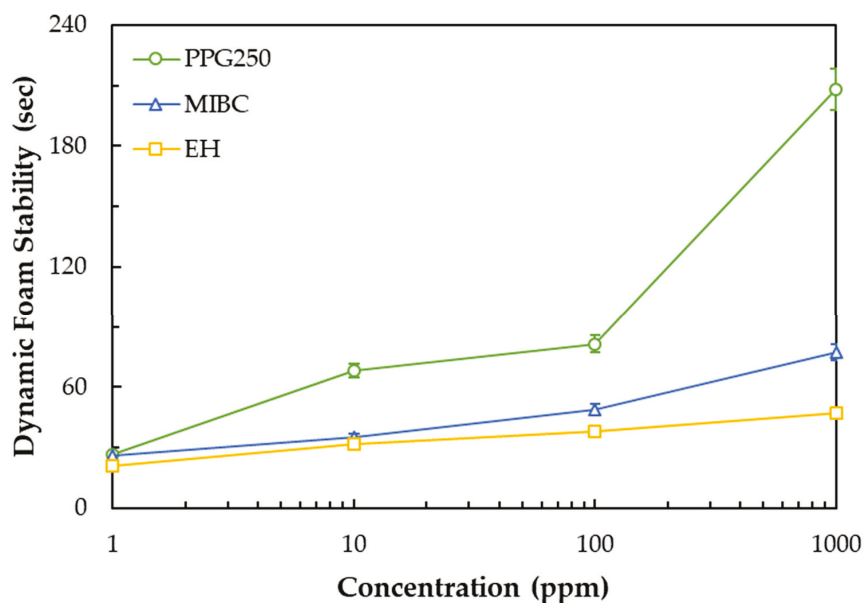


Figure 4. Dynamic foam stability (DFS) of different frothers against concentration.

3.4. Effect of Frother Type on Flotation Recovery

Figure 5 presents the flotation recoveries of three structurally different frothers, polypropylene glycol ether (PPG250), a branched aliphatic primary alcohol (EH), and a branched aliphatic secondary alcohol (MIBC) over a wide concentration range. All frothers exhibited characteristic sigmoidal recovery curves with three distinct regions based on concentration.

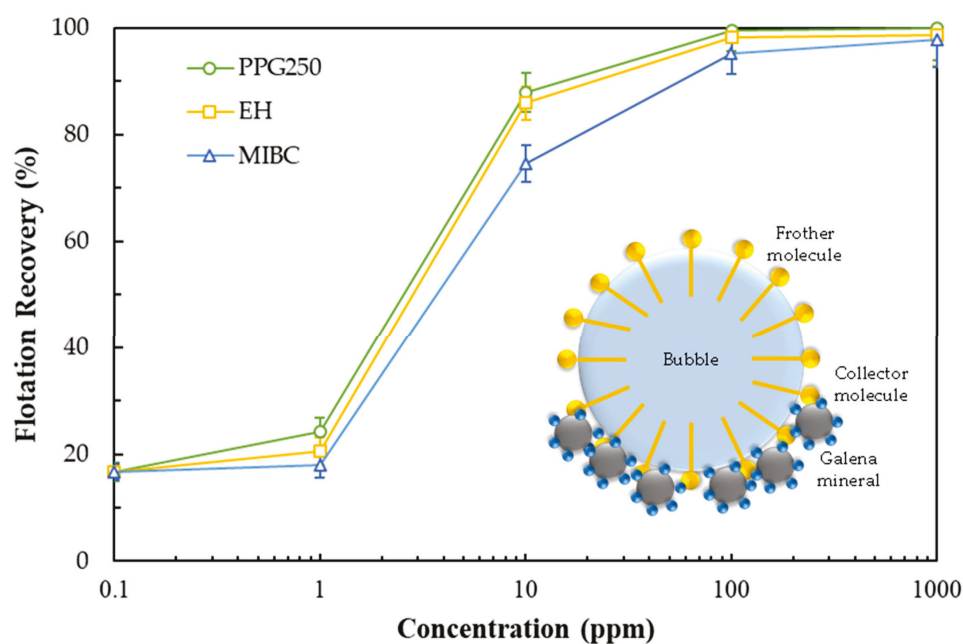


Figure 5. Flotation recovery of different frothers against concentration in the presence of 1 ppm PEX.

In the initial region (≤ 1 ppm), the flotation recoveries remained below 25% for all frothers, indicating that flotation was under sub-CCC conditions, approximately 2 ppm for EH, 3 ppm for PPG250, and 8 ppm for MIBC, where bubble coalescence predominates due to insufficient interface stabilization [26,49]. In the transition region (1–10 ppm), both PPG250 and EH rapidly exceeded their CCCs, achieving 89% and 86% flotation recoveries, respectively. In contrast, MIBC gave only 74% recovery at the same dosage, reflecting its relatively lower surface activity and the need for higher concentrations to effectively suppress bubble coalescence [8,18].

In the saturation region (≥ 100 ppm), all frothers approached their maximal flotation recoveries ($>95\%$). The increases in concentration up to 1000 ppm led to insignificant improvement, indicating that the surface tension had already reached its minimum level, and beyond this, the additional frother had no further effect on bubble stabilization [6,58]. These findings highlight the critical role of molecular structure in governing frother performance, emphasizing that PPG250 and EH in the presence of 1 ppm PEX exhibit superior flotation efficiency at lower dosages due to their enhanced ability to suppress bubble coalescence and reduce surface tension.

4. Conclusions

- In this study, the interfacial behavior and flotation performance of three structurally distinct frothers (EH, PPG250, and MIBC) were systematically investigated using a high-purity galena sample. The results revealed the critical role of frother molecular structure and surface activity in determining surface tension, bubble coalescence, foam stability, and flotation efficiency.
- EH exhibited the highest surface activity, reached the lowest surface tension and CCC value (~ 2 ppm), indicating rapid interface adsorption and effective coalescence suppression.
- PPG250 provided the best dynamic foam stability and flotation recovery by forming persistent interfacial films even at low dosages.
- MIBC, despite its widespread industrial use, showed moderate performance; higher concentrations (~ 8 ppm CCC) were required to achieve comparable stability and recovery due to its weaker surface activity and lower film elasticity.
- The results of the micro-flotation experiments confirmed that all frothers followed a typical flotation recovery curve, with recovery increasing gradually as frother dosage increased; the highest recoveries were obtained with PPG250 (99.45%), EH (98.31%), and MIBC (95.17%).
- In this study, the experiments were carried out using a single high-purity galena mineral. However, industrial flotation processes often involve complex ore bodies and the presence of various gangue minerals, which can significantly affect reagent behavior and overall process performance. Therefore, future research should aim to validate these findings in multi-mineral flotation systems to better represent industrial conditions.
- The results also carry important practical implications for mineral processing operations. Selecting frothers with lower CCC values and higher interfacial activity (such as EH and PPG250) allows reduced reagent consumption. In addition to reducing operational costs and increasing process efficiency, lower dosages contribute to more sustainable flotation practices by minimizing chemical usage, reducing waste generation, and limiting environmental impacts, a critical factor especially in large-scale operations.

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Article

A Surface Chemistry Investigation into Depressants for Minerals Associated with Pyrochlore

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Abstract: Niobium (Nb), a transition element, has been applied mainly as steel additive, among other cutting-edge applications. Nb is mainly produced from pyrochlore-containing ores, dominated by mines at Araxá, Catalão (both from Brazil), and Niobec (Saguenay Region, QC, Canada). At these plants, flotation is employed as the main beneficiation method that all plants apply direct pyrochlore flotation; Catalão and Niobec apply additional reverse flotation prior to pyrochlore flotation. During flotation, depressants are added to improve selectivity, which highlights their importance to Nb mineral flotation. However, most of the available studies related to Nb mineral flotation focus on collectors; the knowledge on depressants is limited. In the present work, various depressants, including sodium silicate, oxalic acid, F100, starch, carboxymethyl cellulose (CMC), and chitosan, are compared for pyrochlore flotation at pH 7 in the presence of sodium oleate and dodecylamine (DDA) collectors. The results are compared with common gangue minerals, including dolomite, calcite, and hematite. It was observed that the performance of depressants is related to the collector applied, which was justified by the mineral surface charge after depressant adsorption and the charge of the collector. Among the tested combinations, 5 kg/t F100 + 2 kg/t DDA and 5 kg/t CMC + 2 kg/t DDA showed potential selectivity toward pyrochlore and hematite, whereas both carbonate minerals could be successfully depressed. Zeta potential measurement and X-ray photoelectron spectroscopy were applied to understand the interaction between depressants and the model minerals.

Keywords: Niobium; pyrochlore; flotation; depressant; surface chemistry

1. Introduction

Nb is a transition element whose major (approximately 90%) consumption is in the steel industry, where it is added in the form of ferroniobium to produce high strength low alloys and stainless steels [1–4]. It also finds applications in other cutting-edge fields, including electronics [5], superalloys [5,6], catalysts, and medical tools [1,7]. Due to there being no effective substitutes, its potential supply risk, as well as its importance to defense, energy, and high-tech industries, Nb is considered a strategic element [2,8].

The global Nb reserves are mainly found in Brazil and Canada, which are also major suppliers of Nb products [4,9,10]. Brazil is currently the largest Nb producer due to mining of the Araxá and Catalão complexes; collectively, they supply more than 90% of the global Nb production [4]. Niobec, located in Canada, is the only active Nb producer in North America, which supplies approximately 7% of the global Nb market [4]. For more details

about the production of Nb, interested readers are suggested to consult Gibson et al. (2015) [11].

Flotation is currently employed as the main beneficiation method to recover Nb minerals (mainly pyrochlore) at these mines. During flotation, collectors, depressants, and activators are typically required to achieve desired selectivity. During direct pyrochlore flotation, at Araxá, amine collectors and sodium fluorosilicate (Na_2SiF_6 , pyrochlore activator) are added under acidic conditions (pH 2.5–3.5) [12–15]; at Niobec, secondary amines are used as collectors [16–20] in addition to sodium silicate (SS) and tapioca starch as gangue depressants [17–20]. Prior to the pyrochlore flotation at Niobec, a carbonate reverse flotation stage is applied, where tall oil fatty acid collector was used during early plant operation, oxalic acid (OA) and hydrofluoric acid (HF, replaced by H_2SiF_6 in the late 1970s) were used to depress pyrochlore [21]. Subsequently, emulsified fatty acid was applied as collector at natural pH (ca. 8) [16–20,22], with SS and starch applied as pyrochlore depressants [16–19]; the latter is also applied to depress pyrochlore during the downstream sulfide reverse flotation stage [16,21]. Similarly to Niobec, reverse flotation is applied at Catalão to remove silicates before pyrochlore flotation, where etheramine and starch are added as silicate collector and pyrochlore depressant, respectively [23].

Limitations are associated with these depressants. For fluorosilicates, the dosage has to be carefully controlled: at a low dosage, they function as an effective gangue depressant and Nb activator [24–26]; at an elevated dosage (e.g., higher than 600 g/t [27] to 1 kg/t [24]), they could depress Nb minerals [21,24,26–28]. Similarly, for SS, a small addition could improve the flotation of Nb mineral; a high dosage could result in Nb mineral depression [29]. Likewise, starch is capable of depressing both gangue and Nb minerals: when organic diphosphonic acids were used as collectors, starch could successfully depress Na-feldspar and hardly affect niobotantalite [30]; other studies found that it could depress fersmite [31] and ilmenorutile [32] significantly. Its depression effect on Nb minerals was also confirmed in ore studies that during silicate flotation using amine collector, starch was applied to depress pyrochlore [23].

As noted, depressants play an important role in Nb mineral flotation; therefore, choosing a selective reagent scheme is essential. However, it appears that the available studies related to Nb flotation reagents focus more on collectors; knowledge related to depressants, and more importantly, their interaction mechanisms with Nb minerals, is limited. Due to this reason, the present work aims to expand the knowledge on depressants applied in Nb mineral flotation. Depressants under different categories were chosen for comparison: SS (a depressant for both pyrochlore [21,33–35] and associated gangue [36,37]), OA (a gangue depressant in Nb mineral flotation [38]), F100 (a commercial lignosulphonate-based carbonate depressant), starch (a common depressant for Fe oxides and a possible depressant for other gangue and Nb minerals as introduced above), carboxymethyl cellulose (CMC, a gangue depressant applied in Nb mineral flotation [39] and appears to be more selective than starch [40]), and chitosan (a novel depressant for Nb mineral flotation). Four model minerals were chosen for investigation: pyrochlore (representative Nb mineral), hematite (representative Fe oxide mineral), dolomite and calcite (common carbonate gangue associated with Nb minerals). Microflotation tests were conducted using sodium oleate (NaOL, representative of fatty acids) and dodecylamine (DDA, representative of amines) as collectors at pH 7, with and without the depressants mentioned previously. Surface chemistry studies, including zeta potential measurements and X-ray photoelectron spectroscopy (XPS), were conducted to understand the interaction mechanism between minerals and reagents.

2. Materials and Methods

2.1. Materials and Reagents

Model minerals of dolomite (Coloured Aggregates Inc., Aurora, ON, Canada), calcite (Ward's Science, Rochester, NY, USA), and hematite (Ward's Science, USA) were ground to $-106\ \mu\text{m}$ using a Pulverisette 6 planetary monomill (Fritsch, Idar-Oberstein, Germany) with agate balls. The pulverized minerals were then wet screened at $38\ \mu\text{m}$ to produce a $-106 + 38\ \mu\text{m}$ fraction for microflotation. For dolomite and calcite, their purity was satisfactory, and they were used as received. Hematite contained a small fraction of quartz, which was rejected using a wet high intensity magnetic separator (WHIMS) at a 0.5 T magnetic field. Due to the difficulty of purchasing pyrochlore with a satisfactory high grade, a plant concentrate was provided by Niobec (Canada) and used in the present work. This pyrochlore concentrate, however, still contained a small amount of iron oxides and light gangue, including silicates and carbonates. To purify this concentrate, it was first sieved into narrow size ranges ($-106 + 75$, $-75 + 53$, and $-53 + 38\ \mu\text{m}$) and passed over a Mozley shaking table to reject the light gangue minerals; the heavy fraction was then passed through WHIMS at 0.5 T to reject iron oxides. The WHIMS nonmagnetic fraction was dried in a lab oven at $93\ ^\circ\text{C}$ before being calcined in a muffle furnace at $300\ ^\circ\text{C}$ for 2 h to remove possible residual organic species. The calcinated materials were then blended into $-106 + 38\ \mu\text{m}$ for microflotation. For surface chemistry studies, the prepared model minerals in the $-106 + 38\ \mu\text{m}$ size range were ground in deionized water to $-10\ \mu\text{m}$ using a Pulverisette 6 planetary monomill (Fritsch, Germany). The obtained slurry was dried in a lab oven at $93\ ^\circ\text{C}$ and collected for later use.

The specific surface areas of the model minerals were determined by the nitrogen Brunauer–Emmett–Teller (N_2 -BET) technique using a TriStar 3000 surface area and porosity analyzer (Micromeritics, Norcross, GA, USA). The particle size of model minerals was determined using a Microtrac Series 5000 Sync Particle Size & Shape Analysis system (Microtrac Inc., USA). The BET and PSA results are shown in Table A1. The purity of model minerals was examined by X-ray fluorescence (XRF), X-ray diffraction (XRD), and scanning electron microscope (SEM) techniques. XRF analysis was conducted at Techni-Lab S.G.B. Abitibi Inc. (Sainte-Germaine-Boulé, QC, Canada) using the fusion method. XRD was conducted using a Bruker (USA) D8 Discovery X-ray diffractometer equipped with a $\text{Co K}\alpha$ source ($\lambda = 0.179\ \text{nm}$). The resultant patterns were processed by DIFFRAC.EVA software (version 6.1, Bruker, Billerica, MA, USA) and compared with the PDF-4+ (ICDD, 2022) database to identify the main minerals present. SEM analysis was conducted using an SU3500 SEM system (Hitachi, Japan) equipped with an $80\ \text{mm}^2$ X-MaxN Silicon Drift energy dispersive spectrometer (EDS) detector (Oxford Instruments, High Wycombe, UK). All tests were performed using a 20 kV accelerating voltage under an environment of 80 Pa. During operation, the deadtime was maintained close to 15%, and count rates were maintained above approximately 6000 cps. The collected data were analyzed using AZtec software (version 3.0, Oxford Instruments, UK) to identify elements present in the samples. The XRF results and XRD spectra are shown in Table A2 and Figure A1, respectively, whereas the false-colored BSE-EDS images are shown in Figures A2–A5. It can be observed that the elemental contents of model minerals are close to the expected values, which could be supported by SEM observation; in addition, their XRD spectra match well with the references. It should be noted that in hematite, a small amount of quartz is still present (as observed from XRD (Figure A1c), XRF (Table A2), and SEM (Figure A4)), possibly due to incomplete liberation between hematite and quartz in coarse ($-106 + 38\ \mu\text{m}$) grains.

All reagents in this work were used as received without further purification. DDA, which is insoluble in water, was first dissolved in acetic acid at a 1:4 (DDA:acetic acid) molar ratio and then diluted to desired concentrations. Deionized water (with a resistance of 18.3 MΩ·m) produced by a reverse osmosis system (Durpro, Candiatic, QC, Canada) was used throughout the research. Information about reagents applied in the present work is detailed in Table A3.

2.2. Microflotation

Microflotation tests were conducted in a modified Hallimond microflotation cell. For each test, 1 g of model mineral ($-106 + 38 \mu\text{m}$) was conditioned for 1 min in 20 mL of collector solution at the desired dosage. The pH was maintained at 7 using diluted hydrochloric acid (HCl) and sodium hydroxide (NaOH) at 1, 0.1, and 0.01 mol/L. In case depressant presents, the mineral was first conditioned with depressant at the desired dosage for 1 min, followed by another minute of conditioning with collector. A stirring bar was used to keep particles suspended throughout the test. After conditioning, the suspension was transferred into the microflotation cell, which was then filled to 160 mL with pH-adjusted water. The air was then turned on and regulated at 40 mL/min during the test. After floating for 1 min, the floated particles were collected into a beaker as concentrate, whereas those left in the cell were collected as tailing. The concentrates and tailings were filtered and dried separately to calculate the recovery (Recovery) using Equation (1):

$$\text{Recovery} = \frac{m_{\text{conc}}}{m_{\text{conc}} + m_{\text{tail}}} \times 100\% \quad (1)$$

where m_{conc} and m_{tail} represent the mass of concentrate and tailing, respectively. Three repeats were conducted at each condition to ensure consistent results were obtained, based on which 95% confidence intervals (C.I.) were calculated and displayed with the flotation results as error bars.

It should be highlighted that due to the already existing frothing effect for both NaOL and DDA, no frother was added during microflotation tests in this work.

2.3. Zeta Potential Measurement

Zeta potential measurement was conducted using a NanoBrook ZetaPlus electrophoretic analyzer (Brookhaven Instruments, Nashua, NH, USA). Model minerals in the $-10 \mu\text{m}$ size range were suspended in 200 mL of 10^{-3} mol/L KCl solution at a mineral/solution ratio of 0.04 wt%. The suspension was dispersed using an ultrasonicator (Hielscher UP400S, Teltow, Germany) for 30 s. A magnetic stirring bar was used to keep particles suspended throughout the test. The pH range investigated was from 3 to 10 due to equipment limitation. Prior to taking measurements, the suspension was allowed to condition for 30 min, and for a minimum of 5 min at each different pH level, which was adjusted using diluted HCl and NaOH. Fresh samples were prepared for measurements in the acidic and basic directions to avoid the hysteresis effect. For cases with reagent, the reagent was added at the beginning of the conditioning stage. The concentration (in kg/t) of reagent was determined by increasing the NaOL dosage until an appreciable shift in the pyrochlore zeta potential was observed. This concentration was kept constant for other reagents and other minerals, which is shown in Table A4. At least three repeats (10 measurements in each repeat) were conducted at each condition to ensure consistent results were obtained; to make visualization easier, the obtained data were fitted by a third order polynomial, on which the calculated 95% C.I. are presented as error bars.

2.4. X-Ray Photoelectron Spectroscopy

To prepare samples for XPS analysis, 1 g of model mineral ($-10\ \mu\text{m}$) was added into 40 mL of pH-adjusted water and sonicated for 30 s to prepare it into suspension. A stirring bar was added to keep particles suspended, and pH was adjusted to the desired level using diluted HCl and NaOH. In case reagents were present, an amount of reagent solution corresponding to 100 kg/t (the same as zeta potential measurement) was added at the beginning of the condition stage. The suspension was then conditioned for 10 min, and the pH was maintained at the desired level using diluted HCl and NaOH. After conditioning, the suspension was transferred into a centrifuge tube and centrifuged at 4000 rpm for 10 min to separate the solid from the solution. The solid was then rinsed using water at the same pH 3 times to wash off residual reagents. The washed solid was then filtered and air-dried for 2 days before being kept in a vacuum oven (vacuum level equivalent to 70 cm Hg) at room temperature for 8 h. The prepared samples were stored in a desiccator before XPS analysis.

XPS analysis was performed using a Thermo Scientific Nexsa G2 spectrometer (Waltham, MA, USA) equipped with an Al K α X-ray source (1489.6 eV). The spot size was 400 μm with 50.0 eV pass energy and 0.1 eV energy step size. A flood gun with low energy electrons was applied during data acquisition to avoid surface charging. The collected spectra were processed using Advantage software (Thermo Fisher Scientific, Waltham, MA, USA), and the binding energies (BE) were calibrated with respect to that of C1s for hydrocarbon (284.8 eV).

3. Results

3.1. Microflotation

3.1.1. Minerals with Collectors

Microflotation results of model minerals with collectors only at pH 7 are shown in Figure 1. For both NaOL and DDA, the recoveries of minerals followed a similar trend in that they gradually increased with respect to the collector dosage; relatively high recoveries (between 70 and 80%) could be achieved with 2 kg/t of collector for all four minerals. As the collector's dosage further increased to 5 kg/t, their recoveries did not increase significantly. The high recoveries and similar recovery trends of all minerals confirm that both collectors are strong but with poor selectivity, which highlights the importance of depressants when these collectors are used in Nb mineral flotation.

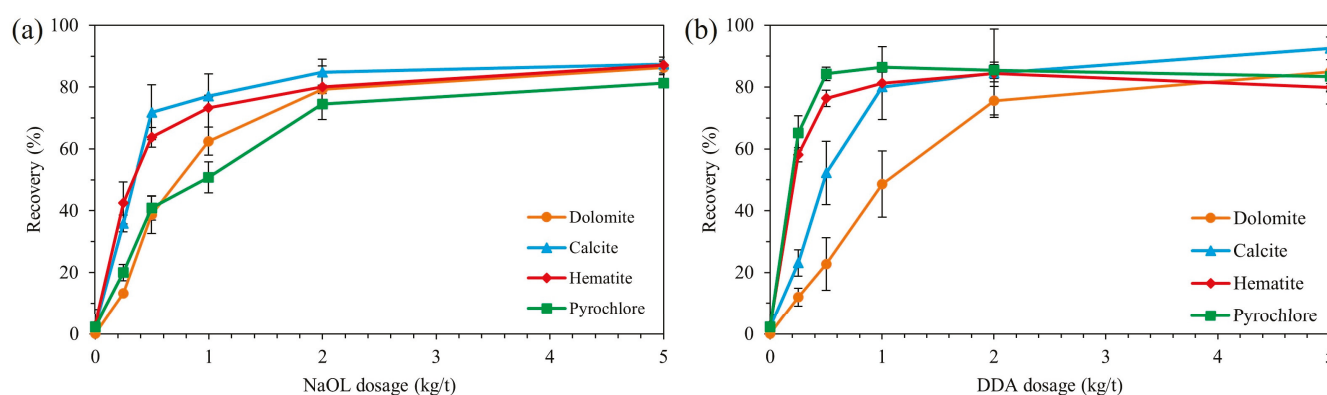


Figure 1. Microflotation results of model minerals with (a) NaOL and (b) DDA at pH 7, error bars denote 95% C.I.

3.1.2. Minerals with Depressants

The performance of depressants was evaluated in the presence of either NaOL or DDA at 2 kg/t, a dosage above which the recoveries of minerals did not increase significantly (as seen in Figure 1). The results are shown in Figure 2 (with NaOL as collector) and Figure 3 (with DDA as collector), respectively.

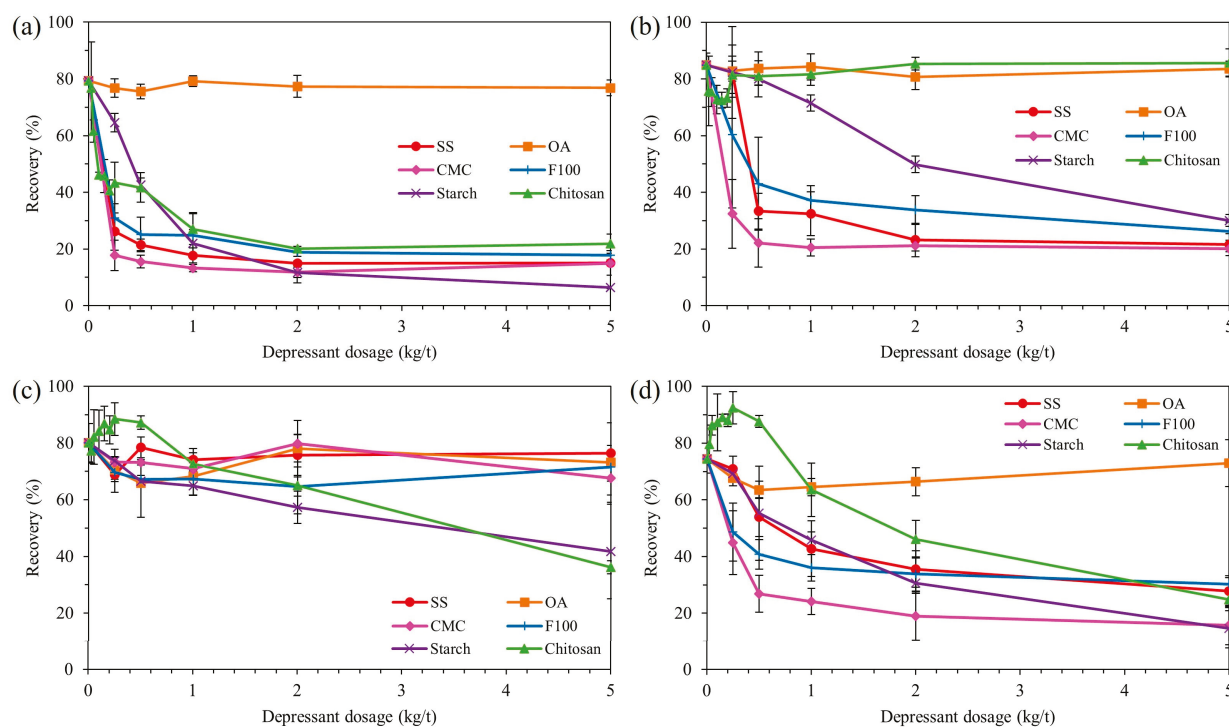


Figure 2. Microflotation results of (a) dolomite, (b) calcite, (c) hematite, and (d) pyrochlore in the presence of depressants and 2 kg/t NaOL, error bars denote 95% C.I.

When NaOL is used as collector, dolomite, as shown in Figure 2a, could be successfully depressed by all tested depressants except OA, and the recoveries follow a similar trend in that they gradually decrease with respect to the depressant dosage. To achieve complete depression (approximately 20% or less), the dosage required was 0.25 kg/t for CMC, 1 kg/t for SS and starch, 2 kg/t for F100 and chitosan. For calcite, it could be depressed by the tested depressants except OA and chitosan. To achieve complete depression, the dosage required was 0.5 kg/t for CMC, 2 kg/t for SS, and 5 kg/t for F100. For starch, at the highest dosage (5 kg/t), the recovery of calcite reduced to approximately 30%. It is interesting to observe the limited depression of chitosan on calcite compared to dolomite; this should be related to the surface composition difference and the interaction mechanism between chitosan and these carbonate minerals. This difference in depression performance might limit the application of chitosan as a carbonate depressant in direct pyrochlore flotation, since dolomite and calcite responded differently under the same condition. For hematite, it could only be depressed significantly by starch and chitosan: when 5 kg/t of chitosan was added, its recovery reduced to approximately 35%; similar depression was achieved with starch. In comparison, SS, OA, F100, and CMC could barely depress hematite such that even at the highest tested dosage (5 kg/t), the recovery of hematite remained at approximately 70–80%. For pyrochlore, it could be depressed by the tested depressants except OA. At 5 kg/t, SS, F100, and chitosan reduced the recovery of pyrochlore to a similar level (approximately 30%). CMC and starch resulted in more severe depression such that the recovery of pyrochlore reduced to approximately 15% at the same dosage (5 kg/t).

This strong depression effect is not surprising since starch has been applied to depress pyrochlore during carbonate reverse flotation at Niobec [17,20,22,35].

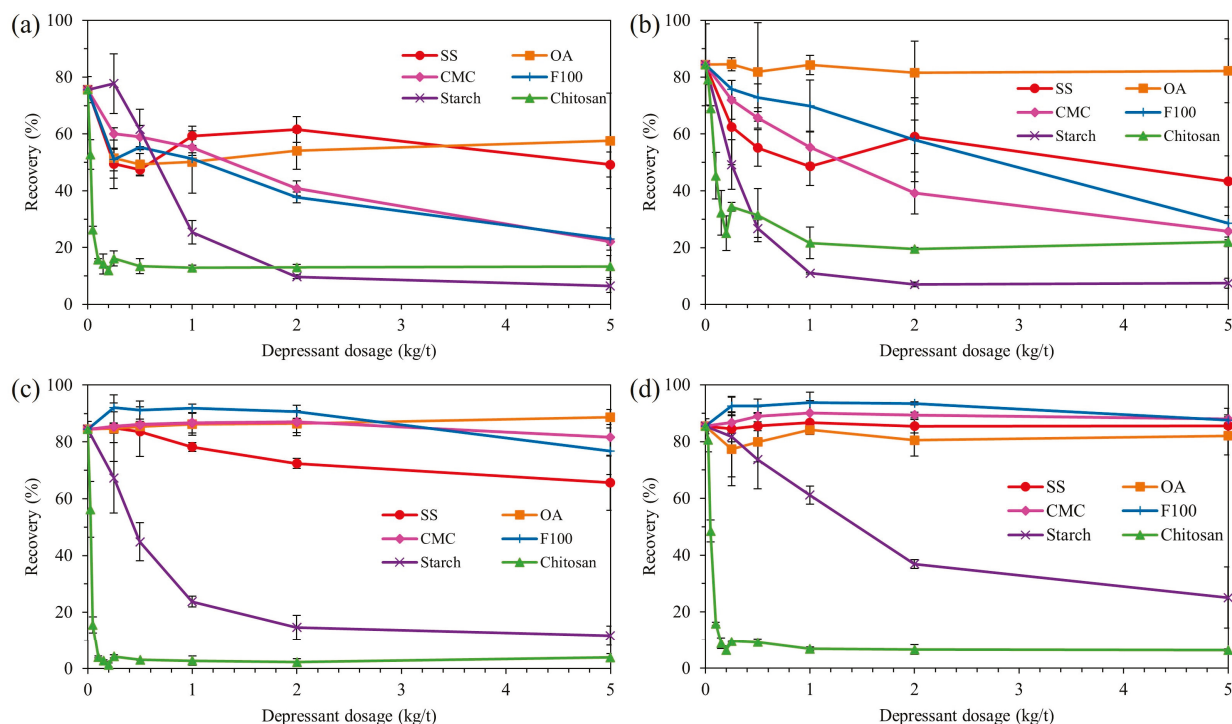


Figure 3. Microflotation results of (a) dolomite, (b) calcite, (c) hematite, and (d) pyrochlore in the presence of depressants and 2 kg/t DDA, error bars denote 95% C.I.

Microflotation results of model minerals in the presence of depressants and 2 kg/t of DDA as collector are shown in Figure 3. During the test, it was noticed that chitosan acts more effectively (i.e., the recovery of minerals already reduced to minimum with 250 g/t chitosan) than when NaOL was used as collector. Due to this reason, chitosan was evaluated at 25, 50, 100, 150, and 200 g/t in addition to the higher dosages.

For dolomite, SS and OA showed limited depression in that with 0.25 kg/t, the recovery of dolomite reduced to approximately 50%, and did not reduce significantly as the depressant dosages increased. Conversely, F100 and CMC followed a similar trend in that the recovery of dolomite kept reducing with respect to their dosages; at 5 kg/t, the recovery of dolomite decreased to approximately 20%. Starch appears to be more effective such that the recovery of dolomite reduced to a similar level (25%) with just 1 kg/t of starch, which could be further reduced to less than 10% with 2 kg/t of starch. Chitosan appears to be the most effective depressant: at 50 g/t, the recovery of dolomite was already reduced to about 15% and remained nearly unchanged as more chitosan was added. For calcite, OA appears to be ineffective in that its recovery remained almost unchanged when OA was added. When 1 kg/t of SS was added, the recovery of calcite reduced to less than 50% and remained almost unchanged as more SS was added. When F100 and CMC were added, the recovery of calcite reduced with respect to the dosage of depressant such that at 5 kg/t, the recovery of calcite reduced to below 30%. Chitosan and starch appear to be the most effective depressants: with a 2 kg/t dosage, chitosan reduced the recovery of calcite to <20%, starch reduced the recovery of calcite to <10%. For hematite, its recovery was not affected significantly by OA, F100, and CMC, so that even with 5 kg/t of these depressants, the recovery of hematite remained above 80%. In the presence of SS, a slight decrease (15%) in the recovery of hematite was observed at the highest tested dosage

(5 kg/t). In comparison, starch and chitosan appear to be much more effective: with 2 kg/t of starch, the recovery of hematite reduced to less than 20%; the recovery of hematite dropped to a similar level with just 50 g/t of chitosan.

For pyrochlore, SS, OA, CMC, and F100 did not affect its recovery significantly: even at a depressant concentration of 5 kg/t, the recovery of pyrochlore remained above 80%. Different depressing effects of OA on pyrochlore have been observed in the literature: in [41], the inhibition effect of OA on pyrochlore was observed, but in [42], its depressing effect on pyrochlore was not evident. This difference might be attributed to the pyrochlore composition, more specifically, the content of Ca, since the inhibition mechanism of OA was proposed as forming calcium oxalate precipitation on mineral surface [41]. Another possible reason is the dosage of OA applied. Pyrochlore could be depressed when OA was used as a pH modifier under acidic conditions (pH 4 and 2) [41]; considering OA is a weak acid, the dosage (in kg/t) applied to achieve an acidic condition might be higher than those tested in this work. Among the tested depressants, only starch and chitosan resulted in appreciable depression on pyrochlore: with 5 kg/t of starch, the recovery of pyrochlore reduced to approximately 25%. Chitosan was more effective in that at 150 g/t, the recovery of pyrochlore was already reduced to <10% and remained almost unchanged as more chitosan was added.

Overall, it could be observed that the performance of depressants is related to the collector applied. Using chitosan as an example, when NaOL was applied as collector, a relatively high dosage (2–5 kg/t) of chitosan was required to completely depress dolomite, hematite, and pyrochlore, whereas calcite could not be depressed; when DDA was used as collector, the dosage of chitosan required to depress the model minerals was much lower: 100 g/t for dolomite, 1 kg/t for calcite, 100 g/t for hematite and pyrochlore. When SS was used as depressant, the recovery of dolomite did not reduce significantly when DDA was used as collector, but the same depressant could reduce its recovery to <20% with NaOL as collector. This should be attributed to the interaction between the adsorbed depressant and the collector added after. One plausible explanation in this case is that the adsorbed anionic SS species (possibly $\text{SiO}(\text{OH})_3^-$, as suggested by [43]) hinders the adsorption of NaOL significantly but does not significantly affect DDA. Surface chemistry study is therefore required to better understand the mechanism.

It is interesting to notice the different performance between dolomite and calcite under the same conditions: when chitosan was used with NaOL, dolomite was significantly depressed, whereas calcite was nearly not affected. This difference should be related to the mineral composition (i.e., the presence of Mg) and how the depressant interacts with the mineral. Both minerals are carbonate gangue minerals; different responses under the same condition will report them in different streams, which could lower the concentrate grade and complicate the overall flowsheet.

It should be highlighted that according to microflotation, selective flotation might be possible with 5 kg/t of either CMC or F100 and 2 kg/t of DDA as collector. Under these conditions, the recoveries of pyrochlore and hematite remained high, whereas both carbonates were significantly depressed. This enables direct pyrochlore flotation, possibly followed by magnetic separation to separate pyrochlore from hematite.

3.2. Zeta Potential Measurement

3.2.1. Minerals with Collectors

The zeta potential of model minerals with and without NaOL and DDA is shown in Figure 4. For dolomite (Figure 4a), within the tested pH range (3–10), the zeta potential of dolomite remained positive, and its IEP is expected to occur at ~pH 10.5 by extrapolation. This is in agreement with [44], who found IEP for dolomite in a very alkaline range. It should

be noted that a wide range of IEP has been reported in the literature related to dolomite, ranging from <2 [45] to 11.2 [44]. This variation in IEP could be attributed to the nature and purity of the minerals [46,47], sample preparation [46], particle size [46], minor surface modifications [48], different Ca/Mg contents on the mineral surface [44,47], different mineral solubility [47], as well as the presence of CO₂ in the solution [48]. After the addition of NaOL, the zeta potential of dolomite shifted to the negative direction remarkably, which is in agreement with [47,49–52]. This shift suggests strong adsorption of the negatively charged oleate groups onto the dolomite surface. DDA, a cationic collector, however, did not result in significant shifts in the zeta potential of dolomite. This is surprising since DDA likely interacts with dolomite due to the high recovery observed during microflotation (Figure 1b). One possible explanation is that the cationic DDA species adsorb on the positively charged dolomite surface through a chemisorption mechanism (since the surface would naturally repel species carrying similar charges); the zeta potential of dolomite did not show significant shifts after reagent adsorption due to the similar charges carried by amine groups and the dolomite surface. This could explain the high recovery achieved when DDA was used as collector; the exact adsorption mechanism of DDA on dolomite, however, remains to be further confirmed using other techniques.

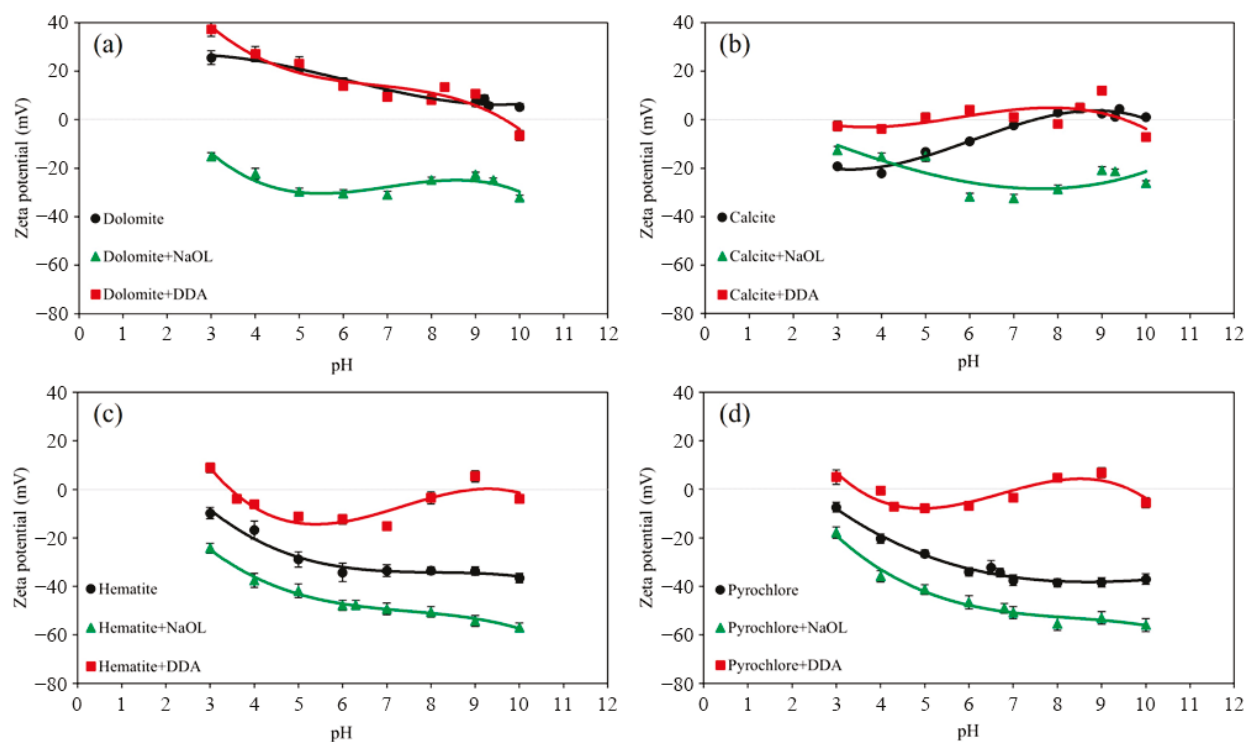


Figure 4. Zeta potential of (a) dolomite, (b) calcite, (c) hematite, and (d) pyrochlore in the presence of collectors, error bars denote 95% C.I.

The zeta potential of calcite obtained in this work follows an unusual ascending trend: it remains negative between pH 3 and 7.5, and becomes slightly positive at pH > 7.5 (as shown in Figure 4b). Similarly to dolomite, a wide range of IEP of calcite has been reported in the literature, ranging from 5.4 [44] to 10.6 [53]. During the test, it was observed that the pH of the suspension was unstable at pH < 7; acid must be constantly added to maintain the pH at the desired value. As pH further decreased, the suspension became more transparent, which was likely due to dissolution of the mineral. However, stable readings could still be obtained, which actually might be measuring the insoluble impurities. According to XRF, a small amount of SiO₂ (0.09%, as shown in Table A2) was present in the sample,

possibly in the form of silica. Its presence might explain the negative zeta potential in the acidic range. The trend of zeta potential appears to be related to the ion species and concentration in the solution. Ascending zeta potential of calcite was also observed in [54], who found that by increasing the salinity of the solution, the trend of zeta potential could change from descending to constant or even ascending. A similar trend was also observed in other research on pyrochlore in that the zeta potential curve became a “U” shape in the presence of Ca^{2+} and Mg^{2+} [35]. In addition, the suspension of carbonate minerals could be affected by CO_2 in the atmosphere [55], which possibly also affects the value and the shape of the zeta potential curve. In the presence of NaOL, similar to dolomite, the zeta potential of calcite observed a significant downward shift, which was also observed in [48,56–58]. This shift suggests the adsorption of NaOL onto the calcite surface, and the adsorption mechanism is likely chemisorption (also suggested by [48]), since the negatively charged calcite surface would naturally repel anionic oleate groups. In the presence of DDA, a notable upward shift was observed at pH 3–8, where the zeta potential of calcite was originally negative; a similar positive shift was also observed in [59,60]. This might suggest the adsorption of DDA, but the adsorption mechanism could not be determined by zeta potential measurements alone. The proposed adsorption mechanisms in the literature include electrostatic attraction and hydrogen bonding between RNH_3^+ and CO_3^{2-} sites [59] and physisorption [61].

For hematite, as shown in Figure 4c, its zeta potential remained negative across the investigated pH range. By extrapolation, its IEP is around pH 2.5, which is in agreement with values reported in [62–64]. Similarly to dolomite and calcite, a large variation in the IEP of hematite has been reported, ranging from 2 [63] to 8.5 [65]. A widely accepted reason for the low IEP of natural hematite is the presence of minor impurities (such as silica) [66,67]. As stated previously in Section 2.1, the hematite sample used in this work is a natural sample containing a small amount of silica impurities (as shown in Figure A1c and Table A2), which might explain the low IEP obtained. Another possible reason is the presence of CO_2 , which could shift the entire zeta potential curve of hematite [67]. In the presence of NaOL, the zeta potential of hematite observed a significant downward shift across the tested pH range, which was also observed in [63,65,68–73]. This significant shift suggests the adsorption of NaOL on hematite, and the adsorption mechanism is likely chemisorption (as proposed by [65,70]) since the negatively charged hematite surface would naturally repel anionic oleate species. In the presence of DDA, the zeta potential of hematite shifted upward, which is in agreement with [74] and suggests adsorption of the cationic amine collector on hematite. The adsorption mechanism, however, could not be determined by zeta potential measurements alone, as the negatively charged hematite surface could naturally attract cationic amine groups.

For pyrochlore, its zeta potential remained negative across the investigated pH range; by extrapolation, its IEP should be around pH 2.5 (as shown in Figure 4d). In the literature, compared to the gangue minerals mentioned above, a relatively narrow IEP ranging from 2.8 [75] to greater than 5 [41] has been reported. The variation in the IEP values might be attributed to the origin of the minerals, difference in surface composition, zeta potential measurement technique, background electrolyte, and concentration. Similarly to the gangue minerals, in the presence of NaOL, the zeta potential of pyrochlore shifted downward significantly, which was also observed in [76], suggesting the adsorption of NaOL on pyrochlore. The adsorption mechanism is likely chemisorption due to the same sign of charge between oleate groups and the pyrochlore surface. In the presence of DDA, the zeta potential of pyrochlore observed a notable shift to the positive direction across the entire tested pH range, which is in agreement with [42]. This suggests the adsorption

of DDA; however, the adsorption mechanism could not be confirmed by zeta potential measurements alone due to the same reason stated previously.

3.2.2. Minerals with Depressants

Zeta potential of dolomite with different depressants is shown in Figure 5a. In the presence of SS, the zeta potential of dolomite shifted slightly (~ 10 mV) to the negative direction, which was also observed in [43]. This shift could be attributed to the adsorption of negatively charged species such as $\text{SiO}(\text{OH})_3^-$, as suggested by the DFT study [43]. In addition, $\text{Si}(\text{OH})_4$ might also interact with dolomite through a weaker interaction mechanism (i.e., hydrogen bonding with O atoms on dolomite) than $\text{SiO}(\text{OH})_3^-$, which interacts through covalent bonding [43]. In the presence of OA, a notable shift in the negative direction was observed. Its adsorption mechanism could not be confirmed by zeta potential alone, since the negatively charged oxalate species could be naturally attracted by the positively charged dolomite surface. One plausible adsorption mechanism is through interactions with Ca sites, which has been confirmed by other studies [41,77].

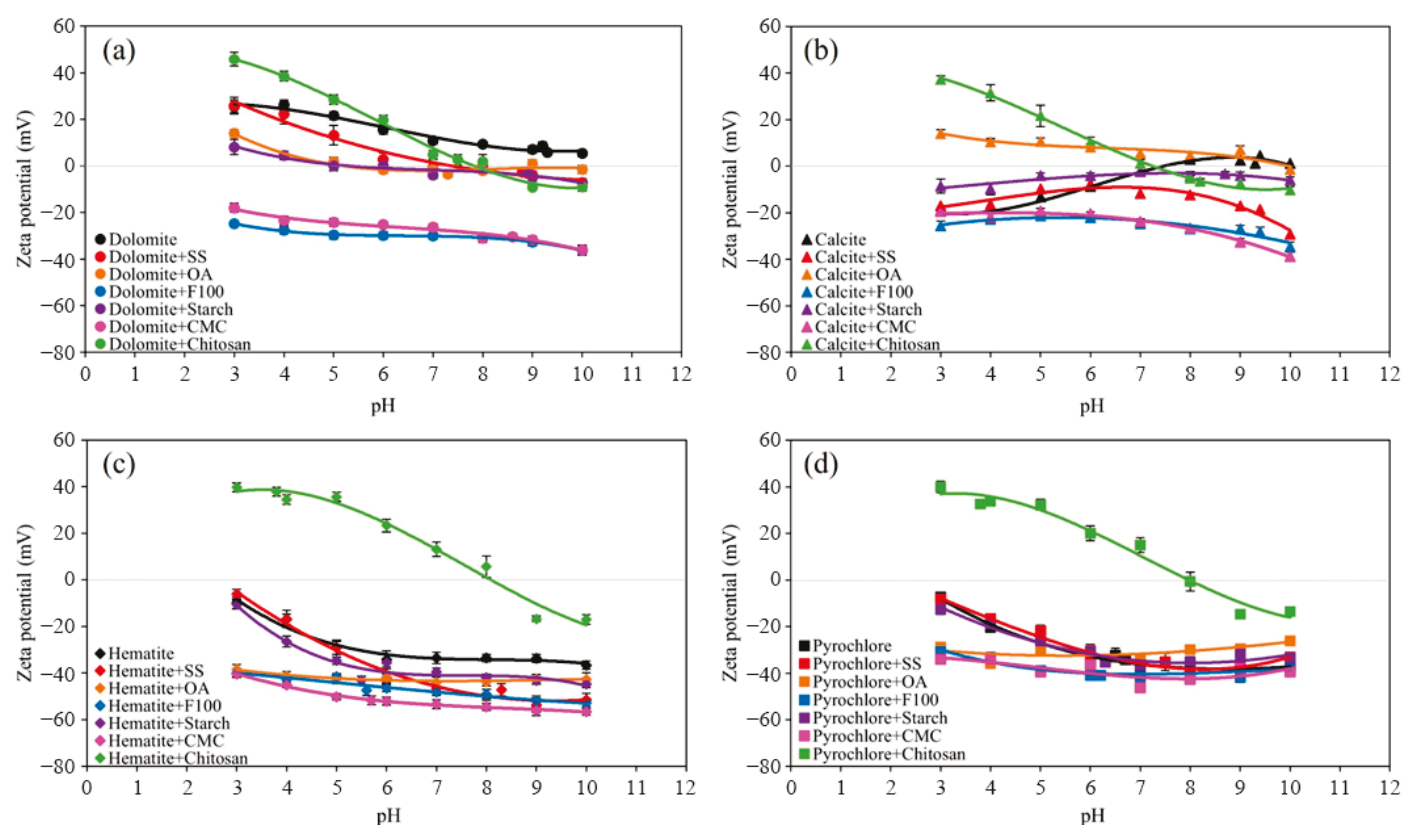


Figure 5. Zeta potential of (a) dolomite, (b) calcite, (c) hematite, and (d) pyrochlore in the presence of depressants, error bars denote 95% C.I.

F100 is a lignosulphonate-based polymer [78], which has been applied as dispersant for clay [78,79] and a depressant for dolomite [80]. A schematic presentation of the structure of lignosulphonate is shown in Figure 6. In the presence of F100, a substantial shift in the negative direction could be observed (as shown in Figure 5a), which was also observed in previous work [80]. This suggests the absorption of anionic lignosulphonate species; however, the adsorption mechanism remains to be further investigated. In previous research, chemisorption has been proposed as the adsorption mechanism of lignosulphonate on dolomite [80].

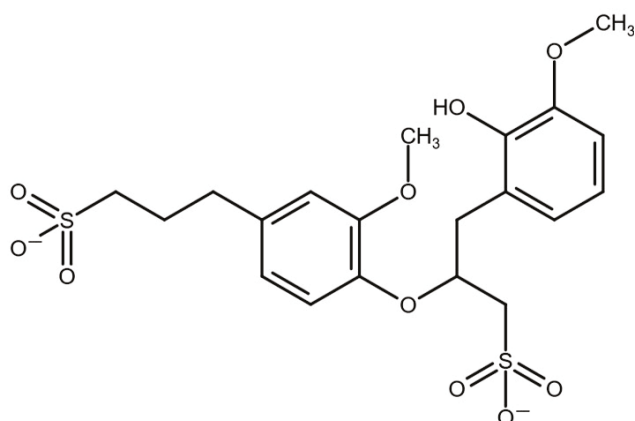


Figure 6. Structure of lignosulphonate, adapted from [81].

In the presence of starch, as shown in Figure 5a, a slight shift to the negative direction was observed on the zeta potential of dolomite, which is in agreement with [51]. Similarly, when CMC was added, significant shifts to the negative direction could be observed (as shown in Figure 5a), which was also observed in [80]. Starch, including amylose and amylopectin types (structures shown in Figure 7), contains hydroxyl groups (—OH) in their molecules [82]. CMC has a similar structure as starch in that it is composed of long chains with hydrophilic hydroxyl and carboxylic groups (as seen in Figure 8). In solution, these groups could undergo hydrolysis and become negatively charged, making the surface they adsorb on negatively charged. However, the adsorption mechanism of starch and CMC on dolomite cannot be confirmed by zeta potential alone due to the same reason stated for OA. Previous studies on dolomite suggested the adsorption mechanism is physisorption for starch [51] and chemisorption for CMC [80].

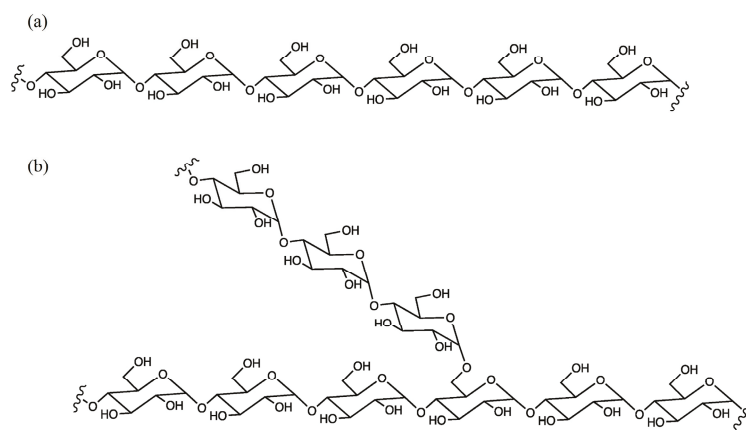


Figure 7. Structure of (a) amylose and (b) amylopectin starches, adapted from [82].

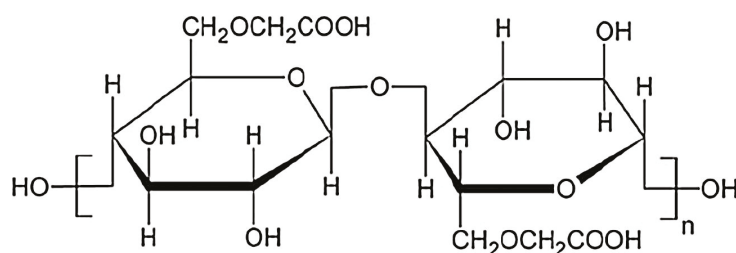


Figure 8. Structure of CMC, adapted from [83].

Chitosan, the main component of crustacean shells, is a natural polyaminosaccharide produced by deacetylating chitin [84]. A schematic presentation of its structure is shown in Figure 9, from which it can be observed that it contains carboxylic acid (—COOH), amine (—NH_3), and hydroxyl (—OH) functional groups. As shown in Figure 5a, in the presence of chitosan, the zeta potential of dolomite showed slight shifts in the positive direction at pH 3–6, and a slight negative shift at pH > 6. The IEP of dolomite shifted correspondingly from approximately 10.5 to 8. This might suggest the adsorption of chitosan and the adsorption mechanism on dolomite might be related to the pH. The adsorption of chitosan on dolomite and the corresponding mechanism remain to be investigated further; previous work on fluorite proposed chitosan chemisorption on Ca sites [85], suggesting its potential affinity to Ca sites.

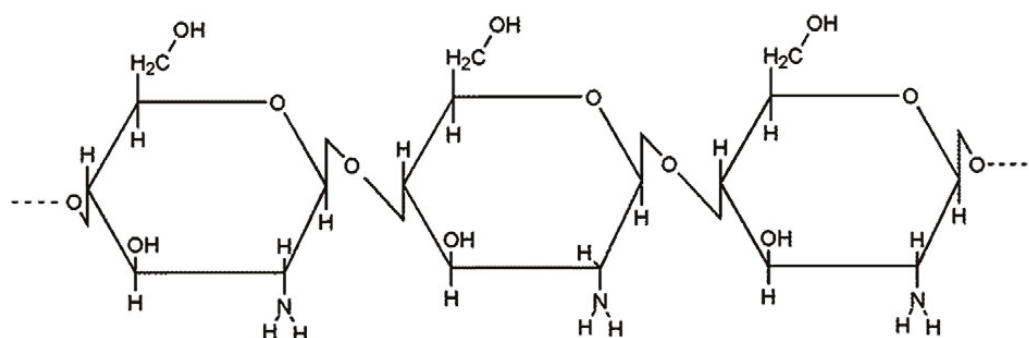


Figure 9. Structure of chitosan, adapted from [84].

Zeta potential of calcite in the presence of depressants is shown in Figure 5b. In the presence of SS, the zeta potential of calcite observed a shift to the negative direction at pH > 6, which is in agreement with [43,86] and might be attributed to the adsorption of SiO(OH)_3^- [43]. Nevertheless, the shift was not obvious at pH < 6, where the zeta potential of calcite was negative. The negative charges on calcite surface in this range might repel SiO(OH)_3^- and inhibit its adsorption, resulting in no shift in zeta potential. It is also plausible that as both calcite and SiO(OH)_3^- carry similar charges, the zeta potential of calcite might remain unchanged after possible adsorption of SiO(OH)_3^- . In the presence of OA, a shift in the positive direction was observed at pH < 9. This might be due to interactions between OA and Ca^{2+} dissolved from the calcite surface, which has been suggested by Chehreh Chelgani and Hart (2018) [77]. Such an interaction forms calcium oxalate with a neutral charge, which could re-deposit onto the calcite surface and result in positive shifts in zeta potential. This process might be less pronounced as pH increases due to less dissolution under alkaline conditions. Another plausible adsorption mechanism is through direct formation of calcium oxalate between OA and Ca on calcite surface [41]. In the presence of F100, the zeta potential of calcite shifted to the negative direction, suggesting the depressant interacted with calcite under the entire tested pH range. This is similar to the trend observed on dolomite, likely due to adsorption of negatively charged lignosulphonate species on calcite surfaces. The exact adsorption mechanism remains to be confirmed by other techniques; one possible mechanism is through interacting with Ca^{2+} [87]. Unlike the case of dolomite, after the addition of starch, the zeta potential of calcite only shifted slightly in the positive direction under acidic conditions (pH < 7) and to the negative direction under alkaline conditions. The resultant zeta potential curve remained at a nearly constant value (approximately -10 mV) across the tested pH range. This is partially in agreement with previous works where the zeta potential of calcite shifted to more negative after adding starch [60,88]. The difference between calcite and dolomite could be due to more dissolution of calcite or different adsorption reactions on the two minerals. When CMC was added, a significant shift to the negative direction was

observed (as shown in Figure 5b); this might suggest its adsorption on calcite, and a similar trend was observed previously by [57]. In solution, the hydroxyl and carboxylic groups of the CMC molecule (as shown in Figure 8) could undergo hydrolysis and become negatively charged; after adsorption on calcite, the mineral surface therefore becomes negatively charged. The adsorption mechanism is likely chemisorption at $\text{pH} < 7$, where calcite is negatively charged. However, the exact adsorption mechanism remains to be confirmed by other techniques. When chitosan was added, the zeta potential of calcite shifted to the positive direction remarkably under acidic conditions ($\text{pH} < 7$) and shifted slightly to the negative direction at $\text{pH} > 7$.

The zeta potentials of hematite with depressants are shown in Figure 5c. In the presence of SS, the zeta potential of hematite shifted to more negative values at $\text{pH} > 5$, and remained almost unchanged at $\text{pH} 3\text{--}5$. The negative shifts might be attributed to the adsorption of negatively charged $\text{SiO}(\text{OH})_3^-$, as discussed previously with dolomite and calcite, and the adsorption mechanism is likely due to chemisorption since a negatively charged hematite surface would repel anionic SS species. With the addition of OA, shifts to the negative direction could be observed across the entire pH range, a similar trend has been observed in previous work [89]. Interestingly, it appears that the adsorption of OA was more intensive in the acidic range as a larger shift could be observed. This might be due to the dissolution of hematite, the correlation between which and OA uptake has been observed by [89]. The adsorption mechanism of OA on hematite is likely chemisorption, since the negatively charged hematite surface would naturally repel anionic oxalic species. With F100, the zeta potential of hematite shifted notably to the negative direction, suggesting the adsorption of negatively charged lignosulphonate species; a similar trend has been observed in previous studies [90,91]. Its adsorption mechanism should be chemisorption, since a negatively charged hematite surface would naturally repel lignosulphonate which carries similar charges. However, electrostatic interaction has been proposed by [91], which might arise from the positive hematite zeta potential (IEP at $\text{pH} 9$) in their study. In the presence of starch, the zeta potential of hematite shifted slightly to the negative direction across the entire tested pH range, possibly suggesting the adsorption of reagent. This is in partial agreement with [92], where the addition of starch resulted in a negative shift at $\text{pH} < \text{IEP}$, and increased the zeta potential significantly at $\text{pH} > \text{IEP}$, likely due to the adsorption of less negatively charged starch [92]. In another study, the zeta potential of hematite became less negative after the addition of starch and became close to that of colloidal starch [93]. In addition, the shift trend was found to be related to the type of starch [94]. The adsorption of starch on hematite has been proposed as $\text{OH}\text{--}\text{OH}$ interaction [94]. Based on the trend observed in the present work, the adsorption mechanism is likely chemisorption, since the negatively charged hematite would naturally repel anionic species. In the presence of CMC, a substantial downward shift could be observed, similar to that reported in a previous study [95]. The negative shift should be due to the adsorption of the negatively charged species, as addressed previously for dolomite and calcite. Similarly to starch, the adsorption mechanism of CMC on hematite is likely chemisorption, since physisorption of such anionic species would be naturally inhibited by the negatively charged hematite surface. With the addition of chitosan, the zeta potential of hematite shifted remarkably in the positive direction such that its IEP shifted from 2.5 to 8. This shift should be due to the adsorption of chitosan; however, the adsorption mechanism could not be confirmed by zeta potential alone due to similar reasons explained above.

For pyrochlore, as seen in Figure 5d, its zeta potential did not significantly shift across the tested pH range in the presence of SS. This could imply that there is no adsorption; however, it is also plausible that adsorption took place, but due to the similar charges carried by the

mineral and SS species, shifts in zeta potential could not be observed. Since SS has been applied as a pyrochlore depressant (as reviewed in the Introduction), it is expected that SS interacts with pyrochlore; the adsorption and mechanism therefore must be confirmed by other techniques such as XPS. The shift in zeta potential of pyrochlore with OA varied under different pH ranges: at pH > 6, a positive shift was observed; at pH < 6, its zeta potential shifted to the negative direction. This might be attributed to the adsorption of negatively charged oxalate groups, possibly on the Ca sites by forming calcium oxalate [41]. With the presence of F100, shifts to the negative direction could be observed at pH < 9. This could be attributed to the adsorption of negatively charged lignosulphonate species, and the adsorption mechanism is likely due to chemisorption, since a negatively charged pyrochlore surface would naturally repel negatively charged depressant molecules and inhibit physisorption. In the presence of starch, the zeta potential of pyrochlore did not observe significant shifts across the tested pH range; similar to the case of pyrochlore with SS, this could imply no adsorption; it is also possible that similar charges carried by the mineral and starch molecules would allow the zeta potential to remain almost identical after adsorption takes place. Since starch has been applied as a pyrochlore depressant (as reviewed in the Introduction), it is expected that starch could interact with pyrochlore; the interactions should be further investigated by other surface chemistry techniques. In the presence of CMC, shifts to the negative direction could be observed at pH < 9. This could be attributed to the adsorption of depressants, and the adsorption mechanism is likely due to chemisorption, since a negatively charged pyrochlore surface would naturally repel negatively charged depressant species and inhibit physisorption. Similarly to dolomite, calcite, and hematite, a substantial shift to the positive direction was observed over the entire pH range when chitosan was added, and as a result, the IEP of pyrochlore shifted from 2.5 to 8. The adsorption mechanism could not be confirmed by zeta potential alone due to similar reasons explained above.

3.3. XPS

As stated previously, in addition to zeta potential, other surface chemistry techniques are required to confirm the adsorption and the corresponding adsorption mechanism of depressants on minerals. Due to this reason, XPS was applied in the present work. From XPS, changes in the surface atomic concentrations could be directly observed if adsorption of reagents takes place; shifts in the binding energy (BE) of elements provide insights on adsorption mechanisms.

3.3.1. Dolomite with Depressants

The atomic compositions of dolomite conditioned with depressants are compared with blank (dolomite conditioned in water at the same pH) in Table 1. Their survey and high-resolution spectra are compared in Figure 10.

Table 1. Atomic concentration of dolomite before and after conditioning with depressants at pH 7.

Sample	Atomic Concentration (%)					
	Ca	Mg	C	O	Si	N
Dolomite	9.9	5.2	26.6	46.2	0.9	-
Dolomite + SS	7.8	5.0	18.1	50.6	6.7	-
Dolomite + OA	9.7	5.1	25.1	47.7	0.8	-
Dolomite + F100	8.7	3.7	28.2	44.2	0.7	-
Dolomite + Starch	9.8	6.2	23.0	48.0	-	-
Dolomite + CMC	9.1	4.1	26.8	48.2	0.5	-
Dolomite + Chitosan	9.0	4.1	27.1	47.2	0.8	0.2

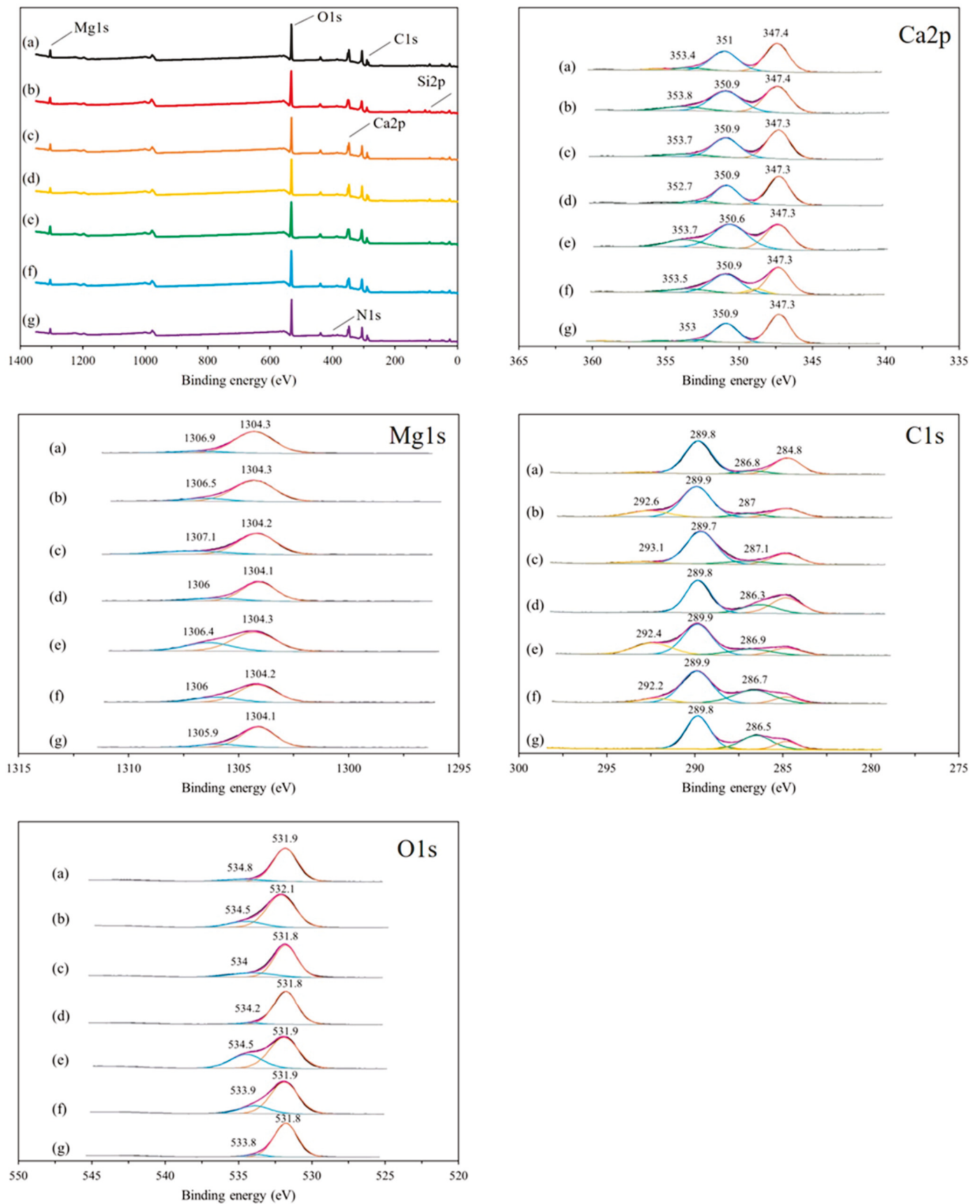


Figure 10. The survey and high-resolution XPS survey spectra of (a) dolomite and dolomite treated with (b) SS, (c) OA, (d) F100, (e) starch, (f) CMC, and (g) chitosan at pH 7.

As shown in Figure 10, the Ca2p peaks at 347.4 and 351 eV on blank dolomite are attributed to Ca2p_{3/2} and Ca2p_{1/2} of Ca in dolomite lattice [50,96–100]. Minor peaks at 353.4 and 355.7 eV might be due to Auger electron and satellite loss [101], which are usually not discussed in XPS spectra analysis in the literature. Therefore, they will be omitted from discussion for the rest of this paper. The Mg1s peak at 1304.3 eV on blank dolomite is attributed to the lattice Mg [50,96,97,101,102], whereas the minor peak at 1306.9 eV is likely due to satellite loss. The C1s peak at 284.8 eV corresponds to hydrocarbon, which was used to calibrate the position of other peaks; the peak at 289.8 eV corresponds to CO₃^{2−} in dolomite lattice [49,80,98,101,103], and the one at 286.8 eV might be attributed to C—O from surface contamination [51,98,101,103]. In the O1s spectrum of blank dolomite, the peak at 531.9 eV is attributed to CO₃^{2−} [80,96,98,99], whereas the peak at 534.8 eV might be due to minor impurities.

After conditioning with SS, as shown in Table 1, the content of Si on dolomite surface increased significantly from 0.9% to 6.7%, and the content of O increased from 46.2% to 50.6%; meanwhile, the contents of Mg, Ca, and C decreased slightly. In addition, Si2p peaks at 103.3 and 105.7 eV could be observed after SS treatment (Figure 11), suggesting the adsorption of SS species. This is in agreement with zeta potential measurement, where a shift to the negative direction was observed with SS (Figure 5a). This might explain the limited depression effect observed when DDA was used as collector (as shown in Figure 3a), since after adsorption, the negatively charged mineral surface might still naturally attract cationic amine species, whereas when NaOL was used as collector (Figure 2a), the negative surface charge would repel anionic oleate species and inhibit their adsorption on dolomite. It should be noted that a weak Si2p peak was observed at 102.8 eV on dolomite before SS treatment (as shown in Figure 11), which might be attributed to silicate impurities present in the model dolomite sample. As seen in Figure 10, the BE of Ca2p and Mg1s peaks did not shift significantly after SS treatment, suggesting their chemical environment did not change after treatment. A slight shift (+0.2 eV) was observed on the O1s peak corresponding to CO₃^{2−}, suggesting its chemical environment was slightly altered after SS treatment. This might suggest the adsorption mechanism of SS (possibly in the form of silica gel Si(OH)₄ at pH 7 [104]) on dolomite is through weak interactions such as hydrogen bonding [43] and electrostatic interaction [86]. The solubility of this gel in water is likely low, which explains the presence of Si on dolomite after washing.

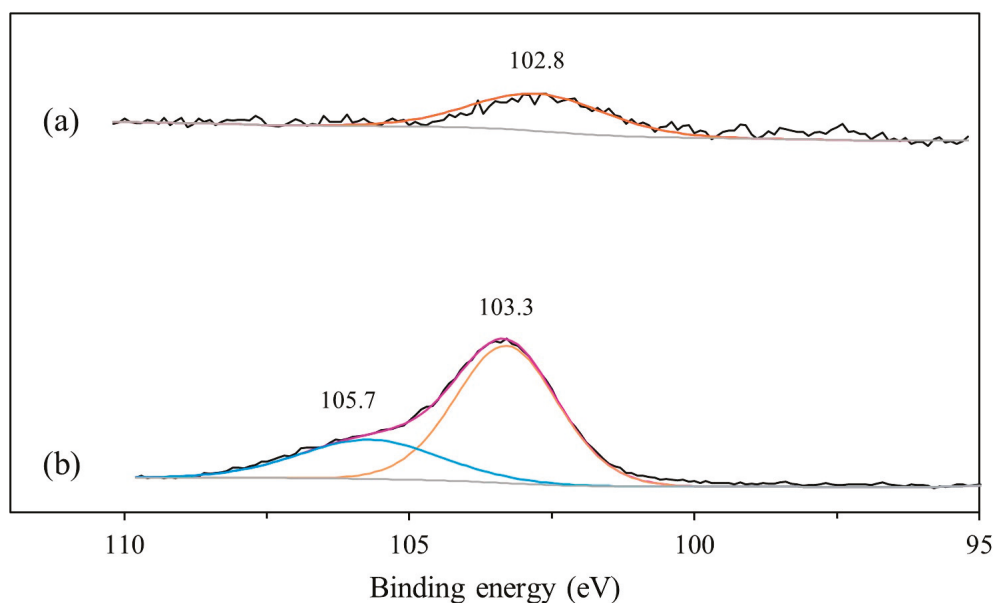


Figure 11. Si2p spectra of (a) dolomite and (b) dolomite + SS at pH 7.

After conditioning with OA, the surface composition of dolomite did not change significantly (as shown in Table 1). The binding energies of Mg1s, Ca2p, C1s, and O1s peaks only shifted insignificantly by 0.1 eV (as shown in Figure 10), which is close to the detection limit of the instrument, suggesting their chemical environment did not change significantly after treatment. These might suggest OA did not adsorb onto the dolomite surface under the tested conditions, which could explain the limited depression effect during microflotation using OA regardless of the collector used (as shown in Figures 2a and 3a).

As shown in Table 1, after conditioning with F100, the C content on dolomite surface increased slightly from 26.6% to 28.2%, and correspondingly, the rest of the elements decreased slightly, possibly indicating the adsorption of depressant. In the high-resolution spectra (Figure 10), the intensified C1s peak at 286.3 eV might be attributed to lignosulfonate molecule. The Mg1s peak at 1304.3 eV shifted slightly to 1304.1 eV, whereas the Ca2p peaks only shifted by 0.1 eV (close to the detection limit of the instrument), suggesting F100 might preferably adsorb on Mg sites. This is in agreement with the negative shift observed in zeta potential measurements (Figure 5) and might explain the reduced dolomite recovery, as shown in Figures 2a and 3a.

After the addition of starch, as shown in Table 1, the surface elemental composition of dolomite only changed slightly (approximately 1–2%, close to the detection limit of the instrument). In the high-resolution spectra, Ca2p peaks at 347.4 and 351 eV shifted to 347.2 and 350.6 eV, respectively, whereas the Mg1s peak at 1304.3 eV did not shift significantly. This suggests starch might adsorb onto dolomite through chemisorption, possibly on Ca sites. In addition, the new C1s peak at 292.4 eV and O1s peak at 534.5 eV suggest new C and O species presented on dolomite after treatment, possibly from starch molecules. It should be noted that the Ca2p peak at 353.7 eV and Mg1s peak at 1306.4 eV intensified, possibly due to hydrolyzation of Ca and Mg atoms on dolomite surface. Overall, according to XPS, starch likely adsorbed onto dolomite through chemisorption; this is in agreement with zeta potential measurement (Figure 5a), where a shift in the negative direction was observed. However, this is contradictory to previous work [51], where physisorption mechanisms such as hydrogen bonding and electrostatic interaction were proposed for starch on dolomite. The adsorption of starch explains the reduced recovery observed during microflotation (Figures 2a and 3a).

Similarly to the case of starch, the surface elemental composition of dolomite did not change significantly after the addition of CMC (as shown in Table 1). Compared to starch, the presence of CMC only created shifts of 0.1 eV in the BE of Ca2p and Mg1s peaks, which is close to the detection limit of the instrument. Similarly to the case of starch, new C1s peaks at 286.7 eV and new O1s peaks at 533.9 eV might be attributed to the adsorbed CMC molecules. This suggests the adsorption of CMC and might explain the shift in zeta potential (Figure 5a) and the reduced recovery in microflotation when CMC was added (Figures 2a and 3a). Its adsorption mechanism appears to be physisorption due to the insignificant shifts in the BE of Ca2p and Mg1s peaks; this is contradictory to previous work [105] where chemisorption was proposed for CMC to adsorb on dolomite through interacting with Ca and Mg. The adsorption of CMC on dolomite remains to be further investigated using other surface chemistry techniques.

After conditioning with chitosan, as shown in Table 1, the contents of O, and C increased slightly, and the content of N increased from non-detectable to 0.2%, suggesting chitosan adsorbed onto dolomite. This could be supported by the presence of the N1s peak at 399.7 eV (as shown in Figure 12), which should be attributed to —NH_2 groups [84, 106]. The binding energies of Ca2p peaks observed insignificant shifts (0.1 eV) after

chitosan treatment, whereas the Mg1s peak observed a larger shift from 1304.3 to 1304.1 eV, suggesting Mg might be the active site for chitosan adsorption, likely following the chemisorption mechanism that has been proposed previously [84]. The adsorption of chitosan is in agreement with the change in zeta potential (Figure 5), and could explain the reduced dolomite recovery during microflotation (as shown in Figures 2a and 3a).

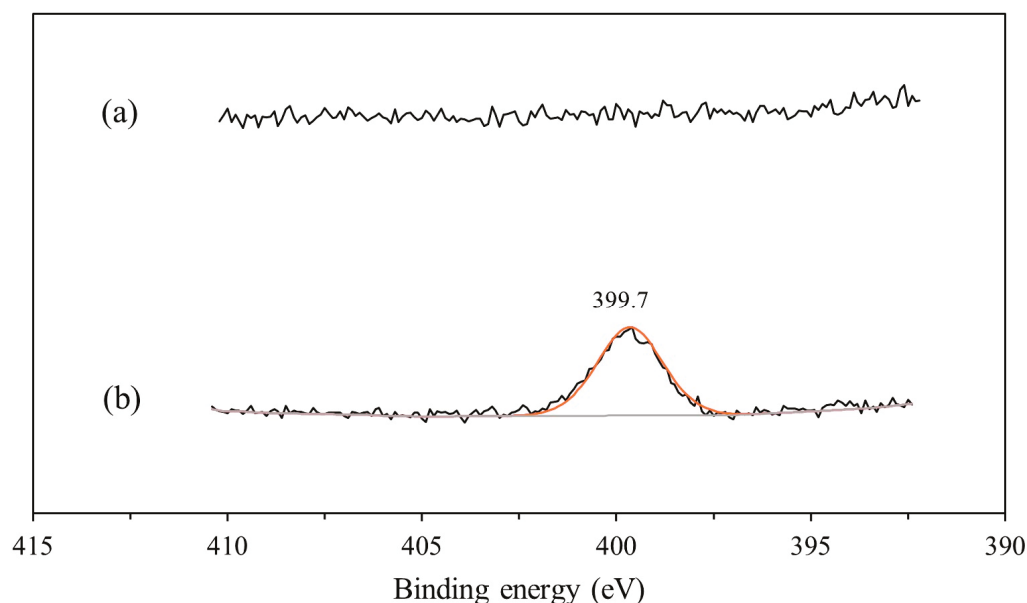


Figure 12. N1s spectra of (a) dolomite and (b) dolomite + chitosan at pH 7.

3.3.2. Calcite with Depressants

The atomic composition of calcite conditioned with different depressants is compared with a blank (calcite conditioned in water at the same pH) in Table 2. Their survey and high-resolution spectra are compared in Figure 13.

Table 2. Atomic concentration of calcite before and after conditioning with depressants at pH 7.

Sample	Atomic Concentration (%)				
	Ca	C	O	Si	N
Calcite	14.7	27.2	47.0	0.1	-
Calcite + SS	11.6	21.1	49.4	6.8	-
Calcite + OA	12.4	30.4	45.7	-	-
Calcite + F100	13.5	30.7	44.3	-	-
Calcite + Starch	14.2	27.3	46.9	-	-
Calcite + CMC	13.3	29.1	46.7	-	-
Calcite + Chitosan	13.3	27.2	47.0	-	1.2

For calcite conditioned in water, the Ca2p spectrum consists of Ca2p_{1/2} and Ca2p_{3/2} doublets at 350.6 eV and 347.1 eV, respectively, which is in good agreement with the values reported in the literature [56–58,107–113]. The minor peaks at around 355.1 and 358.8 eV correspond to satellite loss [107], which holds insignificant roles in spectra analysis and therefore will be excluded in the following analysis. In the C1s spectrum, the peak at 284.8 eV is attributed to hydrocarbons, whereas the peak at 289.6 eV is attributed to CO₃²⁻ in calcite [56,107,109,110,113,114]. The minor peak at 286.8 eV might be attributed to carbon oxides [109,114]. For the O1s spectrum, the peak at 531.5 eV is attributed to C—O present in calcite [57,107,108,111–113], whereas the peak at 533.6 eV might be assigned to Ca—O [111].

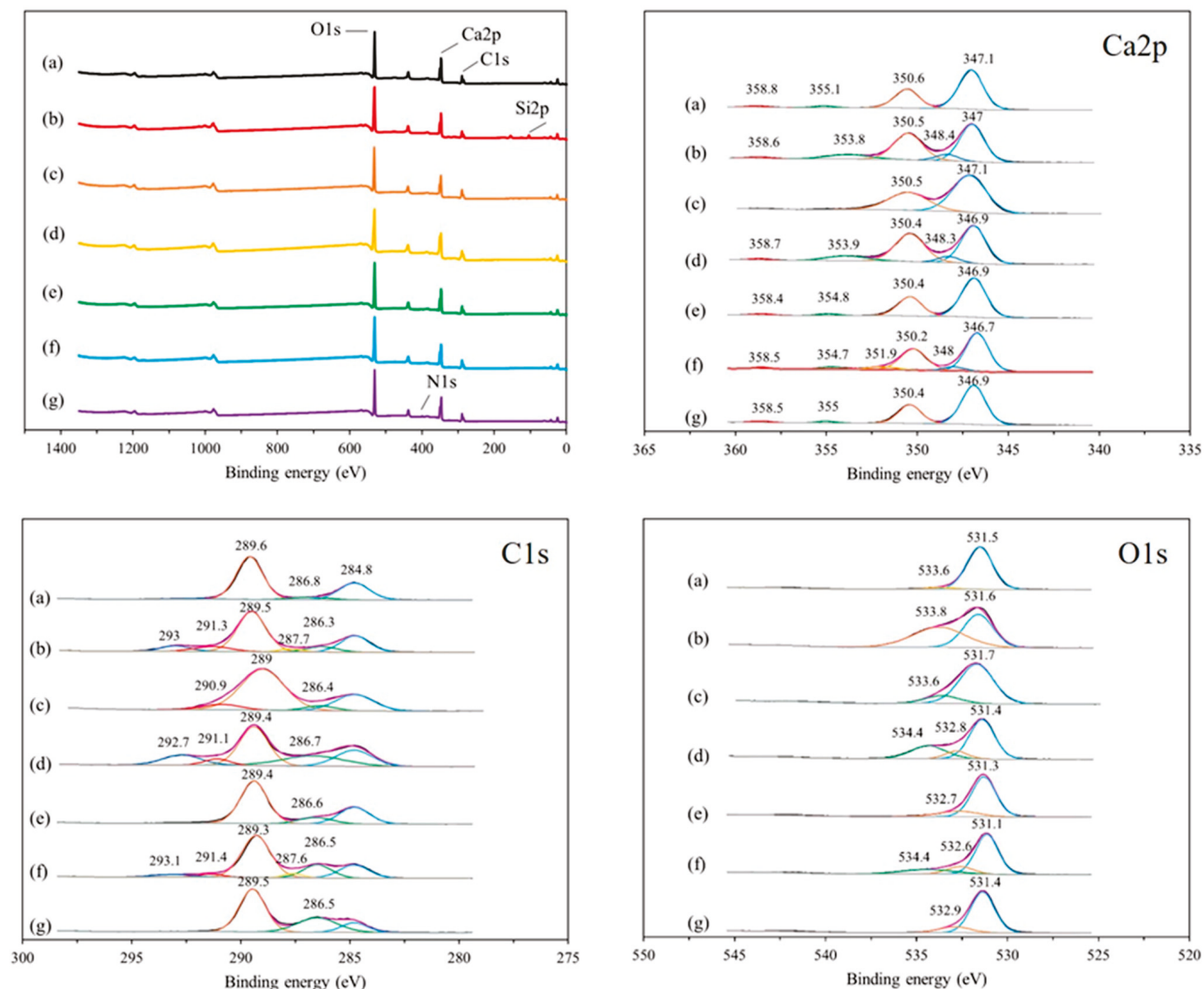


Figure 13. The survey and high-resolution XPS survey spectra of (a) calcite and calcite treated with (b) SS, (c) OA, (d) F100, (e) starch, (f) CMC, and (g) chitosan at pH 7.

As shown in Table 2, after conditioning with SS, the Si content increased significantly from 0.1% to 6.8%, suggesting the adsorption of SS species. This is supported by the presence of Si2p peaks at 103.5 and 105.6 eV after treatment (as shown in Figure 14). In addition, the intense O1s peak at 533.8 eV might be attributed to adsorbed SS species. This is in agreement with zeta potential measurements (Figure 5b), which showed a shift to a more negative value with SS at pH 7. It should be mentioned that a Si2p peak at 103 eV was observed on the blank calcite (as shown in Figure 14), which might be attributed to silicate impurities present in the model calcite sample. For the adsorption mechanism, the BE of Ca2p peaks did not shift significantly after SS treatment, suggesting its chemical environments did not change. It is plausible that SS adsorbs on calcite following a weak interaction mechanism similar to dolomite, where $\text{Si}(\text{OH})_4$ interacts with calcite by hydrogen bonding with O atoms [43]. Electrostatic interaction is also possible between SS and the oppositely charged mineral surface [86]. This is contradictory to [111,115] who proposed a chemisorption mechanism. The adsorbed SS inhibits the adsorption of NaOL, resulting in declined recovery (as observed in Figure 2b), which is in agreement with [104].

This depression was less effective when using DDA (as shown in Figure 3b), possibly because the negative calcite surface after SS treatment could naturally attract cationic amine species.

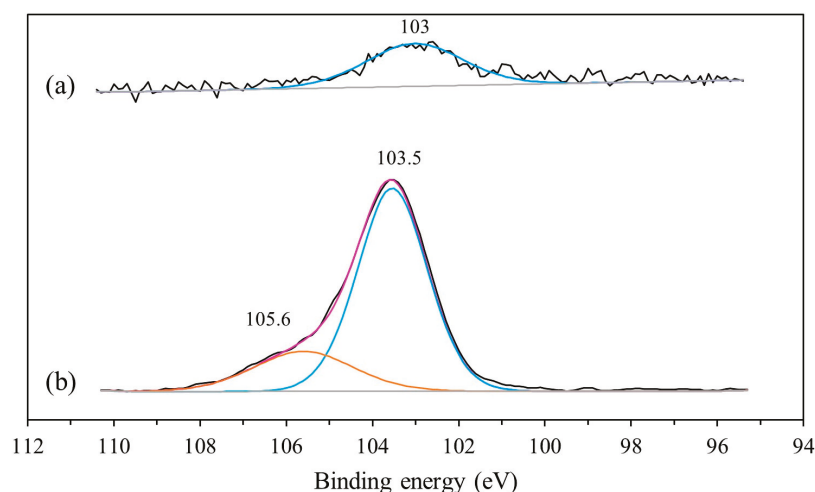


Figure 14. Si2p spectra of (a) calcite and (b) calcite + SS at pH 7.

After conditioning with OA, as shown in Table 2, the surface composition of calcite changed slightly such that its C content increased from 27.2% to 30.4%, whereas the Ca content decreased from 14.7% to 12.4%, which might suggest the adsorption of OA on calcite. In the high-resolution spectra, Ca2p peaks did not shift significantly, suggesting its chemical environment did not change after OA treatment. In contrast, the C1s peak corresponding to CO_3^{2-} observed a significant shift from 289.6 to 289 eV, and correspondingly, the O1s peak corresponding to CO_3^{2-} at 531.5 eV shifted to 531.7 eV after OA treatment. This suggests that OA interacted with CO_3^{2-} on the calcite surface. This is contradictory to previous works that suggested that OA interacted with Ca sites [41,113]. However, this might explain the limited depression achieved when OA was applied during microflotation using NaOL (Figure 2b): Ca, possibly the adsorption sites for NaOL [56,86], remained unaffected by OA, and therefore the adsorption of NaOL was not affected. However, this could not explain the limited depression effect when DDA was used as collector (Figure 3b), since it was proposed that DDA adsorbs on calcite through electrostatic attraction and hydrogen bonding between RNH_3^+ and CO_3^{2-} [59].

As shown in Table 2, after conditioning with F100, the C content on calcite increased slightly from 27.2% to 30.7%, whereas the contents of O and Ca decreased slightly, possibly due to adsorption of the depressant. In the high-resolution XPS spectra (Figure 13), Ca2p peaks shifted from 347.1 to 346.9 eV and from 350.6 to 350.4 eV, suggesting the chemical environment of Ca changed after F100 treatment. Similar interactions between Ca and lignosulphonate have been observed in other published research [87]. In addition, the C1s peak corresponding to CO_3^{2-} shifted from 289.6 eV to 289.4 eV, suggesting CO_3^{2-} sites were also involved in the adsorption of F100. This suggests the adsorption of F100 is likely chemisorption, which explains the reduced recovery in calcite flotation when F100 was added as depressant (as shown in Figures 2b and 3b).

After conditioning with starch, no significant changes in the atomic concentrations could be observed (as shown in Table 2). In the higher-resolution spectra, the major peaks of Ca2p observed shifts of 0.2 eV after conditioning with starch, which was also observed in [88,112,116]. Similar shifts could also be observed in C1s and O1s peaks corresponding to CO_3^{2-} (at 289.6 and 531.5 eV, respectively), suggesting starch interacted

with both Ca and CO_3^{2-} sites. This suggests the adsorption of starch on calcite and could explain the decreased calcite recovery when starch was added as depressant (as shown in Figures 2b and 3b). It should be highlighted that different interaction mechanisms between starch and calcite have been reported: interacting with Ca and O by forming Ca—O and hydrogen bonds [116,117], chemisorbing on Ca [88,112,118], (dextrin) chemisorbing on —OH and Ca [110], as well as interacting with O [88].

As shown in Table 2, the atomic composition of the calcite surface observed small changes after conditioning with CMC: C content increased slightly from 27.2% to 29.1%, and the contents of both Ca and O decreased slightly. In the high-resolution XPS spectra, Ca2p peaks shifted from 347.1 to 346.7 eV and from 350.6 to 350.2 eV, respectively, suggesting the chemical environment of Ca has been altered after CMC treatment. Similar shifts in Ca2p peaks have also been observed in other work [57]. In addition, the C1s and O1s peaks corresponding to CO_3^{2-} shifted significantly from 289.6 eV to 289.3 eV and from 531.5 eV to 531.1 eV, respectively. This suggests that CMC interacted with both Ca and CO_3^{2-} sites, likely through a chemisorption mechanism. This is in agreement with the conclusion drawn from zeta potential measurements (Figure 5b) and explains the reduced calcite recovery when CMC was added as depressant, as seen in Figures 2b and 3b.

After conditioning with chitosan, as shown in Table 2, the N content on calcite increased from non-detectable to 1.2%. This could be supported by the appearance of the N1s peak at 399.7 eV after conditioning (as shown in Figure 15), which might be attributed to —N=CH— [119], N—C=O [106], or —NH₂ groups [84,106,120] from chitosan. As shown in Figure 13, Ca2p peaks shifted slightly from 347.1 to 346.9 eV and from 350.6 to 350.4 eV. Meanwhile, only small shifts (0.1 eV) were observed on C1s and O1s peaks, which are close to the detection limit of the instrument. These shifts in the BE suggest Ca might be the adsorption site for chitosan, which is in agreement with previous work [120]. The adsorption of chitosan could explain the reduced calcite recovery when DDA was used as collector (Figure 3b) but could not explain the unaffected recovery when NaOL was used as collector (Figure 2b). One possible explanation is that the calcite surface became positively charged after the addition of chitosan (as shown in Figure 5b), which might naturally attract anionic oleate groups.

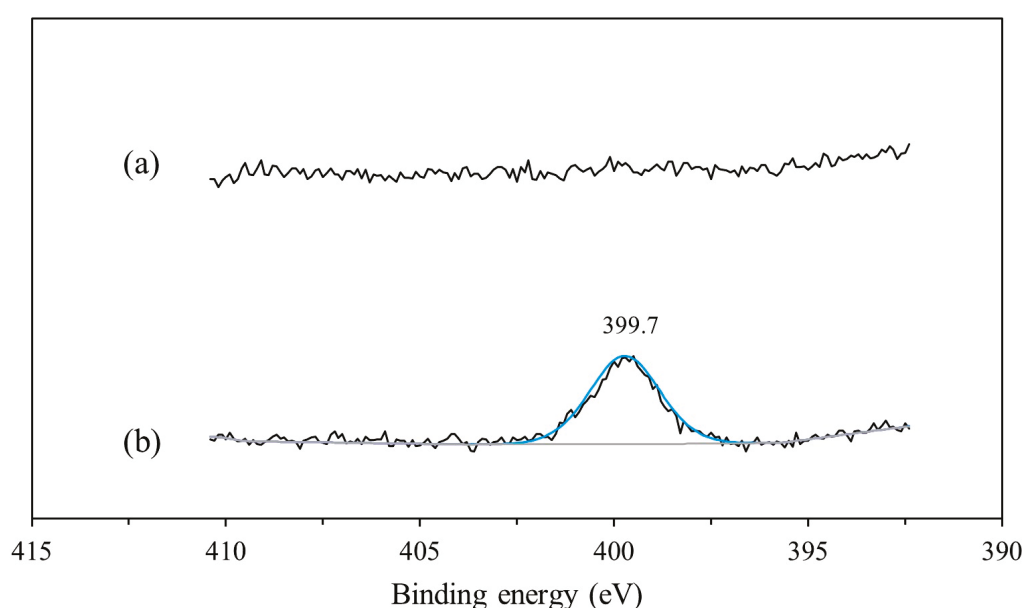


Figure 15. N1s spectra of (a) calcite and (b) calcite + chitosan at pH 7.

3.3.3. Hematite with Depressants

The atomic composition of hematite conditioned with different depressants is compared with the blank (hematite conditioned in water at the same pH) in Table 3. The survey and high-resolution spectra of key elements are compared in Figure 16.

Table 3. Atomic concentration of hematite before and after conditioning with depressants at pH 7.

Sample	Atomic Concentration (%)				
	Fe	C	O	Si	N
Hematite	13.1	11.3	54.1	8.3	-
Hematite + SS	17.3	9.7	52.9	9.1	-
Hematite + OA	14.2	12.9	54.6	6.5	-
Hematite + F100	14.4	13.8	53.9	5.8	-
Hematite + Starch	12.5	16.2	53.3	6.7	-
Hematite + CMC	13.7	13.3	54.2	6.6	-
Hematite + Chitosan	9.3	20.5	50.2	5.3	3.0

As seen in Figure 16 for hematite, the C1s peaks at 284.8, 286.5, and 289 eV were observed, which could be attributed to C—C, C—O, and C=O, respectively, from surface contamination [72,73,121]. O1s peaks at 529.9, 531.7, and 535.5 eV might be assigned to Fe—O (in Fe_2O_3) [73,92,121], O—H (in FeO—OH) [73,92,121], and Si—O (as quartz impurity) [122], respectively. On blank hematite, major Fe2p peaks were located at 711.2 and 724.3 eV, corresponding to $\text{Fe}2p_{3/2}$ and $\text{Fe}2p_{1/2}$, respectively [93,123]; peaks at 718.6 and 732 eV are assigned to their satellite signals [93,121]. It could be observed that these peaks are broad with a different shape compared to other elements (e.g., C1s and O1s in Figure 16), likely due to their being composed of several individual peaks that correspond to different chemical states of Fe. How to analyze and compare these broad peaks appears to be debatable in the literature: they have been compared as is (without deconvoluting) [90,123,124] or deconvoluted into two [90], three [92,93,121,125,126], or more [127,128] sub-multiplets corresponding to different chemical states of Fe. Some studies only focus on one of the doublets (i.e., $\text{Fe}2p_{3/2}$) [92,125,126,128] in their analyses, possibly due to simplicity. During XPS data analysis in this work, attempts have been made at deconvoluting the broad $\text{Fe}2p_{3/2}$ and $\text{Fe}2p_{1/2}$ peaks into three sub-multiplets according to the reported BE in [92,93,121,125,126]: the broad peak at 711.2 eV could be deconvoluted into 710.2, 711.3, and 713.8 eV, whereas the broad peak at 724.3 eV could be deconvoluted into 723.2, 724.9, and 727.3 eV. Peaks at 710.2 and 723.2 eV could be assigned to Fe^{2+} ; the remaining are assigned to Fe^{3+} [92,93,121,125,126]; among them, peaks at 713.8 and 727.3 eV could be assigned to FeO—OH as a result of hydrolyzation of Fe^{3+} [93,121]. Nevertheless, it was later noticed that the Fe2p doublets in other samples could be fit by peaks with similar binding energies; adjusting their heights and broadness was sufficient to fit the doublets well. This might give misleading information on the BE and, consequently, the change in chemical environment of Fe. Due to this reason, for the rest of the work, the broad Fe2p doublets will be compared as is without deconvoluting.

As shown in Table 3, after conditioning with SS, the Si content on hematite increased slightly from 8.3% to 9.1%; meanwhile, Si2p peaks appeared at 103.6 and 107 eV after treatment (as shown in Figure 17). This might indicate the adsorption of SS species on hematite; this is in agreement with zeta potential measurements (Figure 5c), which showed a shift to more negative values in the presence of SS at pH 7. In addition, the O1s peak corresponding to Si—O at 532.7 eV [122] significantly intensified after SS treatment, suggesting the presence of SS species on hematite. It should be emphasized that Si2p peaks at 102.5 and 99.6 eV on hematite before SS treatment (as shown in Figure 17) should be attributed

to silicate impurities in the hematite sample, which has been confirmed previously by XRD and XRF analyses (as shown in Figure A1c and Table A2, respectively). The adsorption mechanism of SS on hematite is likely chemisorption through interactions with Fe sites. As shown in Figure 16, the binding energies of Fe2p doublets shifted from 711.2 to 712.2 eV and from 724.3 to 725 eV after SS treatment, suggesting its chemical environment changed during the treatment. This is in agreement with the conclusion from zeta potential measurement, and might explain the insufficient depression when DDA was used as collector: after SS treatment, the hematite surface was negatively charged, which could naturally attract cationic DDA collector. However, this could not explain the high recovery of hematite achieved when NaOL was used as collector. The interaction between adsorbed reagents and the hematite surface remains to be further investigated.

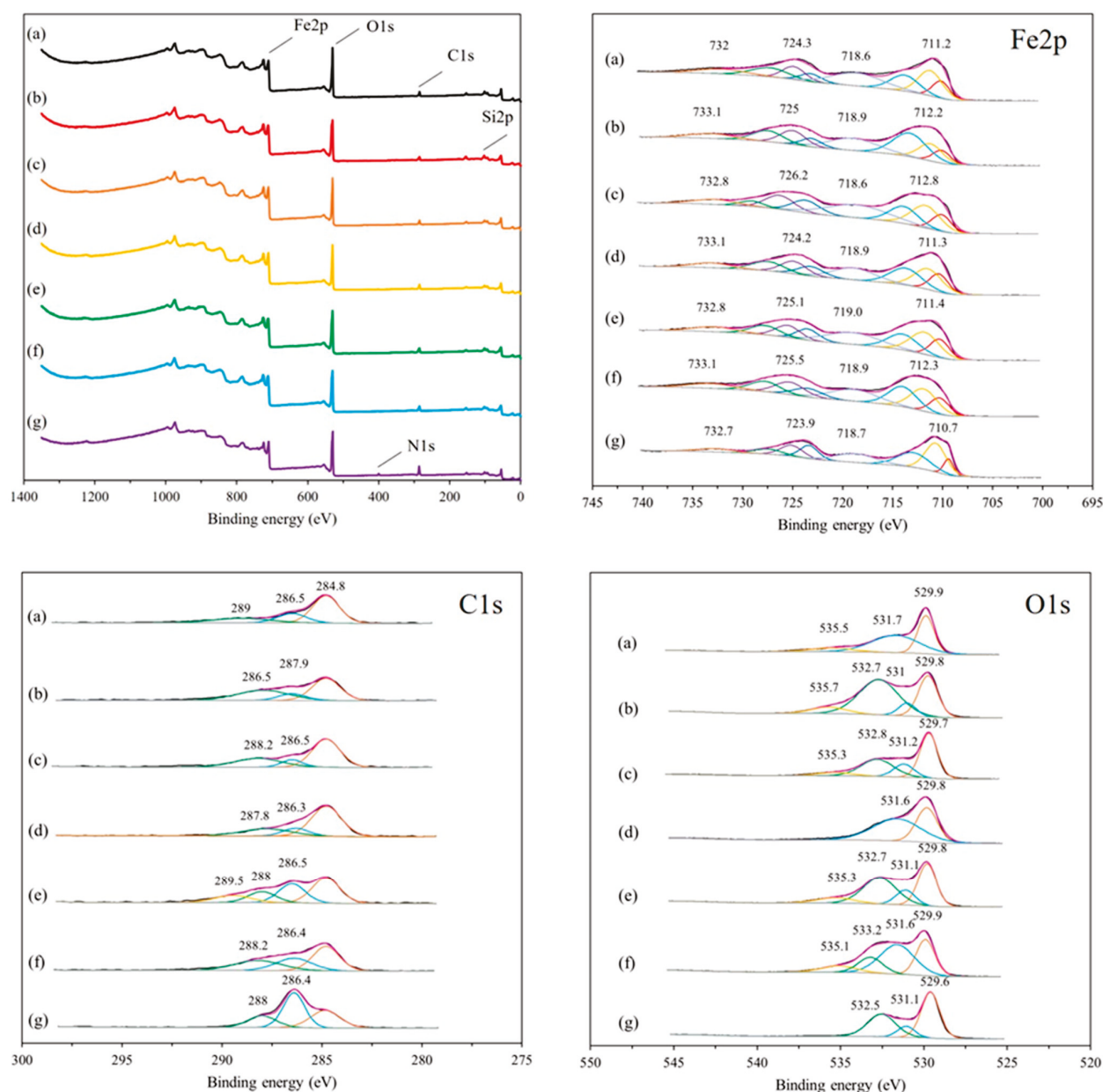


Figure 16. The survey and high-resolution XPS spectra of (a) hematite and hematite with (b) SS, (c) OA, (d) F100, (e) starch, (f) CMC, and (g) chitosan at pH 7.

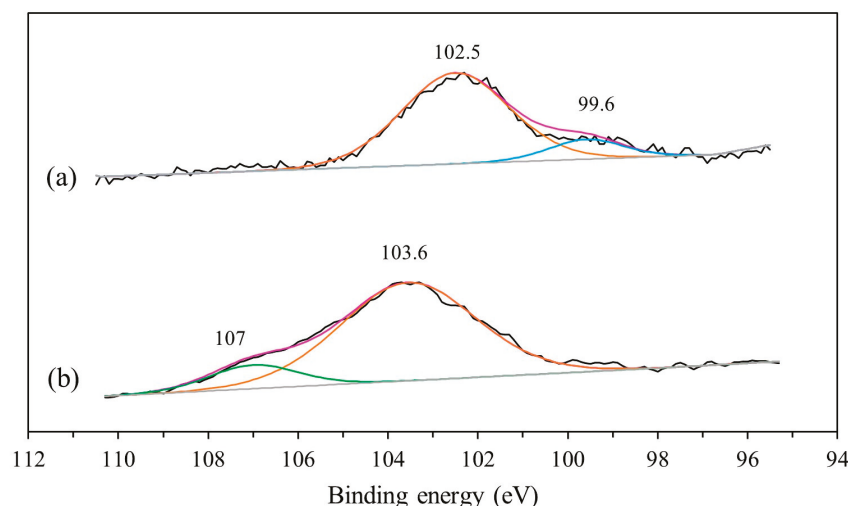


Figure 17. Si2p spectra for (a) hematite and (b) hematite + SS at pH 7.

After OA treatment, as shown in Table 3, the surface C content of hematite increased slightly from 11.3% to 12.9%, which might imply the adsorption of OA. In the high resolution C1s spectrum (Figure 16), the C1s peak at 288.2 eV after conditioning with OA might be attributed to C—O [129]; correspondingly, the O1s peak of the same bond could be observed at 532.8 eV [129], suggesting OA adsorbed on hematite. This could be supported by the negative shift in zeta potential of hematite with the presence of OA (as shown in Figure 5c). The adsorption mechanism of OA on hematite is likely chemisorption, as the BE of Fe2p peaks shifted significantly after OA treatment: peaks at 711.2 and 724.3 eV shifted to 712.8 and 726.2 eV, respectively, suggesting the chemical environment of Fe changed substantially. This might be attributed to the interaction between —COOH (from OA) and Fe—OH, which could be supported by the shift in the Fe—OH peak at 531.7 eV [73,92,121] to 531.2 eV after OA treatment. Correspondingly, the O1s peak at 531.7 eV (from Fe—OH [129]) shifted to 531.2 eV, suggesting the —OH group was involved in OA adsorption. However, this does not explain why the recovery remained nearly unaffected in the presence of OA (as shown in Figures 2c and 3c). The interactions between OA, the collectors, and the hematite surface should be further investigated.

As shown in Table 3, the surface composition of hematite only changed slightly after conditioning with F100. In addition, no significant shifts in the major peaks in Fe2p, C1s, and O1s spectra were observed, suggesting the presence of F100 did not change the chemical environment of these elements. This could explain the limited depression observed on hematite when F100 was added during microflotation (as shown in Figures 2c and 3c). Previous work proposed physisorption as the interaction mechanism between F100 and hematite [90]; this could not explain the negative shift in the zeta potential of hematite in the presence of F100 (as shown in Figure 5c), since negatively charged hematite would naturally repel anionic lignosulphonate groups and inhibit physisorption. One possible reason for the shift in zeta potential might be the presence of F100 depressed electrical double layer of hematite particles, shifting its zeta potential to more negative values. The interaction mechanism between F100 and hematite therefore remains to be further investigated.

As shown in Table 3, after conditioning with starch, the surface C content on hematite increased significantly from 11.3% to 16.2%, whereas the contents of other elements reduced correspondingly, suggesting the adsorption of starch on hematite. This could explain the reduced recoveries of hematite (as shown in Figures 2c and 3c). The presence of starch

could be further supported by the changes in C1s and O1s spectra: after starch treatment, C1s peaks at 288 and 289.5 eV appeared, which might be attributed to C—O/COO[−] and COOH, respectively, in starch [121,129]. In the O1s spectrum, the new peak at 532.7 eV (corresponding to C—O from starch [93,121,129]) suggests starch adsorbed on hematite. The adsorption mechanism of starch is likely through interactions with the —OH groups on the hematite surface: it could be observed that the O1s peak at 531.7 eV (corresponding to Fe—OH [129]) shifted to 531.1 eV, suggesting the hydroxyl group was involved in starch adsorption. A similar mechanism (as shown in Figure 18) was also proposed by [94], who also suggested that the selectivity of the oxygen atoms was related to the polarity and its solubility in water [94]. In addition to the —OH groups, Fe might also participate directly in starch adsorption since Fe2p peaks shifted from 711.2 and 724.3 eV to 711.4 and 725.1 eV, respectively. However, its role should be further confirmed since the magnitudes of shift for the doublets are very different. Other studies [92,125] have confirmed the role of Fe in starch adsorption, possibly through the formation of a stable five-atom ring with the C—O groups from starch [92].

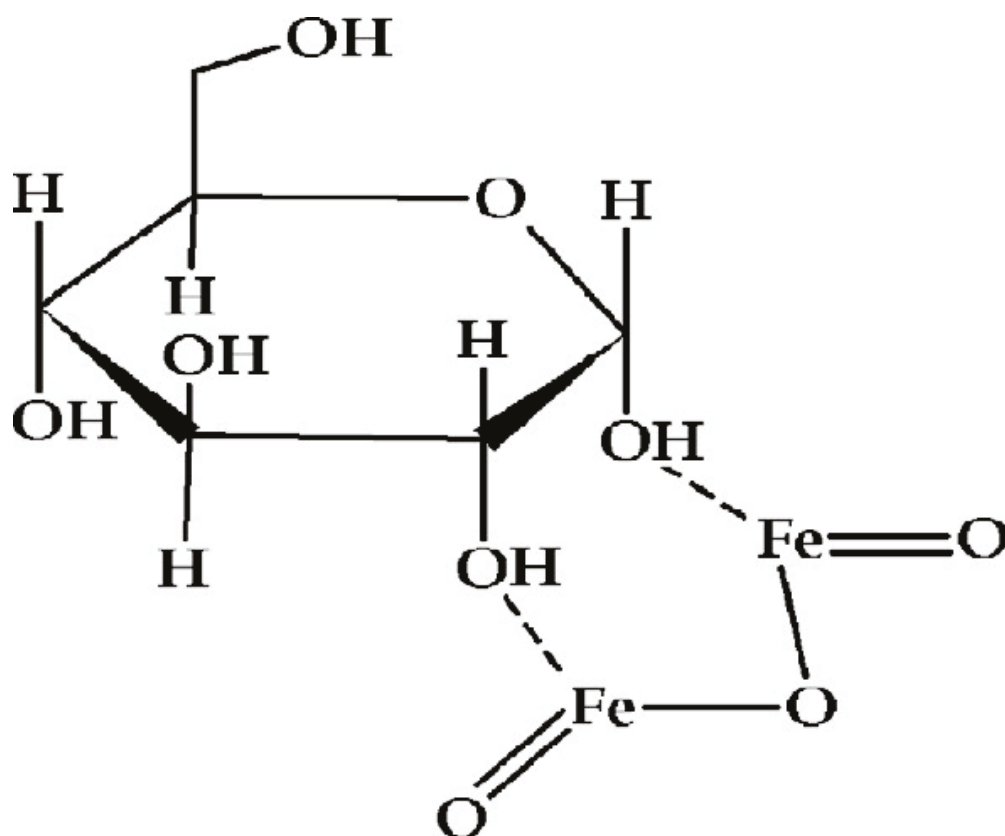


Figure 18. A schematic presentation of hematite-starch interaction, adapted from [94].

As shown in Table 3, the surface C content of hematite increased slightly from 11.3% to 13.3% after CMC treatment, possibly due to the adsorption of CMC. This is supported by the appearance of a new O1s peak at 533.2 eV, which could be attributed to C—OH and C—O—C from CMC [121]. Meanwhile, the peak corresponding to —OH at 531.6 eV intensified, likely due to the increased —OH population on hematite as a result of CMC adsorption. The adsorption mechanism of CMC on hematite is likely chemisorption. As shown in the Fe2p spectrum in Figure 16, the doublets shifted from 711.2 and 724.3 eV to 712.3 and 725.5 eV, respectively, after CMC treatment, suggesting the chemical environment of Fe has been significantly changed. A similar mechanism was proposed by other

researchers as follows: chemical bonds formed between Fe^{3+} and —COO^- from CMC [95]. As a result, a hydration repulsive force was produced due to the hydrophilic groups (—OH and —COO^-), allowing hematite depression [95]. However, this is contradictory to flotation results (Figures 2c and 3c) that CMC showed limited depression effect to the hematite when either NaOL or DDA was used as collector.

As shown in Table 3, the surface C content on hematite observed a remarkable increase from 11.3% to 20.5% after conditioning with chitosan; meanwhile, its N content increased from non-detectable to 3.0%, suggesting the adsorption of chitosan. This could be supported by the presence of N1s peaks at 399.6 and 401.7 eV (Figure 19), which might be attributed to —NH_2 [106,130] and —NH_3^+ [130], respectively. In addition, the C1s peak corresponding to C—O at 286.4 eV became dominant after treatment, and correspondingly, the O1s peak corresponding to C—O at 532.5 eV [93,121,129] intensified, confirming the adsorption of chitosan. The adsorption mechanism of chitosan on hematite is likely chemisorption. As shown in Figure 16, the Fe2p peaks shifted from 711.2 and 724.3 eV to 710.7 and 723.9 eV, respectively, suggesting the chemical environment of Fe changed during conditioning with chitosan. In addition, the O1s peak at 531.7 eV corresponding to —OH shifted to 531.1 eV, suggesting the hydroxyl groups were involved in chitosan adsorption. A similar chemisorption mechanism between —COOH (and —NH—) and Fe^{3+} was also proposed by [126], who also suggested that this interaction was stronger than hydrogen bonding between —OH groups from starch and the hydroxylated hematite surface; therefore, chitosan was a stronger hematite depressant than starch [126]. This explains the strong depression effect of chitosan on hematite, as observed during microflotation (Figures 2c and 3c).

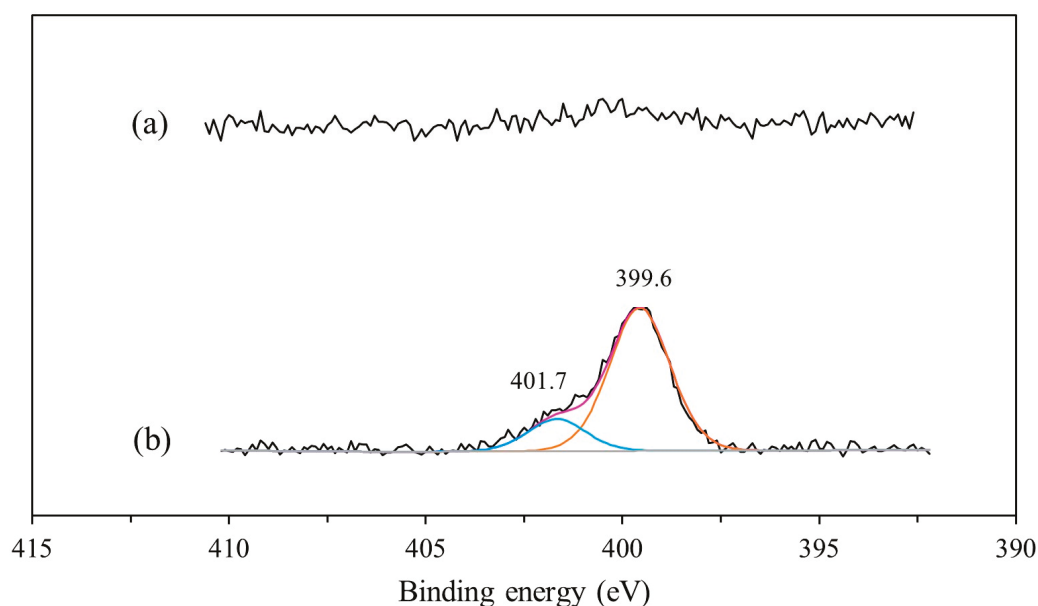


Figure 19. N1s spectra for (a) hematite and (b) hematite + chitosan at pH 7.

3.3.4. Pyrochlore with Depressants

The atomic composition of pyrochlore conditioned with different depressants is compared with blank (pyrochlore conditioned in water at the same pH) in Table 4. The survey and high-resolution spectra of key elements are compared in Figure 20.

Table 4. Atomic concentration of pyrochlore before and after conditioning with depressants pH 7.

Sample	Atomic Concentration (%)						
	Nb	Ca	Fe	C	O	Si	N
Pyrochlore	9.3	5.6	2.8	13.1	47.0	2.3	-
Pyrochlore + SS	8.8	5.1	2.2	13.3	47.0	5.3	-
Pyrochlore + OA	9.0	5.6	2.0	20.3	43.8	2.0	-
Pyrochlore + F100	9.5	5.3	2.3	18.2	44.6	2.3	-
Pyrochlore + Starch	8.8	5.2	2.3	16.8	45.8	2.7	-
Pyrochlore + CMC	9.3	5.2	2.3	17.7	46.4	2.1	-
Pyrochlore + Chitosan	7.1	3.8	1.7	21.6	43.8	1.7	4.5

On blank pyrochlore, Nb3d_{5/2} and Nb3d_{3/2} peaks were observed at 206.9 and 209.6 eV, respectively, which are in close agreement with previous studies [41,42,75,76,131]. Ca2p peaks are observed at 347 and 350.7 eV, which are in good agreement with [42,75,76]. The minor Ca2p peak at 343.9 eV was also observed in [42,75,76,131] but was not discussed by the authors. In addition to Nb and Ca, Fe signals could be detected and were included for comparison. As shown in Figure 20, Fe2p doublets were identified at 711 and 723.5 eV; compared to Nb and Ca, the signals for Fe are noisier, possibly due to its low concentration in pyrochlore (as seen in Table A2). On the blank pyrochlore, C1s peaks at 284.8 and 286.5 eV could be assigned to C—C and C—O, respectively, possibly from surface contamination [132]; the peak at 289 eV might be attributed to CO₃^{2−} from carbonate impurity such as dolomite [49,98,101,103] and calcite [56,107,109,110,113,114]. O1s peaks at 530 and 531.8 eV might be attributed to Nb—O [132] and C—O (possibly from calcite [57,107,108,111–113] and dolomite [99]), respectively.

After conditioning with SS, as shown in Table 4, the Si content on pyrochlore increased from 2.3% to 5.3%. This might suggest the adsorption of SS and could be supported by the presence of Si2p peaks at 102.4 and 104.1 eV after SS treatment (Figure 21). It should be noted that a peak at 102 eV was observed on blank pyrochlore before SS treatment, which might be due to silicate impurities present in the pyrochlore sample. The adsorption mechanism of SS on pyrochlore appears to be chemisorption on Ca sites. From Figure 20, the Ca2p peak at 347 eV shifted to 347.3 eV, suggesting it interacted with SS, which was also observed in [111,115]. In comparison, the Nb3d peaks did not shift significantly after SS treatment, suggesting it was not involved during SS adsorption. Shifts in BE were also observed on Fe2p peaks; however, its role in SS adsorption should be further confirmed due to its noisier signals and broad feature. The adsorbed SS could inhibit the adsorption of NaOL, resulting in declined recovery in microflotation (as observed in Figure 2d). However, similar depression was not observed when DDA was used as collector, possibly due to the fact that the negatively charged pyrochlore surface after SS treatment could still attract cationic collector DDA through electrostatic interaction.

As shown in Table 4, after conditioning with OA, the C content on pyrochlore increased from 13.1% to 20.3%, whereas the contents of other elements decreased slightly, suggesting the adsorption of OA. This might be supported by the intensive O1s peak at 532.2 eV in Figure 20, which could be attributed to C—O bonding from OA [129]. However, this is not in agreement with zeta potential results, where the zeta potential of pyrochlore remained almost unchanged in the presence of OA (as shown in Figure 5). The XPS result is also not supported by microflotation results that OA showed almost no depression to pyrochlore (Figures 2d and 3d). The adsorption mechanism of OA on pyrochlore might be through chemical interaction with Ca and Fe sites. As shown in Figure 20, a shift of 0.3 eV was observed on one of the Ca2p doublets at 350.7 eV, suggesting it might be involved in OA adsorption. However, the

other peak at 347 eV did not shift by a significant amount; therefore, the role of Ca sites in OA adsorption remains to be further investigated. Fe might be involved in adsorption since its peaks shifted significantly from 711 and 723.5 eV to 712.5 and 725 eV, respectively; however, due to its noisy signals and broad peaks, its role in the adsorption remains to be confirmed. In comparison, the Nb3d peaks did not shift by significant amounts.

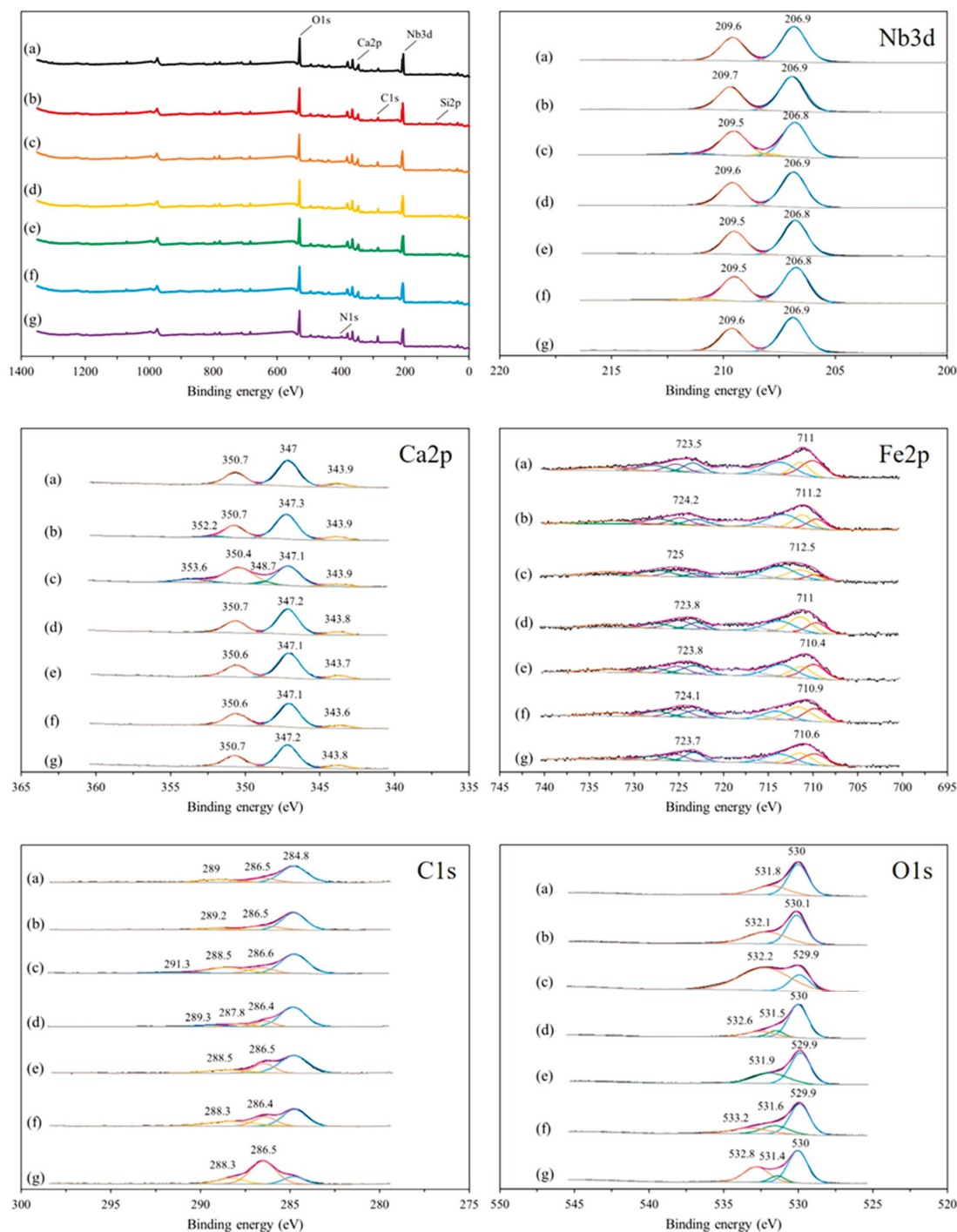


Figure 20. The survey and high-resolution XPS spectra of (a) pyrochlore and pyrochlore with (b) SS, (c) OA, (d) F100, (e) starch, (f) CMC, and (g) chitosan at pH 7.

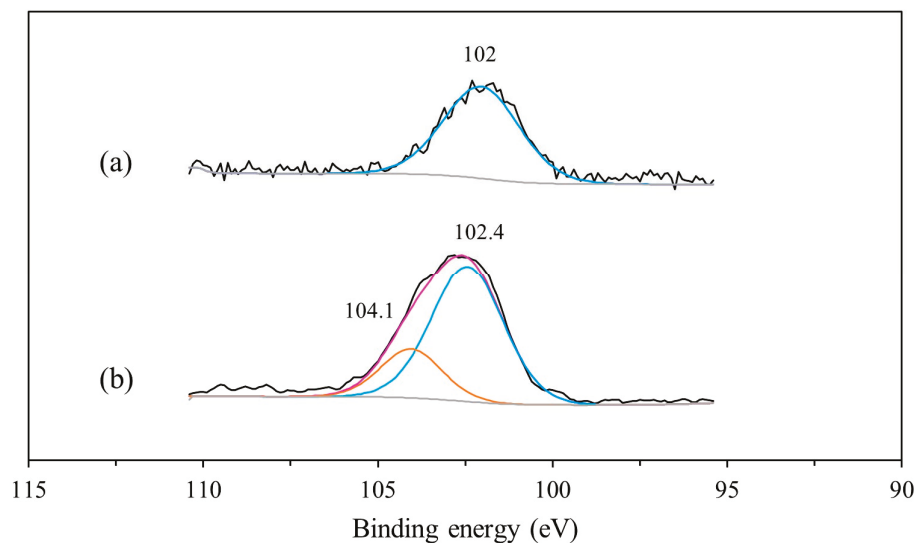


Figure 21. Si2p spectra for of (a) pyrochlore and (b) pyrochlore + SS at pH 7.

As shown in Table 4, after conditioning with F100, the C content of pyrochlore increased slightly from 13.1% to 18.2%, which implies the adsorption of F100 and could be supported by zeta potential measurements (as shown in Figure 5d). As shown in Figure 20, the Ca2p_{3/2} peak at 347 eV shifted slightly to 347.2 eV after F100 treatment, whereas the Fe2p_{1/2} peak at 723.5 shifted to 723.8 eV. In comparison, the BE of Nb3d peaks did not shift. The changes in the binding energies suggest F100 might interact with the Ca and Fe sites on pyrochlore. However, it should be highlighted that due to the relatively small shifts in the binding energies and only one of the doublets shifted after treatment, the adsorption of F100 on pyrochlore and its mechanism remain to be further confirmed. The possible adsorption might explain the reduced pyrochlore recovery when using NaOL as collector (as observed in Figure 2d). Nevertheless, its depression effect when using DDA was limited, possibly because the negatively charged mineral surface could still attract cationic DDA collectors through electrostatic forces.

After conditioning with starch, as shown in Table 4, the C content of pyrochlore increased slightly from 13.1% to 16.8%, and the contents of other key elements observed slight decreases, suggesting starch might adsorb onto the pyrochlore surface. This is supported by the intensified C1s peak at 286.5 eV, which is attributed to C—O bond in starch [129,132]. Correspondingly, the O1s peak at 531.9 eV from the same bonding also intensified, suggesting the adsorption of starch on pyrochlore. The adsorption of starch might explain the decrease in pyrochlore recovery observed in microflotation (as observed in Figures 2d and 3d). Compared to Nb and Ca, it appears that Fe interacted more intensively with starch as its peaks shifted from 723.5 and 711 eV to 723.8 and 710.4 eV, respectively, whereas the peaks in Nb3d and Ca2p spectra only shifted by a magnitude of 0.1 eV, close to the detection limit of the instrument. However, due to the broad feature and noisy signals associated with Fe2p peaks, its role in starch adsorption should be further confirmed by other techniques.

As shown in Table 4, the C content of pyrochlore increased slightly from 13.1% to 17.7% after conditioning with CMC, while the contents of other key elements decreased slightly, suggesting CMC might adsorb onto the pyrochlore surface. This could be supported by the appearance of a new O1s peak at 533.2 eV, which might be attributed to —OH and C—O—C from CMC [121]. Similarly to the case of starch, significant shifts in the BE were observed only on Fe2p: its peaks shifted from 723.5 and 711 eV to 724.1 and 710.9 eV, respectively,

after CMC treatment. In comparison, shifts observed in Nb3d and Ca2p spectra were only 0.1 eV, suggesting their chemical environments did not change significantly after CMC treatment. This might explain the reduced recovery (as observed in Figure 2d) when NaOL was used as collector. However, when DDA was applied (Figure 3d), high pyrochlore recovery could still be observed, possibly due to the adsorption of cationic collectors on the negatively charged mineral surface through electrostatic interactions.

After conditioning with chitosan, as shown in Table 4, the C content of pyrochlore increased significantly from 13.1% to 21.6%, and the N content increased from non-detectable to 4.45%, suggesting the presence of chitosan on the pyrochlore surface. This could be supported by the presence of N1s peaks (as shown in Figure 22) at 399.7 eV, which can be attributed to —N=CH— [119], N—C=O , or NH_2 [106] from chitosan. In addition, the C1s peak at 286.5 eV, corresponding to C—O in chitosan, became dominant after treatment; correspondingly, the O1s peak corresponding to the same bonding at 532.8 eV [93,121,129] intensified, further confirming the adsorption of chitosan. The adsorption of chitosan could explain the reduced flotation recovery (Figures 2d and 3d). It appears that the depression effect was stronger when DDA was used as collector (shown as a lower dosage of chitosan was required to achieve complete depression). This might be explained by the positively charged pyrochlore after chitosan treatment (shown in Figure 5d) repelling cationic DDA. It appears that chitosan adsorbs on pyrochlore by interacting with Fe, possibly also Ca sites. From Figure 20, it could be observed that Fe2p peaks at 723.5 and 711 eV shifted to 723.7 and 710.3 eV, respectively, suggesting its chemical environment changed during chitosan treatment. In the Ca2p spectrum, the Ca2p_{3/2} peak at 347 eV shifted by 0.2 eV after conditioning with chitosan, suggesting it might also participate in the adsorption. In comparison, the Nb3d peaks remained unchanged after conditioning with chitosan, suggesting its chemical environment did not change.

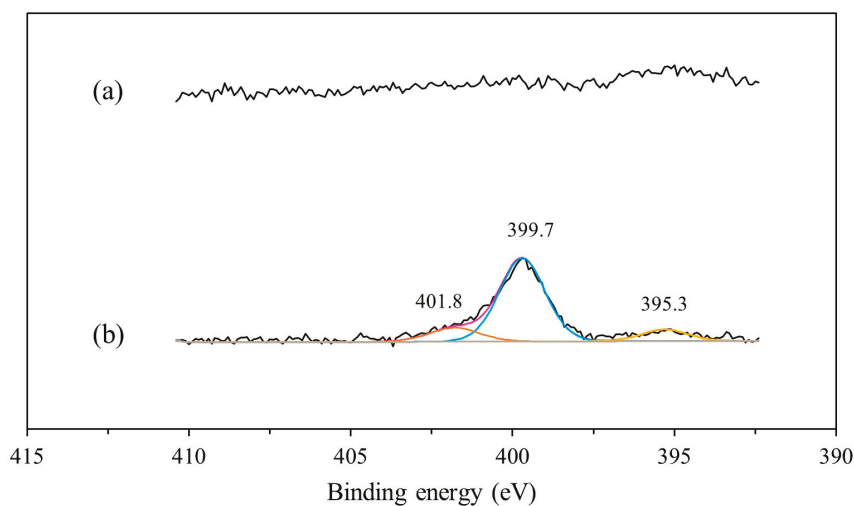


Figure 22. N1s spectra for of (a) pyrochlore and (b) pyrochlore + chitosan at pH 7.

4. Discussion

In the present work, different depressants, including SS, OA, F100, starch, CMC, and chitosan, are compared in the flotation of pyrochlore, dolomite, calcite, and hematite. Their performance was evaluated at pH 7 in the presence of NaOL and DDA as collectors. Microflotation tests were conducted on model minerals; zeta potential and XPS techniques were employed to understand the reagent-mineral interaction. Key findings are highlighted as follows:

1. When either NaOL or DDA was used as collector, the recoveries of the model minerals followed a similar trend and reached relatively high recoveries (between 70 and 80%) with 2 kg/t of collector; as the collector's dosage further increased to 5 kg/t, their recoveries did not increase significantly. This suggests these collectors are strong with poor selectivity. In order to achieve separation between pyrochlore and the gangue minerals using these collectors, depressants are required.
2. The performance of tested depressants appears to be related to the collector applied. This difference in performance was justified by the surface charge of minerals after depressant adsorption and the charge of the collector. For example, the depression effect of chitosan was more severe when DDA was applied as collector, possibly because the positively charged mineral surfaces after chitosan adsorption would naturally repel cationic amine collectors.
3. Among the tested conditions, 5 kg/t F100 + 2 kg/t DDA and 5 kg/t CMC + 2 kg/t DDA showed potential selectivity in that pyrochlore and hematite were nearly unaffected, whereas dolomite and calcite were significantly depressed. Future work will focus on investigating these potential selective conditions and exploring other selective reagent schemes. It is recommended to test the potential selective reagent conditions on a synthetic mixture of the minerals to confirm their selectivity.
4. Surface chemistry study suggests SS interacts with dolomite and calcite through weak interaction mechanisms (e.g., hydrogen bonding and electrostatic interaction); it interacts with hematite and pyrochlore through chemisorption by interacting with Fe (on hematite) and Ca (on pyrochlore) sites. OA seems to not adsorb on dolomite; it might adsorb on other minerals through interacting with CO_3^{2-} (for calcite), Fe and OH groups (for hematite), and Ca and Fe (on pyrochlore). For F100, it might interact with Mg on dolomite, Ca and CO_3^{2-} sites on calcite, Ca and Fe sites on pyrochlore, but it did not interact with hematite. For starch, it might interact with Ca sites on dolomite, Ca and CO_3^{2-} sites on calcite, Fe and OH groups on hematite, and Fe on pyrochlore. For CMC, it adsorbs onto dolomite, possibly through physisorption; it likely interacts through chemisorption at Ca and CO_3^{2-} sites on calcite, Fe and OH groups on hematite, Fe on pyrochlore. For chitosan, it adsorbs on dolomite likely through interacting with Mg sites, Ca sites on calcite, Fe and OH groups on hematite, Fe and Ca sites on pyrochlore.
5. It should be highlighted that the applied techniques have their limitations: zeta potential is less useful when the added reagents carry similar charges as the mineral surfaces; it also gives limited information on the adsorption mechanisms. For XPS, it is sensitive to surface contamination; for some elements (e.g., Fe), how to deconvolute their peaks appears to be arguable; therefore, their roles in reagent adsorption remain to be further investigated. To achieve better understanding of the reagent adsorption mechanisms, other techniques such as FTIR, ToF-SIMS, Raman spectroscopy, AFM, and DFT simulation might be useful in future investigation.
6. It is also recommended to investigate the performance and interaction mechanism of the depressants and minerals at other pH values. By doing so, the knowledge on the application of depressants for Nb mineral flotation could be further expanded.

5. Conclusions

The current production of Nb is dominated by beneficiating pyrochlore-containing ore using flotation. During flotation stages, depressants are added to improve selectivity, which highlights their importance to Nb mineral flotation. However, it appears that compared to collectors, the knowledge on depressants is limited in the context of Nb mineral flotation.

Due to this reason, this work compared different depressants, including SS, OA, F100, starch, CMC, and chitosan, in the flotation of pyrochlore and its common gangue minerals, where NaOL and DDA were used as collectors. It was observed that the performance of depressants was related to the collector applied. For example, a relatively high dosage (2–5 kg/t) of chitosan was required to completely depress dolomite, hematite, and pyrochlore when NaOL was used as collector, whereas calcite was not depressed; in comparison, when DDA was used, the dosage of chitosan required to achieve complete depression was much lower (0.1–1 kg/t). This was justified by the surface charge of model minerals after depressant adsorption repels collector species.

The reagent-mineral interaction was investigated by zeta potential measurement and XPS techniques. Shifts in zeta potential after reagent addition might suggest adsorption, which was further confirmed by the change in surface composition using XPS. In addition, shifts in the BE of elements give insights into the adsorption mechanism, as detailed during the Results and Discussion sections. It should be highlighted that due to the limitation of techniques, other surface chemistry techniques might be helpful to further investigate the interaction between reagents and minerals.

Author Contributions: Conceptualization, R.L. and K.E.W.; methodology, R.L. and K.E.W.; software, R.L.; validation, R.L.; formal analysis, R.L.; investigation, R.L.; resources, K.E.W.; data curation, R.L.; writing—original draft preparation, R.L.; writing—review and editing, R.L. and K.E.W.; visualization, R.L.; supervision, K.E.W.; project administration, K.E.W.; funding acquisition, K.E.W. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AFM	Atomic force microscopy
BE	Binding energy
BSE	Backscattered electron
C.I.	Confidence intervals
CMC	Carboxymethyl cellulose
DDA	Dodecylamine
DFT	Density functional theory
EDS	Energy dispersive spectrometer
FTIR	Fourier transform infrared spectroscopy
NaOL	Sodium oleate
OA	Oxalic acid
PSA	Particle size analysis
SEM	Scanning electron microscopy
SS	Sodium silicate
ToF-SIMS	Time-of-Flight Secondary Ion Mass Spectrometry

WHIMS	Wet high intensity magnetic separator
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

Appendix A

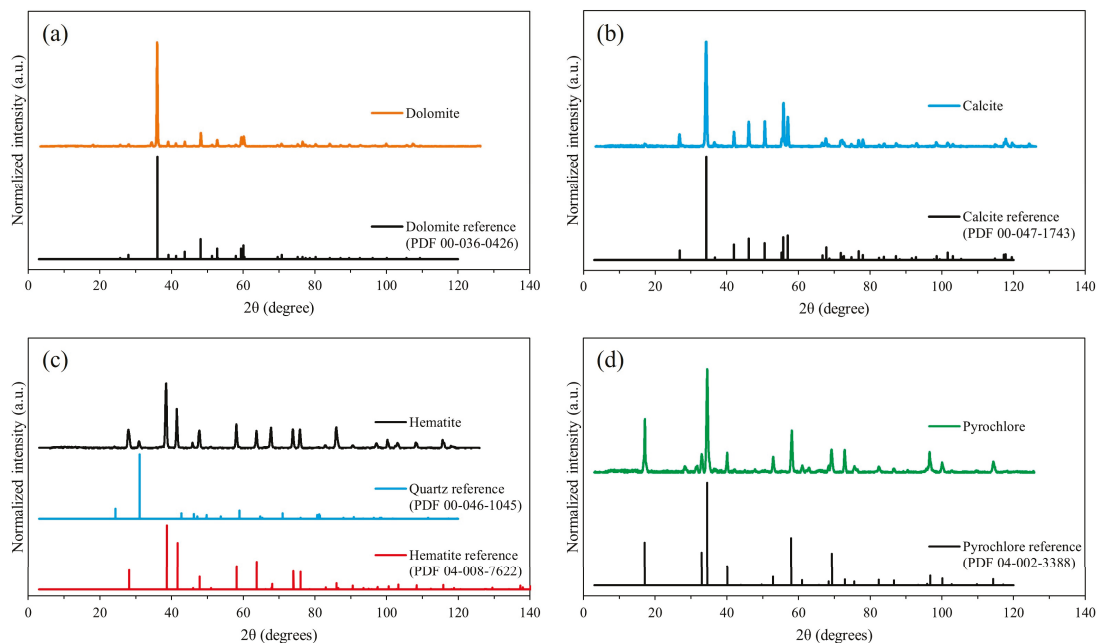


Figure A1. XRD spectra of (a) dolomite, (b) calcite, (c) hematite, and (d) pyrochlore model minerals.

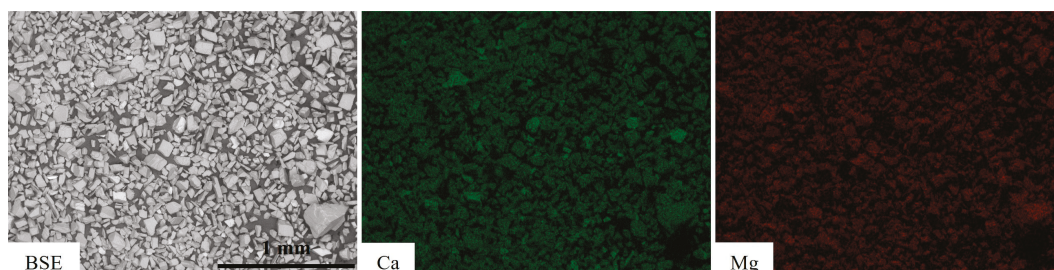


Figure A2. SEM images of the dolomite model mineral.

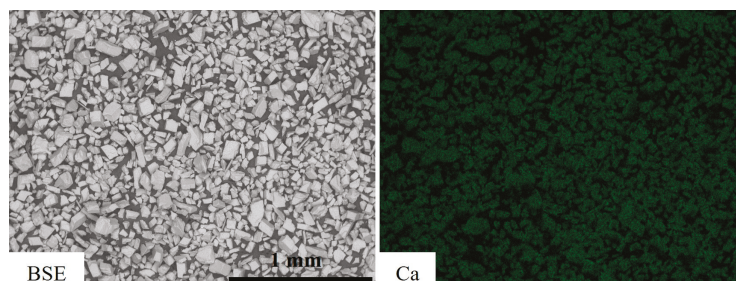


Figure A3. SEM images of the calcite model mineral.

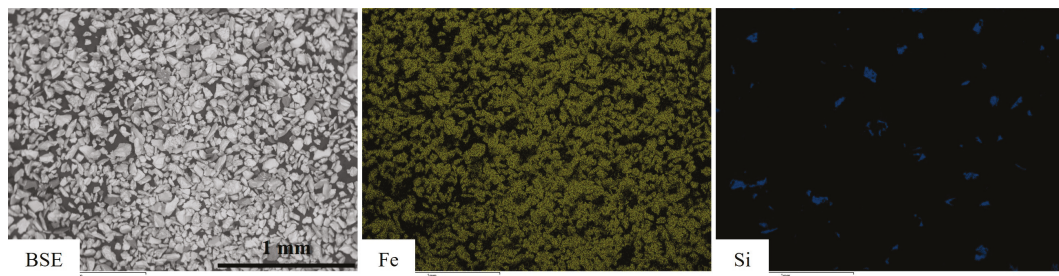


Figure A4. SEM images of the hematite model mineral.

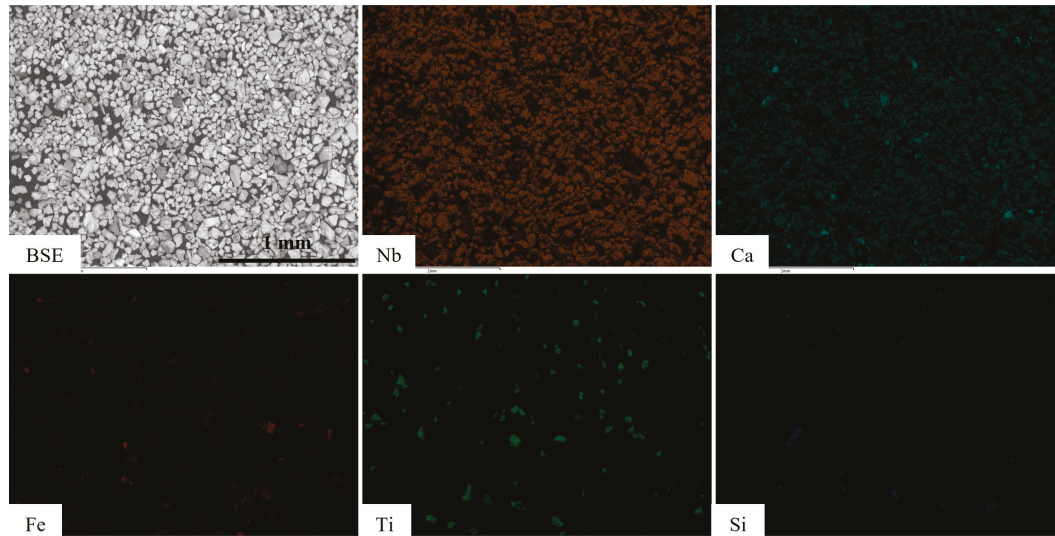


Figure A5. SEM images of the pyrochlore model mineral.

Table A1. Particle size and BET surface area of the model minerals.

Mineral	Size Range (μm)	D ₅₀ (μm)	D ₈₀ (μm)	D ₉₀ (μm)	BET Surface Area (m^2/g)
Dolomite	−106 + 38	108.4	152.0	199.2	0.14
	−10	4.2	10.0	14.6	5.18
Calcite	−106 + 38	102.7	131.6	146.9	0.10
	−10	3.2	7.0	9.9	3.68
Hematite	−106 + 38	84.1	111.6	127.2	0.18
	−10	4.6	8.8	12.2	2.69
Pyrochlore	−106 + 38	86.2	109.5	123.0	1.25
	−10	6.2	11.8	15.6	3.10

Table A2. XRF analysis result of the model minerals.

Mineral	Category	CaO (%)	MgO (%)	Fe ₂ O ₃ (%)	SiO ₂ (%)	Nb ₂ O ₅ (%)	LOI (%)
Dolomite	Model	31.58	19.28	0.37	0.43	-	46.31
	Theoretical	30.41	21.86	-	-	-	47.73
Calcite	Model	54.99	0.17	0.01	0.09	-	43.23
	Theoretical	56.03	-	-	-	-	43.97
Hematite	Model	0.24	0.01	98.21	1.84	-	0.41
	Theoretical	-	-	100	-	-	0
Pyrochlore	Model	13.4	0.12	4.49	0.93	58.87	2.18
	Theoretical	Varies	-	Varies	-	65 *	0

* composition might vary between samples from different origins; value adapted from [28].

Table A3. Summary of reagents applied in this work.

Category	Reagents	Assay *	Manufacturer
Collector	Dodecylamine Sodium oleate	98% ≥82%	Aldrich Sigma-Aldrich
Solvent	Acetic acid	99.7%	Fisher Scientific
Depressant	Sodium silicate Oxalic acid dihydrate Carboxymethyl cellulose ** F100 Starch Chitosan	40% 100.2% N/A N/A N/A 10%	Fisher Scientific Fisher Scientific Sigma Pionera Fisher Scientific Tidal Vision Products Inc.
pH modifier	Hydrochloric acid Sodium hydroxide	37% 99.2%	Spectrum Chemical Mfg. Corp. Fisher Scientific
Zeta potential background electrolyte	Potassium chloride	N/A	Fisher Scientific

* as indicated on the original packaging. In case the assay was not provided (indicated as N/A in the above table), 100% purity was assumed when use. ** high viscosity sodium salt, molecular weight unknown; on the packaging, it was provided that the viscosity of 1% aqueous solution at 25 °C equals 1500–3000 cps.

Table A4. Reagent dosage for zeta potential measurements.

Reagent	Mineral	Reagent Dosage			
		kg/t	g/m ²	mmol/L	mmol/m ²
DDA	Dolomite		0.019	0.216	0.104
	Calcite		0.027	0.216	0.147
	Hematite		0.037	0.216	0.201
	Pyrochlore		0.032	0.216	0.174
NaOL	Dolomite		0.019	0.131	0.063
	Calcite		0.027	0.131	0.089
	Hematite		0.037	0.131	0.122
	Pyrochlore		0.032	0.131	0.106
SS	Dolomite		0.019	0.328	0.158
	Calcite		0.027	0.328	0.223
	Hematite		0.037	0.328	0.305
	Pyrochlore		0.032	0.328	0.265
OA	Dolomite		0.019	0.444	0.215
	Calcite		0.027	0.444	0.302
	Hematite		0.037	0.444	0.413
	Pyrochlore		0.032	0.444	0.359
F100	Dolomite	100	0.019		
	Calcite		0.027		
	Hematite		0.037	N/A *	N/A *
	Pyrochlore		0.032		
Starch	Dolomite		0.019		
	Calcite		0.027		
	Hematite		0.037	N/A *	N/A *
	Pyrochlore		0.032		
CMC	Dolomite		0.019		
	Calcite		0.027		
	Hematite		0.037	N/A *	N/A *
	Pyrochlore		0.032		
Chitosan	Dolomite		0.019		
	Calcite		0.027		
	Hematite		0.037	N/A *	N/A *
	Pyrochlore		0.032		
KCl	Dolomite	186.378	0.036	1	0.483
	Calcite	186.378	0.051	1	0.680
	Hematite	186.378	0.069	1	0.930
	Pyrochlore	186.378	0.060	1	0.808

* Unable to compute due to their unknown molar weights.

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