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Optimized flotation of smithsonite and hemimorphite using mixed PAX–Armac C collectors: synergistic effects and desliming strategies

Amir Mabudi [a, *]

[a] *Department of Mining Engineering, Sahand University of Technology, Tabriz, Iran.*

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ABSTRACT

The progressive depletion of zinc sulfide ores and growing environmental constraints have shifted attention toward the beneficiation of zinc oxide ores, which are inherently more challenging due to their complex mineralogy and poor floatability. This study investigates the flotation behavior of a low-grade zinc oxide ore from the Barmalek deposit in Iran, with a focus on the synergistic effects of mixed collectors. The ore, composed predominantly of smithsonite and hemimorphite with significant calcite and magnesite gangue, was characterized using XRD and liberation analysis. Three collector regimes, potassium amyl xanthate (PAX), cocoalkyl amine acetate (Armac C), and their mixture, were tested under different process parameters using Taguchi orthogonal designs. Results showed that the mixed collector system significantly improved zinc recovery and selectivity compared to single collectors. Notably, desliming (removal of <20 µm particles) enhanced flotation performance, increasing zinc recovery from ~63% (without desliming) to over 80% under optimal conditions, while also reducing gangue entrainment. The optimal reagent scheme, determined via statistical modelling and ANOVA, provided a favorable balance between zinc grade and calcium rejection. Validation experiments confirmed the model's reliability, albeit with some zinc loss attributed to desliming. The findings demonstrate the efficacy of synergistic collector systems and tailored reagent schemes in overcoming the metallurgical challenges of oxidized zinc ores. This approach contributes to the sustainable processing of alternative zinc resources, offering insights into reagent design, process optimization, and slime management for industrial applications.

Keywords: *Flotation, Mixed collectors, Smithsonite, Hemimorphite, Sulfidization, Desliming.*

1. Introduction

Zinc is an essential base metal with wide-ranging industrial applications, particularly in galvanizing steel to prevent corrosion [1], producing brass and other alloys [2], fabricating batteries (including emerging zinc-based energy storage systems) [3], and formulating pharmaceutical and cosmetic products due to its antimicrobial properties [4]. The strategic importance of zinc in both mature and emerging technologies—such as electric vehicles and renewable energy infrastructure—has intensified global demand in recent years [5]. Traditionally, zinc is extracted primarily from sulfide ores, with sphalerite (ZnS) being the most significant source due to its abundance and amenability to established beneficiation techniques like froth flotation [6–8]. However, the progressive depletion of high-grade sulfide deposits, coupled with rising environmental and regulatory pressures on sulfide mining and smelting, has driven growing interest in alternative resources, particularly oxidized zinc ores formed through weathering and supergene enrichment processes [9]. These oxidized deposits, once considered secondary, are increasingly recognized as critical to the long-term sustainability of zinc supply chains [10].

Despite their increasing strategic importance, zinc oxide ores present significant metallurgical challenges that differentiate them markedly from their sulfide counterparts [11]. These ores are typically formed through the weathering of primary sulfide deposits, resulting in secondary zinc-bearing minerals such as smithsonite ($ZnCO_3$), hemimorphite ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$), and hydrozincite ($Zn_5(CO_3)_2(OH)_6$) [12]. These minerals are often finely disseminated and intimately associated with gangue phases such as quartz, dolomite, and calcite, which complicate liberation and separation processes [13]. In addition to their complex mineralogy, oxide zinc ores are generally of lower grade than sulfide ores, which increases the mass of material that must be processed and raises energy and reagent demands [14]. Moreover, their surface chemistry is fundamentally different; zinc oxide minerals possess naturally hydrophilic surfaces under typical flotation conditions, making them less amenable to conventional flotation using thiol collectors like xanthates [15].

The complex surface characteristics result in poor collector adsorption and weak attachment to air bubbles, which ultimately lead to reduced flotation recovery and selectivity [16]. The problem is further exacerbated by the presence of carbonate gangue minerals that share similar surface properties and particle sizes, often causing high entrainment and dilution of the concentrate [17]. Additionally, oxide minerals are more sensitive to changes in pulp chemistry, including pH and redox potential, which complicates process control [18]. These constraints underscore the need for more sophisticated and selective flotation strategies that enhance recovery while minimizing reagent consumption and environmental impact [19].

To overcome these limitations, sulfidization–flotation has become the standard approach for oxide zinc ores, whereby sodium sulfide (Na_2S) is used to render the mineral surface more sulfide-like and receptive to xanthate adsorption [20]. However, this method often suffers from inconsistent flotation response, excessive reagent consumption, and surface passivation, leading to suboptimal recovery and selectivity [21]. Direct flotation using cationic collectors (primary

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* Corresponding author. *E-mail address:* mabudi@sut.ac.ir (A. Mabudi).

amines or quaternary ammonium salts) has also been investigated, but issues related to high gangue entrainment and poor selectivity remain [22].

Recent advances in reagent chemistry have spurred interest in mixed collector systems—combinations of different collectors—to address the shortcomings of traditional approaches [23]. These systems exploit synergistic interactions between collectors of differing polarities or functional groups, improving adsorption, hydrophobicity, and selectivity [24]. For zinc oxide minerals, combinations such as xanthate–amine [25] or xanthate–hydroxamate [26] have demonstrated enhanced performance compared to single collectors. Such approaches not only boost recovery but can also reduce reagent dosages, making them attractive economically and environmentally [27]. The present study investigates a mixed collector system composed of potassium amyl xanthate (PAX) and Armac C (a cationic fatty amine) for a low-grade zinc oxide ore from the Barmalek deposit, comparing it with individual collectors in terms of recovery, selectivity, and gangue rejection. The roles of sulfidizing agents, depressants, and desliming are also examined to improve flotation efficiency. The results provide critical insights into the design of more effective reagent schemes for complex oxide ores and contribute to the sustainable exploitation of zinc oxide resources as sulfide reserves continue to decline.

2. Materials and methods

2.1. Material preparation

A representative sample of low-grade zinc–lead oxide ore was collected from the Barmalek deposit in Iran. The bulk sample was air-dried, homogenized, and subjected to particle size distribution analysis using standard ASTM sieves ranging from +10 to −200 mesh (+2000 to −75 µm). Each size fraction was weighed, and cumulative weight percentages were recorded to construct the particle size distribution curve. The head grade was approximately 13–14 wt.% Zn and 3–4 wt.% Pb, as determined by atomic absorption spectroscopy (AAS). To examine the distribution of metals across size fractions, each sieve fraction was subjected to acid digestion followed by AAS analysis for zinc and lead. The coefficients of variation for Zn (0.074) and Pb (0.259) indicated minimal grade fluctuations across size classes, suggesting a relatively uniform distribution of valuable metals throughout the particle size range. The results are presented in Figure 1.

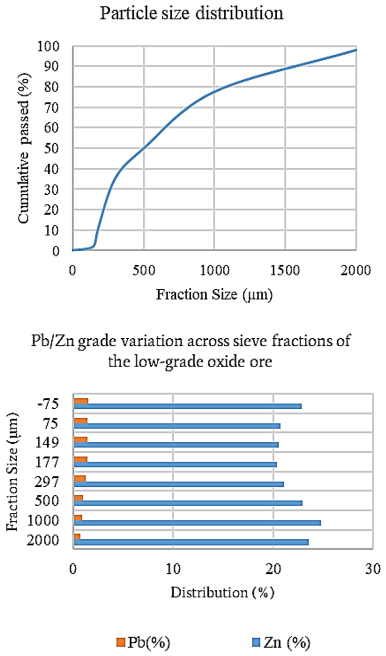


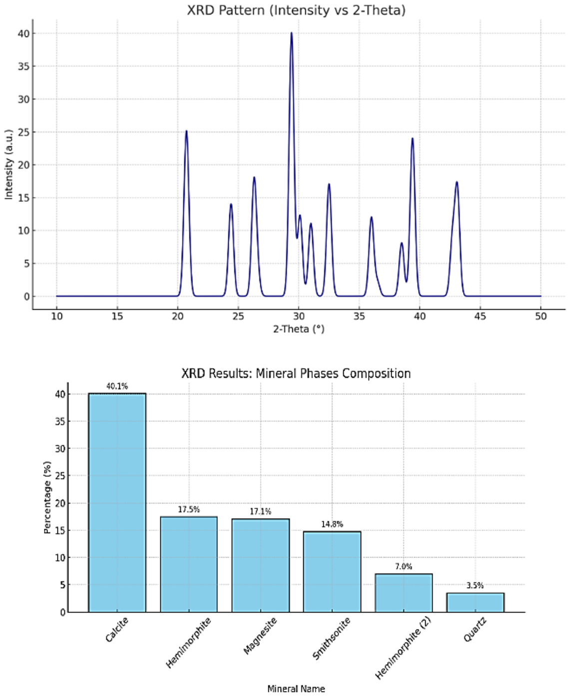
Figure 1. Particle size distribution and Pb/Zn grade variation across sieve fractions of the low-grade oxide ore.

In conclusion, the results of feed analyses showed that:

- Most material lies in the 500–1000 µm range.
- Zinc peaks in the +1000 µm fraction (24.79%).
- Lead concentration increases with decreasing particle size.

2.2. Mineralogical characterization

X-ray diffraction (XRD) analysis (Figure 2) was carried out using Cu-Kα radiation (λ = 1.5406 Å). The data were processed with X'Pert software, and quantitative phase analysis was performed through Rietveld refinement. Calcite ($CaCO_3$) was identified as the dominant gangue mineral (40.1 wt.%), followed by hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$, 17.5 wt.%) and smithsonite ($ZnCO_3$, 14.8 wt.%) (Figure 3). Additional non-sulfide gangue minerals included magnesite ($(Mg,Fe)CO_3$, 17.1 wt.%) and quartz (SiO_2, 3.5 wt.%). The abundance of carbonate and silicate gangue—particularly calcite, which shares similar surface chemistry with smithsonite—was identified as a major challenge for selective flotation. The presence of hemimorphite, a zinc silicate known for its poor floatability, further highlighted the need for a customized reagent scheme capable of selectively recovering both carbonate- and silicate-hosted zinc minerals.



Mineral name	Mineral phase	(%)
Calcite	$CaCO_3$	40.1
Hemimorphite	$Zn_4Si_2O_7(OH)_2, H_2O$	17.5
Magnesite	$(Mg.Fe)CO_3$	17.1
Smithsonite	$ZnCO_3$	14.8
Hemimorphite	$Zn_2(SiO_4).H_2O.2ZnO(SiO_2).H_2O$	7.0
Quartz	SiO_2	3.5

Figure 2. Particle size distribution and Zn grade variation across sieve fractions of the low-grade oxide ore.

2.3. Evaluation of degree of liberation

Understanding the liberation behavior of ore minerals is fundamental to optimizing mineral beneficiation, particularly for complex and finely intergrown oxidized zinc ores. These ores often present significant processing challenges due to their intricate mineral textures, variable gangue associations, and high sensitivity to overgrinding. Liberation analysis enables the evaluation of the extent to which valuable minerals, such as smithsonite and hemimorphite, are physically detached from gangue minerals including calcite, quartz, and iron oxides. Such insights are critical for determining the optimal grind size that balances mineral exposure with flotation efficiency and cost-effectiveness. This section presents a detailed liberation study based on microscopy and electron imaging techniques to inform processing strategies for a refractory zinc ore. Liberation analysis was conducted through a comprehensive mineralogical investigation involving both reflected and transmitted light microscopy on thin and polished sections (Figure 4) prepared from representative size fractions (−212+150 μm, −150+125 μm, and −125+75 μm). The results of the mineralogical investigation indicate that, given the inherently heterogeneous textures and complex intergrowths typical of oxidized zinc ores, quantitative liberation assessment was performed using point-counting methods at 200× magnification. The analysis revealed that smithsonite ($ZnCO_3$), the predominant zinc-bearing phase, attained approximately 80% liberation at particle sizes below 75 μm. However, comminution to this degree introduced a significant proportion of ultrafine particles (<20 μm), which pose operational challenges during flotation—primarily through elevated reagent consumption, entrainment losses, and diminished selectivity.

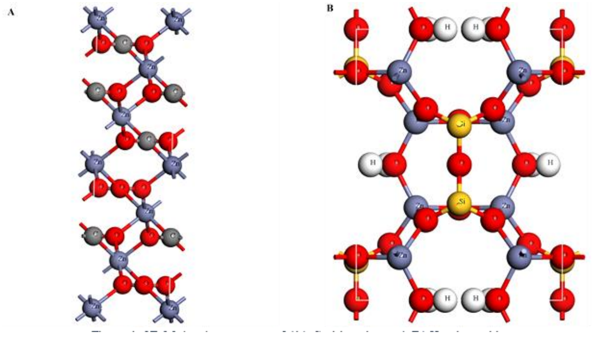


Figure 3. 3D Molecular structure of (A). Smithsonite, and (B) Hemimorphite.

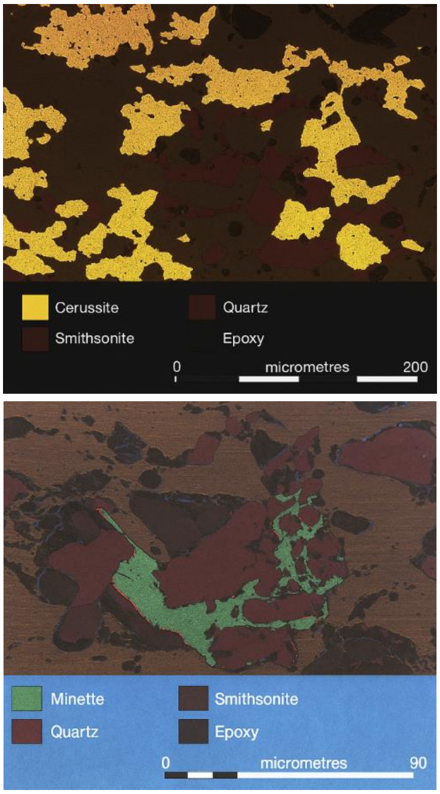


Figure 4. Entrapment of Smithsonite particles within Cerussite.

Microscopic and back-scattered electron (BSE) imaging revealed complex mineral associations, including fine-grained smithsonite encapsulated within cerussite ($PbCO_3$) and hemimorphite intergrown with iron oxides. These intimate associations indicate that complete mineral liberation would require grinding to sub-40 μm sizes, which is generally considered industrially unfeasible due to increased energy demands and the detrimental effects of excessive slime generation on flotation performance. Complementary energy-dispersive X-ray spectroscopy (EDS) confirmed the spatial relationships among zinc, lead, and iron phases and provided quantitative data on phase abundance and liberation characteristics. Overall, the findings highlight a critical processing dilemma: while finer grinding enhances mineral exposure, it simultaneously results in a disproportionate increase in slimes, which adversely affects downstream processing efficiency.

To address this trade-off, alternative beneficiation approaches—such as staged grinding, selective desliming, and the incorporation of advanced reagents (e.g., polymer-based dispersants or hydrophobic flocculants)—are increasingly recommended to enhance flotation selectivity without compromising throughput. These strategies are particularly relevant for refractory oxidized zinc ores, where liberation efficiency is closely linked to economic viability.

2.4. Assessment of the comminution behavior

Comminution represents a critical stage in mineral processing, directly influencing subsequent liberation and separation efficiency [28]. The energy intensity of this phase is determined by the ore's inherent grindability, which must be accurately characterized to guide circuit design and forecast energy consumption [29]. For complex oxide ores, particularly those rich in zinc carbonates and silicates, grindability is further complicated by heterogeneous textures and variability in mineral hardness [30]. This section evaluates the grindability behavior of a representative oxidized zinc ore using the Bond Work Index (BWi) methodology, providing insights into its comminution energy requirements relative to other ore types

The grindability of the representative ore sample was quantitatively assessed by determining the Bond Work Index (BWi) in accordance with the standardized Bond ball mill testing protocol (ASTM G408-93). The resulting BWi value of 10.5 kWh/sh.t classifies the ore as moderately hard from a comminution perspective, consistent with values typically reported for oxidized zinc ores in the literature [31]. In comparison with conventional sulfide-based zinc ores, which often exhibit BWi values in the range of 9.0–10.0 kWh/sh.t, this sample demonstrates an approximately 15–20% higher energy requirement, reflecting its more resistant grinding characteristics. This elevated BWi is primarily attributed to the presence of abrasive gangue constituents, notably quartz and magnesite, as confirmed through detailed mineralogical and XRD analyses. These findings underscore the necessity of adopting energy-efficient grinding strategies, particularly in the processing of low-grade or refractory oxidized zinc ores.

2.5. Reagents and flotation conditions

lead–zinc ores, particularly those containing both sulfide and oxidized phases. Its effectiveness depends on the careful selection of reagents, precise control of pulp chemistry, and the physical properties of the ore. In oxidized zinc ores, where surface chemistry differs markedly from that of sulfides, flotation performance is hindered by poor collector adsorption, slime coatings, and fine particle effects [32]. Consequently, tailored reagent regimes and pre-treatment steps—such as sulfurization and desliming—are critical to achieving acceptable metallurgical performance [33]. This section outlines the flotation methodology adopted in the present study, incorporating established reagent schemes and preparatory treatments to address the specific challenges posed by oxide-rich zinc ores.

Flotation tests were conducted to evaluate the separation efficiency of valuable base metal minerals—primarily lead and zinc compounds—from associated gangue phases. The experimental procedure was designed in accordance with standard laboratory-scale protocols commonly employed in both academic research and industrial pilot studies. The test program included three collector regimes: potassium amyl xanthate (PAX), a well-established thiol collector for sulfide minerals; cocoalkylamine acetate (Armac C), a cationic collector typically effective for zinc silicates and carbonates; and a synergistic PAX–Armac C mixture, intended to enhance flotation performance across mixed mineral phases.

To enhance the floatability of oxidized zinc species (e.g., smithsonite and hemimorphite), sodium sulfide (Na_2S) was employed as a sulfurizing agent to render mineral surfaces more hydrophobic by converting oxide surfaces into pseudo-sulfide layers—a process critical for effective collector adsorption. In addition, sodium silicate was introduced as a dispersant to control gangue slimes, while sodium hexametaphosphate (Calgon) (Figure 5A) and natural starch (Figure 5B) served as depressants, selectively inhibiting gangue minerals and mitigating the adverse effects of fine particles and slime coatings. To further improve flotation selectivity, a pre-flotation desliming stage was incorporated to remove particles smaller than 20 µm.

This step has been shown to reduce reagent consumption, improve concentrate grade by eliminating ultrafines that would otherwise increase entrainment, and minimize interference with bubble–particle attachment. The combination of chemical treatment and physical desliming was designed to optimize surface chemistry conditions and maximize the recovery of valuable phases, particularly in this challenging oxidized ore system.

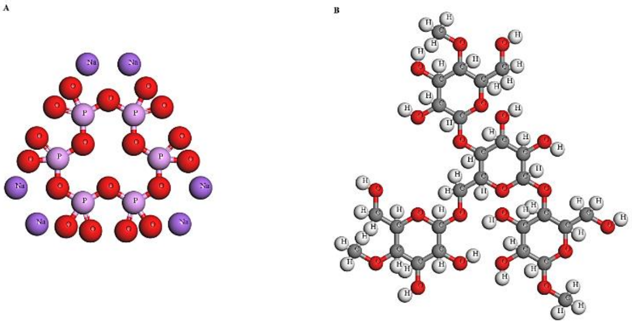


Figure 5. molecular structure of (a). Sodium hexametaphosphate (Calgon), and (B) Starch.

3. Results and discussions

3.1. Flotation using potassium amyl xanthate

Xanthates, particularly potassium amyl xanthate (PAX) (Figure 6), are among the most extensively utilized collectors in the flotation of sulfide minerals such as galena and sphalerite, owing to their strong affinity for metal sulfide surfaces and their ability to form hydrophobic metal–xanthate complexes [34]. Despite their proven efficacy in sulfide systems, the application of xanthates to oxidized zinc ores, including smithsonite and hemimorphite, remains limited due to fundamental differences in surface chemistry. Oxide minerals lack the surface sulfur species required for direct xanthate adsorption, resulting in significantly lower flotation recoveries [35].

In aqueous systems, xanthates undergo hydrolysis and oxidation, producing a mixture of reactive species including xanthate ions (AX^-), xanthic acid (ROCSH), carbon disulfide (CS_2), monothiocarbonates, and dixanthogen (ROCSSCRO). These species influence flotation behavior through complex interactions with mineral surfaces and the pulp environment. For example, in sphalerite–xanthate systems, AX^- remains the dominant species at pH values between 8 and 10, whereas acidic conditions promote the formation of xanthic acid and other unstable intermediates [36]. Such pH-dependent equilibria become even more critical when treating oxidized ores, where collector adsorption mechanisms are highly surface-sensitive and kinetically constrained.

To evaluate the suitability of PAX for oxidized zinc ore flotation, a series of preliminary batch flotation tests were conducted. These experiments were designed to determine reagent dosages and reduce the number of full-scale test iterations by identifying key process parameters. A Taguchi L8 orthogonal array was employed to examine the effects of seven process variables, each at two levels: pH, PAX dosage, Na_2S (sulfidizing agent), $CuSO_4$ (activator), sodium silicate (dispersant), Calgon (slime depressant), and flotation time. Zinc grade and recovery were selected as the primary responses (Table 1).

Analysis of the Taguchi test results revealed that Na_2S concentration had the most significant influence on both zinc grade and recovery. This finding supports previous studies emphasizing the critical role of sulfurization in enhancing collector adsorption on oxidized surfaces by forming a pseudo-sulfide layer, thereby increasing mineral hydrophobicity. Other notable variables included $CuSO_4$, which likely improved zinc surface reactivity by forming copper–zinc sulfide films, and Calgon, which contributed to improved dispersion and slime suppression. Regression plots (Figure 7 and Figure 8) demonstrated a strong correlation between experimental and predicted values ($R^2 = 0.99$ for grade, $R^2 = 0.96$ for recovery), confirming the robustness of the fitted models.

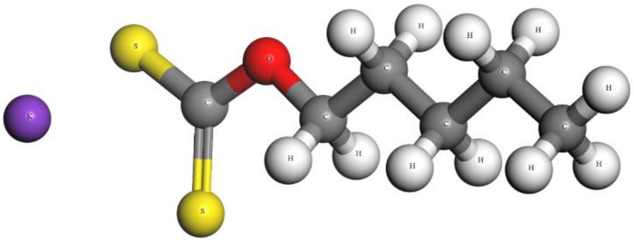


Figure 6. Molecular structure of potassium amyl xanthate (PAX).

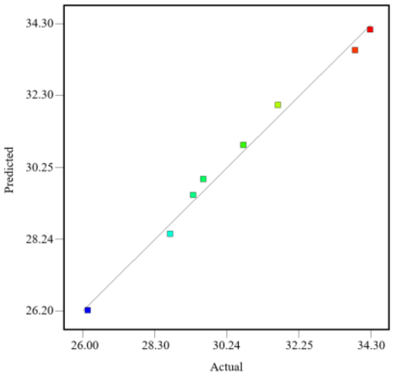


Figure 7. Regression plot of actual versus predicted values for zinc grade (R^2 = 0.99).

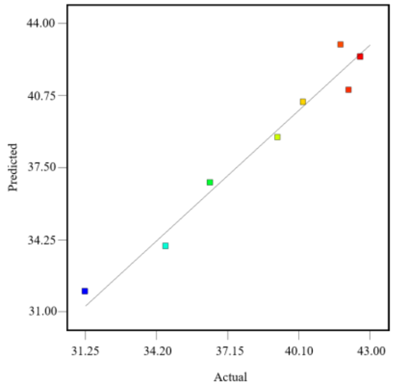


Figure 8. Regression plot of actual versus predicted values for zinc recovery (R^2 = 0.96)

However, despite careful optimization, overall zinc recoveries remained suboptimal when PAX was used as the primary collector. The poor flotation performance was attributed to the instability of Zn–xanthate surface complexes, which are prone to desorption and oxidation under mildly alkaline conditions. In addition, froth stability was a recurring issue across tests. The froth phase was transient and collapsed rapidly, leading to significant detachment and re-entrainment of floated particles. Notably, variations in frother concentration, sulfurizing agent levels, and collector dosage had minimal impact on froth volume or persistence, suggesting that collector–mineral interaction was the dominant limiting factor rather than froth phase chemistry. Although slimes are known to affect flotation selectivity and reagent consumption, their impact in the xanthate system was less pronounced and could not, by itself, account for the low recoveries observed. These findings reinforce the growing consensus that xanthates are fundamentally unsuitable for oxidized zinc ores and underscore the need to explore alternative collectors, such as amine-based reagents and chelating agents.

3.2. Flotation Using cocoalkyl amine acetate

Cationic collectors, particularly alkyl amines, have emerged as promising agents for the flotation of oxidized zinc ores, offering an alternative to traditional xanthate-based systems [37]. Unlike xanthates, which function via chemisorption, amines primarily interact with mineral surfaces through electrostatic attraction between their protonated head groups and negatively charged mineral surfaces [38]. This interaction is generally weaker than the covalent bonding observed with xanthates, resulting in less robust surface hydrophobization [39]. Nevertheless, cationic collectors are especially well suited for the flotation of oxidized, carbonate, and silicate ores, as well as alkaline earth minerals such as barite, carnallite, and sylvite [40]. The flotation performance of amines is highly sensitive to the pH of the pulp [41]. These reagents are most effective in mildly acidic to neutral environments, whereas strongly acidic or alkaline conditions can significantly reduce their efficiency. For example, dodecyl amine, a well-studied cationic collector, exhibits solubility and phase behavior that are strongly dependent on pH [42]. At neutral pH, un-ionized amine species predominate, while at pH 10.6 and above, the equilibrium shifts toward protonated and dimeric forms, thereby reducing collector availability. In the present study, the cationic collector cocoalkyl amine acetate—commercially known as Armac C, with the chemical formula $[R\text{-}NH_2]\bullet[CH_3COOH]$—was employed (Figure 9).

Armac C is widely applied in the industrial-scale flotation of oxidized zinc ores. Adsorption of the collector onto smithsonite surfaces, particularly following sulfidization with sodium sulfide (Na_2S), is a crucial step in promoting hydrophobicity and flotation. To evaluate the influence of various process parameters, a Taguchi L8 orthogonal array design was employed, considering seven variables at two levels. These tests assessed the effects of Calgon, sodium silicate, Na_2S, $CuSO_4$, pH, Armac C concentration, and flotation time on zinc grade and recovery. The outcomes (Table 2) indicated that Na_2S concentration had the most significant positive impact on both grade and recovery. Increasing flotation time enhanced zinc recovery but simultaneously reduced concentrate grade, likely due to entrainment effects. Among the reagents tested, sodium silicate, sodium sulfide, copper sulfate, and Armac C all exhibited a synergistic effect: as their dosages increased, both grade and recovery improved.

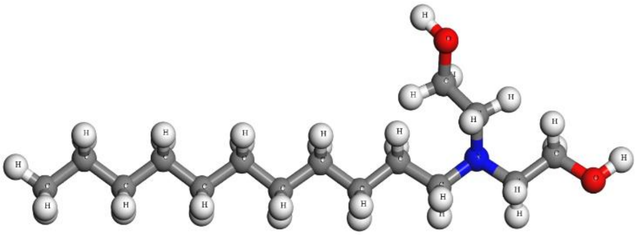


Figure 9. Molecular struture of potassium amyl xanthate (PAX).

All flotation tests were conducted without desliming. Although recovery and grade were generally higher with Armac C compared to xanthate-based flotation, the overall performance still fell short of industrially acceptable levels. This suggests that while cationic collectors offer certain advantages, particularly in oxide ore flotation, further optimization—potentially through reagent combinations or surface modification strategies—is required to achieve satisfactory results. Recent studies have emphasized the importance of hydrocarbon chain length in amine collectors. Longer hydrocarbon chains have been shown to enhance the hydrophobic association ability of amines, facilitating selective adsorption onto sulfurized smithsonite particles and thereby improving flotation performance. For example, ether amines with longer chains, such as OPA 1214, have demonstrated superior performance compared to shorter-chain amines like dodecyl amine. This improvement is attributed to stronger hydrophobic interactions and better molecular alignment of the collector on the mineral surface.

Table 1. Zinc grade and recovery results from flotation experiments using a xanthate collector (PAX).

	Flotation Condition							Zn Results	
	PAX (g/t)	Sodium Silicate (g/t)	Na_2S (g/t)	Calgon (g/t)	$CuSO_4$ (g/t)	pH	Flotation time(min)	Grade (%)	Recovery (%)
1	300	800	1600	500	400	10	2	31.7	42.2
2	600	400	800	500	400	10	4	28.7	36.4
3	300	400	800	500	200	8	2	29.3	31.3
4	600	800	1600	500	200	8	4	34.3	40.3
5	600	800	800	1000	200	10	2	26.4	34.6
6	300	400	1600	1000	200	10	4	30.7	42.7
7	300	800	800	1000	400	8	4	29.6	39.2
8	600	400	1600	1000	400	8	2	33.8	41.8

Table 2. Zinc grade and recovery results from flotation experiments using armac c

	Flotation Condition							Zn Results	
	Armac C (g/t)	Sodium silicate (g/t)	Na_2S (g/t)	Calgon(g/t)	$CuSO_4$ (g/t)	Flotation time (min)	pH	Grade (%)	Recovery (%)
1	600	400	1600	1000	400	2	8	38.5	45.4
2	300	800	1600	500	400	2	10	40.0	46.1
3	600	800	800	1000	200	2	10	32.7	39.7
4	300	400	1600	1000	200	4	10	31.0	43.6
5	600	400	800	500	400	4	10	31.3	42.3
6	300	800	800	1000	400	4	8	33.3	43.6
7	600	800	1600	500	200	4	8	37.6	44.7
8	300	400	800	500	200	2	8	33.6	34.3

In conclusion, while cationic collectors such as Armac C show promise in the flotation of oxidized zinc ores, their performance is influenced by several factors, including pH, collector dosage, and the presence of sulfidizing agents. Further research into the molecular structure of collectors and their interactions with mineral surfaces is essential to optimize flotation processes for oxidized zinc ores. All flotation tests in this study were conducted without desliming. Although recovery and grade were generally higher with Armac C compared to xanthate-based flotation, the overall performance still fell short of industrially acceptable levels. This suggests that while cationic collectors provide certain advantages, particularly in oxide ore flotation, further optimization—potentially through reagent combinations or surface modification strategies—is required to achieve satisfactory results.

3.2.1 Flotation without de-sliming

To better elucidate the complex interactions involved in the flotation of zinc oxide ores using a mixed collector system, a preliminary experimental campaign was conducted employing a Taguchi L12 orthogonal array design. This approach enables the systematic investigation of multiple variables with a reduced number of experiments, thereby enhancing efficiency while maintaining statistical validity. Eleven process parameters, each evaluated at two levels, were selected based on prior flotation studies and their established influence on the flotation behavior of oxidized ores. The tested variables included pulp pH, reagent dosages (e.g., collectors, dispersants, sulfidizers, and depressants), conditioning durations, and flotation times. These factors are summarized in Table 3, process variables and levels used in the taguchi l12 orthogonal design.

Twelve experimental runs were conducted according to the Taguchi L12 matrix, with each run duplicated to improve reproducibility and enable the calculation of signal-to-noise (S/N) ratios. The results are presented in Table 4. The flotation process was carried out in two sequential stages to reflect industrial practice and enhance separation efficiency. In the first stage, starch and sodium silicate were introduced as depressants to control slime coating and dispersion, followed by Na_2S addition and pH adjustment. Xanthate was then conditioned with the pulp prior to flotation. The second stage involved fresh Na_2S dosing, pH adjustment, and the addition of Armac C (cationic collector) together with xanthate. Air was introduced after two minutes to initiate froth formation. Notably, no frother was added in the second stage, allowing for a clear assessment of froth-forming behavior induced solely by the collectors.

Collector interaction and froth behavior

Observations indicated that froth characteristics were highly dependent on the Armac C dosage. Interestingly, lower Armac concentrations resulted in improved flotation performance, potentially due to reduced surface tension effects and enhanced selectivity. This behavior is consistent with literature reports suggesting that excess amine can cause froth instability or bubble coalescence as a result of surfactant saturation. The primary response variables were zinc and calcium recoveries in the combined flotation concentrates. Calcium recovery served as a proxy for gangue entrainment, particularly from dolomite or calcite, the presence of which is undesirable due to increased acid consumption during subsequent hydrometallurgical leaching stages. Accordingly, the flotation strategy aimed to simultaneously maximize zinc recovery while minimizing calcium content.

Statistical analysis and optimization

Analysis of variance (ANOVA) revealed several parameters with statistically significant effects. For zinc recovery, flotation time, sodium silicate and Na_2S dosages in Stage 1, Armac C dosage, and pulp pH were the most influential factors. In contrast, calcium recovery was primarily affected by conditioning time, starch dosage, and xanthate addition in the first stage, underscoring the importance of early-stage dispersion and surface modification. Optimization was performed using a weighted desirability function that prioritized zinc recovery while constraining calcium recovery. The optimal operating conditions are summarized in Table 5. Under these conditions, model predictions yielded a zinc recovery of 63.5% and a calcium recovery of 19.1%. Validation tests under the optimized regime confirmed the general trend, with zinc recovery ranging from 53.2% to 54.4% and calcium recovery between 21.8% and 22.7%. The slight underperformance relative to the model is likely attributable to the presence of ultrafine particles and slimes, which were not removed prior to flotation. These fine materials are known to interfere with particle–bubble attachment and to adsorb reagents non-selectively, thereby reducing flotation efficiency.

Table 3. Process variables and levels used in the taguchi l12 orthogonal design.

N.	Factor	Unit	Low level	High level
1	PAX Concentration 1	g/t	300	600
2	Sodium Silicate Concentration 1	g/t	500	1000
3	Na_2S Concentration 1	g/t	1500	3000
4	Starch	g/t	400	800
5	Conditioning Time	min.	5	10
6	pH	-	9	11
7	Flotation Time	min.	3	6
8	PAX Concentration 2	g/t	200	400
9	Armac C Concentration	g/t	100	200
10	Sodium Silicate Concentration 2	g/t	2000	4000
11	Na_2S Concentration 2	g/t	800	1600

Table 4. Experimental results from Taguchi L12 design (two replicates per run).

Run	Zn Recovery		Ca Recovery	
	R1 (%)	R2 (%)	R1 (%)	R2 (%)
1	39.3	43.5	8.3	6.8
2	52.7	61.2	19.9	17.9
3	53.2	55.0	24.1	19.0
4	63.5	68.4	20.1	22.4
5	55.8	58.8	21.5	20.3
6	57.3	55.1	23.5	20.9
7	63.5	69.7	27.8	22.1
8	53.9	52.4	19.0	20.1
9	46.5	50.3	18.4	11.6
10	52.6	60.1	15.6	14.4
11	58.3	64.3	23.5	19.2
12	66.5	62.5	25.3	26.5

3.2.3 Flotation with de-sliming

To enhance the flotation performance of zinc oxide ores and mitigate the adverse effects of ultra-fine particles, a desliming process was implemented to remove particles smaller than 20μm from the feed prior to flotation.

Table 5. The identified optimal operating conditions for flotation using mixed collectors.

pH	Sodium Silicate		Starch (g/t)	Na_2S		Conditioning Time (min)	PAX		Armac C (g/t)	Flotation Time (min)
	Stage1 (g/t)	Stage2 (g/t)		Stage1 (g/t)	Stage1 (g/t)		Stage1 (g/t)	Stage1 (g/t)		
10.8	2.0	2.5	400	2195	1090	5	`435	375	100	6

This approach is consistent with findings from previous studies, which have demonstrated that desliming can significantly improve flotation efficiency by reducing slime coatings on mineral surfaces and minimizing reagent consumption. Subsequent flotation tests were conducted using a mixed collector system within the framework of a Taguchi L8 ($2^1 \times 3^7$) orthogonal array design. This design incorporated eight factors, one at two levels and the remaining seven at three levels, as detailed in Table 6. A series of 18 experiments were performed based on the L18 matrix, with randomized test orders to minimize systematic errors. The factors investigated included pulp pH, concentrations of sodium silicate, starch, sodium sulfide, xanthate (at two stages), Armac C dosage, and flotation time. The primary responses analyzed were zinc recovery, zinc grade in the concentrate, and calcium recovery in the concentrate.

Table 6. Key factors and their levels for flotation experiments with desliming.

No.	Factors	Unit	Level 1	Level 2	Level 3
1	PAX Concentration 1	g/t	250	500	750
2	Sodium Silicate Concentration	g/t	400	800	1200
3	Starch	g/t	400	700	1000
4	Na_2S Concentration	g/t	800	1800	2800
5	pH	-	9	10	11
6	Flotation Time	min	2	4	6
7	PAX Concentration 2	g/t	200	400	-
8	Armac C Concentration	g/t	100	200	300

Analysis of variance (ANOVA) revealed that sodium sulfide concentration was the most significant factor affecting zinc grade in the concentrate ($p = 0.009$), followed by xanthate dosage in the second stage ($p = 0.034$). The overall model was statistically significant ($F = 4.54$, $p = 0.038$), indicating a good match between predicted and experimental data. Regarding calcium recovery, starch concentration exhibited a strong effect ($p = 0.010$), with additional contributions from xanthate 1, flotation time, and Armac C dosage ($p < 0.1$). The model for calcium recovery was also significant ($F = 4.52$, $p = 0.038$), and the predicted versus actual calcium recovery values confirmed the model's validity.

The experimental results, summarized in Table 7, demonstrated that desliming significantly improved flotation performance. Zinc recoveries exceeded 80%, and higher zinc grades were achieved while maintaining acceptable levels of calcium recovery in the concentrate. These findings highlight the importance of proper feed preparation and reagent dosage optimization in the flotation of zinc oxide ores.

Overall, the integration of desliming and a carefully designed reagent scheme, guided by a Taguchi experimental design, has proved effective in enhancing the flotation performance of zinc oxide ores. This approach offers a systematic methodology for optimizing flotation parameters and can be adapted to similar mineral processing challenges.

3.3. Optimization of flotation conditions for selective zinc recovery

To achieve the dual objectives of maximizing zinc recovery and concentrate grade while minimizing calcium contamination, a critical factor in downstream hydrometallurgical processing, the flotation process was systematically optimized. The optimization employed a multi-response strategy using desirability functions within a defined range of factor levels based on prior experimental data. Parameters included reagent dosages, pulp pH, flotation time, and desliming conditions. Weights were assigned to response variables based on their relative importance: higher weight was given to zinc recovery and grade, and lower weight to calcium recovery, consistent with economic and operational priorities in zinc oxide ore beneficiation.

Using predictive modeling with statistical software (e.g., Design-Expert), the system generated ten optimized scenarios (Table 8 and Table 9), each meeting the objective of enhanced zinc flotation performance with suppressed calcium entrainment. Among these, Case 1 emerged as the most favorable, predicting a zinc recovery of 84.27%, a zinc grade of 41.52%, and a calcium recovery of only 13.85%. These results represent a favorable balance between flotation selectivity and overall metallurgical performance. The confidence intervals associated with each optimized prediction confirmed the statistical robustness of the model. Validation experiments conducted under the conditions specified in Case 1 yielded results closely aligned with model predictions. However, actual zinc recoveries were slightly lower than predicted values, a discrepancy attributed to the loss of ultra-fine particles during the desliming stage, a common issue in oxide ore flotation. After accounting for the desliming losses, where a significant fraction of zinc and calcium-bearing fines were removed the corrected zinc recoveries ranged from 64.7% to 74.2%, with calcium recoveries remaining within acceptable limits.

This outcome indicates a trade-off between improved concentrate quality and overall metal recovery. These findings underscore the necessity of integrating particle size classification strategies, such as staged desliming or selective flocculation, to mitigate zinc losses without compromising flotation selectivity. Moreover, the optimized reagent regime, particularly the synergistic use of sulfidizing agents and mixed collectors (PAX and Armac C), demonstrated effective surface modification and collector adsorption.

In conclusion, the application of statistical design and modelling tools enabled a data-driven approach to flotation optimization. While desliming enhanced the flotation response by reducing gangue interference, attention must be given to minimizing metal losses in the slimes fraction. Future work could explore alternative desliming thresholds, flocculant-assisted classification, or reprocessing strategies for the slime tailings to enhance overall resource efficiency.

4. Conclusion

This study confirms the synergistic use of potassium amyl xanthate and Armac C significantly enhances the flotation performance of oxidized zinc minerals, particularly smithsonite and Hemimorphite. The mixed collector system demonstrated superior zinc recovery and grade compared to single collectors, especially when combined with pre-flotation desliming. Sodium sulfide proved essential for effective sulfidization, facilitating collector adsorption. Optimization via Taguchi design and desirability functions enabled a robust parameter selection for maximizing zinc recovery while minimizing calcium contamination. Despite some zinc losses during desliming, the process improvements affirm the potential of mixed reagent schemes in addressing the complexities of oxidized zinc ore beneficiation.

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