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Optimized Flotation of Zinc Oxide Ores: Synergistic Effects of Mixed Collectors and Desliming

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ABSTRACT

The flotation of zinc oxide ores presents significant technical challenges due to their complex surface chemistry and fine particle size. This study investigates the flotation behavior of a zinc oxide ore (13–14% Zn, 3–4% Pb) from the Barmalek deposit using different collector systems—potassium amyl xanthate (KAX), cocoalkylamine acetate (Armac C), and a mixed collector system. Comprehensive mineralogical and liberation analyses confirmed the oxide-dominated nature of the ore and the presence of slime-generating fractions, which negatively affect flotation performance. Systematic flotation experiments were conducted using Taguchi design arrays (L8, L12, L18) to evaluate the effects of various parameters, including reagent dosages, pH, and flotation time, both with and without desliming. Results showed that KAX or Armac C alone provided limited recovery and selectivity. In contrast, the mixed collector system significantly enhanced zinc recovery and concentrate grade, particularly when combined with desliming. Under optimized conditions—pH 11, Na_2S 2800 ppm, starch 1000 ppm, sodium silicate 400 ppm, flotation time 4 minutes, xanthate 500 ppm (stage 1), xanthate 400 ppm (stage 2), and Armac C 300 ppm—zinc recovery reached 84.3% and concentrate grade exceeded 42%, while calcium recovery was minimized to 13.85%. Validation experiments confirmed the model predictions, although actual recoveries slightly decreased after accounting for slime losses. The findings demonstrate the synergistic potential of mixed collectors and highlight the critical role of desliming and reagent optimization in improving the flotation of refractory zinc oxide ores.

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1 .Introduction

Zinc is a strategically important non-ferrous metal extensively used across a wide range of industries, including galvanization, alloy production, electrochemical energy storage, and pharmaceuticals [1, 2]. Its widespread application stems from its favorable physicochemical properties, such as high corrosion resistance and biocompatibility [3]. Globally, zinc production has historically relied on the exploitation of sulfide ores, primarily sphalerite (ZnS) [4]. However, the increasing depletion of high-grade sulfide deposits and growing environmental concerns have prompted the mining industry to explore alternative sources of zinc, notably zinc oxide ores such as smithsonite ($ZnCO_3$), hemimorphite ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$), and willemite ($Zn_2SiO_4$) [5]. These oxidized ores are abundant in many parts of the world, including Iran, China, and North Africa, but their complex mineralogy and poor surface hydrophobicity pose significant challenges for conventional beneficiation processes [6].

The flotation of zinc oxide minerals is particularly problematic due to their inherently hydrophilic nature and their frequent occurrence in fine particle size fractions [7-10]. In contrast to sulfide minerals, oxide minerals do not readily form stable surface complexes with standard thiol collectors like xanthates [11]. As a result, sulfidization has traditionally been employed as a pre-conditioning step to render oxide surfaces more reactive by forming a pseudo-sulfide layer [12-14]. Despite its widespread use, sulfidization is associated with several operational limitations, including reagent overconsumption, surface passivation, inconsistent performance, and poor selectivity in complex ore matrices [15]. These drawbacks become especially severe when dealing with ores containing significant amounts of carbonate gangue, such as calcite or dolomite, which compete for reagent adsorption and contaminate the flotation concentrate [16-17]. Therefore, there is a growing need to develop more selective, cost-effective, and environmentally sustainable reagent schemes for the flotation of oxidized zinc ores [8, 18, 19].

Recent research has shifted toward the use of mixed collector systems that exploit the synergistic interactions between different classes of surfactants—typically combining anionic xanthates with cationic amines or amphoteric reagents [20-22]. These systems offer several advantages over single collectors, including improved adsorption kinetics, enhanced surface hydrophobicity, and greater control over froth characteristics. For instance, recent studies show that combining potassium amyl xanthate (KAX) with cationic collectors such as Armac C significantly improved both zinc recovery and concentrate grade in oxidized ores [23-25]. The dual action of xanthates targeting sulfide or sulfurized sites and amines interacting with negatively charged mineral surfaces enhances collector coverage and selectivity [11]. Furthermore, mixed systems can reduce the overall reagent dosage, which not only decreases operational costs but also minimizes secondary environmental impacts, such as residual toxicity and wastewater treatment burdens [26, 27]. These findings suggest that the intelligent design of reagent combinations may be key to unlocking the flotation potential of complex oxide ores [28].

Another critical factor influencing the flotation performance of oxidized zinc ores is the presence of slimes—ultra-fine particles (<20 μm) that result from overgrinding or natural weathering of ore bodies [29]. Slimes hinder flotation by increasing pulp viscosity, obstructing bubble-particle collisions, and stabilizing unwanted froth phases, thereby reducing both recovery and concentrate purity. Desliming, the selective removal of these fine particles before flotation, has emerged as a practical and effective strategy to mitigate these issues [30]. Recent studies demonstrated that pre-flotation desliming significantly improved zinc recovery and reduced gangue entrainment, particularly for ores containing high levels of clay minerals or carbonates [9, 13, 25, 31, 32]. In addition, desliming improves froth stability and reagent efficiency by reducing the surface area available for non-selective adsorption. However, it must be carefully controlled, as excessive removal of fine particles may lead to the loss of valuable zinc-bearing minerals. Therefore, process design must balance desliming intensity with mineral liberation to maximize overall metallurgical efficiency.

Against this backdrop, the present study aims to systematically investigate the flotation behavior of a refractory zinc oxide ore from the Barmalek deposit in Iran using a mixed collector strategy comprising potassium amyl xanthate (KAX) and cocoalkylamine acetate (Armac C). The research adopts a comprehensive experimental approach, incorporating Taguchi orthogonal design methodologies to evaluate the influence of process parameters such as pH, reagent dosages, flotation time, and desliming. Through statistical optimization (ANOVA and model validation), the study seeks to establish optimal operating conditions that maximize zinc recovery and grade while minimizing the recovery of unwanted gangue minerals, especially calcium, which adversely affects downstream hydrometallurgical processing. The findings provide valuable insights into the synergistic mechanisms of mixed collectors and offer a practical framework for improving the flotation efficiency of complex, low-grade zinc oxide ores in industrial settings.

2. Materials and Methods

2.1. Sample Preparation and Characterization

A representative sample of zinc-lead oxide ore was carefully homogenized and subjected to sieve analysis to evaluate its particle size distribution. The ore, with an average assay of 13–14% Zn and 3–4% Pb, was dry-sieved using standard ASTM meshes (10 to −200 mesh), and the weight percentage retained on each sieve was recorded (Table 1). To assess the distribution of valuable metals across different size fractions, each fraction was chemically analyzed for Zn and Pb content using atomic absorption spectroscopy (AAS, PerkinElmer AAnalyst 400, USA). The results demonstrated a relatively uniform distribution of metals, as evidenced by low coefficients of variation (0.074 for Zn and 0.259 for Pb), indicating that grade fluctuations were statistically insignificant across the size classes.

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

Size (µm)	Remain Mass (gr)	Remain Mass (%)	Cumulative passed (%)	Zn (%)	Pb (%)
+2000	44.15	2.23	97.77	23.5	0.7
+1000	400.82	20.27	77.5	24.79	0.84
+500	544.84	27.55	49.95	22.96	0.97
+297	290.83	14.71	35.24	21.1	1.22
+177	481.38	24.34	10.9	20.35	1.39
+149	161.94	8.19	2.71	20.58	1.42
+75	38.46	1.95	0.76	20.68	1.43
-75	14.98	0.76	0	22.85	1.5
Bulk S.				21.52	0.98

To further characterize, X-ray diffraction (XRD Philips PW1730-Netherlands) analysis equipped with Cu Kα radiation (λ = 1.5406 Å), operating at 40 kV and 40 mA was performed (**Error! Reference source not found.**).

Table 2. XRD analysis results.

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

The XRD results identified calcite ($CaCO_3$, 40.1%) as the predominant gangue mineral, followed by zinc-bearing phases such as Hemimorphite ($Zn_4Si_2O_7(OH)_2.H_2O$, 17.5%) and Smithsonite ($ZnCO_3$, 14.8%). Non-sulfide gangue minerals included Magnesite ($(Mg,Fe)CO_3$, 17.1%) and quartz (SiO_2, 3.5%). This mineralogical profile confirmed the oxide-dominant nature of the ore, with calcite posing a key challenge due to its floatability interference and similar physicochemical properties to zinc carbonate minerals. The presence of Hemimorphite, a zinc silicate, further highlighted the ore's complexity, necessitating tailored beneficiation strategies to address both carbonate and silicate-hosted zinc.

2.2. Degree of Liberation

Liberation analysis was conducted through a comprehensive mineralogical assessment using reflected and transmitted light microscopy (a Leica DM2700M optical microscope-Leica Microsystems GmbH, Germany) on thin and polished sections prepared from the sieved size fractions (−212+150, −150+125, and −125+75 µm). Given the heterogeneous texture and complex mineral associations typical of oxidized zinc ores, the liberation degree was quantified for each fraction using particle counting methods under 200× magnification. The results revealed that smithsonite, the primary zinc-bearing mineral, required grinding to a particle size of ≤75 µm to achieve 80% liberation from the gangue matrix (predominantly calcite and quartz [33]). However, this degree of comminution risked generating excessive slimes (−20 µm), which could adversely affect downstream flotation performance through increased reagent consumption and reduced selectivity.

Detailed microscopic examination further identified intricate mineral intergrowths, particularly smithsonite grains encapsulated within Cerussite ($PbCO_3$) (Fig. 1), as well as complex boundaries between Hemimorphite and iron oxides.

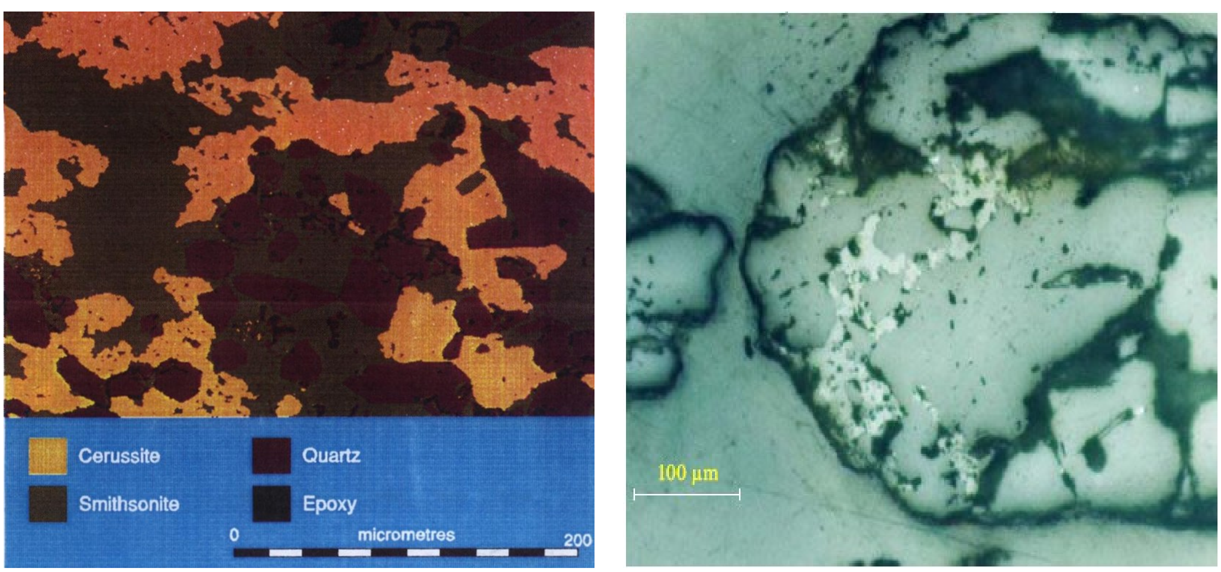

Fig. 1. Entrapment of Smithsonite particles within Cerussite.

These textural relationships indicated that complete liberation would require ultra-fine grinding to 20–40 µm, which was deemed impractical for industrial flotation due to high-energy costs and exacerbated slime-related challenges. Back-scattered electron (BSE) imaging coupled with energy-dispersive X-ray spectroscopy (EDS) confirmed these mineral associations and provided quantitative phase distribution data.

The liberation analysis underscored a critical trade-off: while finer grinding improved zinc mineral exposure, it simultaneously increased slime generation and operational costs. This finding highlighted the need for alternative beneficiation strategies, such as staged grinding or slime rejection, to optimize the liberation-flotation efficiency balance for this refractory ore type.

2.3. Bond Work Index Determination

The grindability of the ore sample was quantitatively evaluated through the determination of the Bond work index (W_i) using the standardized Bond ball mill test procedure (ASTM G408-93 protocol). The calculated Bond work index of 10.76 kWh/short ton (equivalent to W_i = 10.76 (kWh/(sh.t))) indicates moderately hard grinding characteristics, comparable to values reported for similar oxidized zinc ores. This result suggests the ore requires approximately 15-20% more energy for comminution than typical sulfide zinc ores (≈ 9-10(kWh/(sh.t))). The relatively high work index can be attributed to the presence of hard, abrasive gangue minerals (quartz and magnesite) identified in the mineralogical analysis.

2.4. Flotation Reagents and Conditions

Flotation experiments were carried out using a laboratory-scale mechanical flotation machine (Denver D12, Metso, USA) equipped with a 1.5 L cell. The impeller speed was maintained at 1200 rpm, and the air flow was kept constant at 2.5 L/min. All tests were conducted at ambient temperature (22–24°C). A fixed pulp density of 20% solids by weight was maintained in each experiment.
The general flotation procedure was as follows:

1. Ore conditioning: 300 g of the representative ore sample was ground (if required) and transferred to the flotation cell with distilled water to form a slurry.
2. pH adjustment: The pulp pH was adjusted to the target level (between 9 and 11) using either HCl or NaOH.
3. Addition of modifiers: Dispersants such as sodium silicate and depressants like Calgon or starch were added and conditioned for 3 minutes.
4. Sulfidization: Sodium sulfide (Na_2S) was added and conditioned for 5 minutes to sulfidize the zinc oxide mineral surfaces.
5. Collector addition (Stage 1): Xanthate (KAX) was added and conditioned for 3 minutes.
6. First flotation stage: Froth was collected for 3–6 minutes (depending on test design).
7. Reconditioning (if applicable): For tests involving two-stage collector addition, further Na_2S was added, followed by Armac C and a second dose of KAX.
8. Second flotation stage: Froth was collected for another 3–5 minutes (no frother used in stage 2).
9. Concentrate and tailings separation: The products were filtered, dried, and weighed. Zinc and calcium contents were analyzed using AAS (PerkinElmer AAnalyst 400, USA).

Each test was repeated at least twice to ensure reproducibility, and the average values were reported. The effects of different reagents and operating parameters were systematically evaluated using Taguchi design matrices (L8, L12, and L18).

3. Results and Discussion

3.1. Flotation Using Xanthate Collectors

Xanthates, particularly potassium amyl xanthate (KAX), are among the most widely used collectors in the flotation of sulfide minerals. Due to their established efficacy, their application has also been explored for oxide zinc ores, despite the significant differences in surface chemistry. The hydrolysis of xanthates in aqueous systems results in several decomposition products, including xanthate ions (AX^-), monothiocarbonates, xanthic acid, carbon disulfide (CS_2), and dixanthogen, each contributing to the complex chemistry of flotation pulp. In sphalerite-KAX systems, AX^- is the dominant phase at pH values between 8 and 10, while lower pH values favor the formation of other species. Before designing full-scale flotation tests, a series of preliminary experiments was conducted to assess the general flotation behavior of zinc oxide ore using KAX as the primary collector. These trials helped determine feasible reagent ranges and minimized the number of tests required by identifying critical factors influencing flotation. An L8 Taguchi design was implemented to evaluate seven factors, each at two levels, affecting zinc recovery and grade. These factors included pH, KAX dosage, sulfidization using Na_2S, and auxiliary reagents such as Calgon, sodium silicate, $CuSO_4$, and flotation time. The results (Table 3) revealed that Na_2S concentration had the most significant impact on both zinc grade and recovery.

Table 3. Zinc grade and recovery results from flotation experiments using a xanthate collector (KAX).

N	Calgon (ppm)	Sodium Silicate (ppm)	Na_2S (ppm)	$CuSO_4$ (ppm)	pH	KAX (ppm)	Flotation time(min)	Grade (Zn)%	Recovery (Zn) %
1	500	400	800	200	8	300	2	29.3	31.26
2	500	400	800	400	10	600	4	28.66	36.43
3	500	800	1600	200	8	600	4	34.26	40.27
4	500	800	1600	400	10	300	2	31.68	42.16
5	1000	400	1600	200	10	300	4	30.71	42.64
6	1000	400	1600	400	8	600	2	33.84	41.83
7	1000	800	800	200	10	600	2	26.35	34.59
8	1000	800	800	400	8	300	4	29.59	39.22

According to the analysis, Na_2S, $CuSO_4$, and Calgon concentrations, along with flotation time, significantly affected flotation responses. For the concentrate grade, pH was also a notable factor. Regression plots (Fig. 2 and Fig. 3) show strong agreement between experimental and predicted values ($R^2 = 0.99$ for Zn grade, $R^2 = 0.96$ for recovery), confirming the reliability of the developed models.

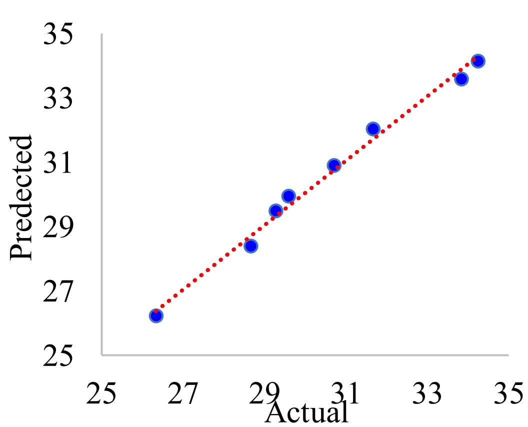

Fig. 2. Regression plot of actual versus predicted values for zinc grade ($R^2 = 0.99$).

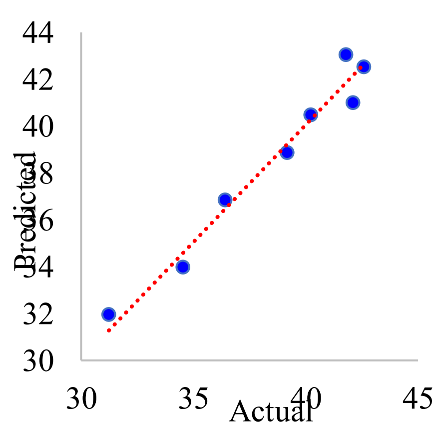

Fig. 3. Regression plot of actual versus predicted values for zinc recovery ($R^2 = 0.96$).

Despite optimization efforts, the overall zinc recovery using KAX was relatively low, suggesting the limited suitability of xanthates for oxidized zinc ores. This limitation is attributed to the instability of Zn–xanthate surface complexes and the poor froth stability observed during tests. The froth generated was short-lived, rapidly collapsing and releasing attached particles back into the pulp. Notably, froth volume appeared unaffected by variations in frother concentration, collector dosage, or sulfidizing reagents, implying that collector–mineral interactions are the primary control mechanism. Although the presence of slimes negatively affected flotation efficiency, their effect in xanthate-based flotation of oxidized zinc ore was not significant enough to account for the poor performance. Overall, the findings confirm that xanthates, while effective for sulfide minerals, are not suitable collectors for the flotation of zinc oxide ores. Their poor interaction with oxide surfaces and unstable froth behavior necessitate the exploration of alternative or synergistic reagent systems for enhanced flotation performance.

3.2. Flotation Using Cationic Collectors

Unlike xanthates, which function via chemisorption, cationic collectors such as amines rely primarily on electrostatic attraction between their polar head groups and the electrical double layer at the mineral surface. These interactions are generally weaker than the covalent bonding observed with xanthates, resulting in less robust surface hydrophobization. Cationic collectors are particularly suited for the flotation of oxidized, carbonate, and silicate ores, as well as alkaline earth minerals like barite, carnallite, and Sylvite. Among cationic collectors, primary amines, amine salts, and quaternary ammonium compounds are commonly used. Their flotation performance is highly sensitive to the pH of the pulp. These reagents tend to be most active in mildly acidic to neutral environments, while strong acidic or alkaline conditions can significantly reduce their effectiveness. For instance, dodecyl amine, a well-studied cationic collector, exhibits solubility and phase behavior highly dependent on pH. At neutral pH, the un-ionized amine species predominates, whereas at pH 10.6 and above, the equilibrium shifts toward protonated and dimeric forms, reducing collector availability.

In the present study, the cationic collector cocoalkyl amine acetate, commercially known as Armac C with the chemical formula $[R\text{-}NH_2]\cdot[CH_3COOH]$, was used. Armac C is widely applied in industrial-scale flotation of oxidized zinc ores. Adsorption of the collector onto smithsonite surfaces, particularly after 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 impact of Calgon, sodium silicate, Na_2S, $CuSO_4$, pH, Armac C concentration, and flotation time on the grade and recovery of zinc. Outcomes (Table 4) clearly show that Na_2S concentration had the most significant positive impact on both grade and recovery. Increasing flotation time improved 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 showed a synergistic effect: as their dosage increased, both grade and recovery improved.

Table 4. Zinc grade and recovery results from flotation experiments using an amine collector (Armac C).

N	Calgon (ppm)	Sodium silicate (ppm)	Na_2S (ppm)	$CuSO_4$ (ppm)	pH	Armac C (ppm)	Flotation time (min)	Grade Zn (%)	Recovery Zn (%)
1	500	400	800	200	8	300	2	33.61	34.29
2	500	400	800	400	10	600	4	31.29	42.32
3	500	800	1600	200	8	600	4	37.56	44.68
4	500	800	1600	400	10	300	2	39.98	46.09
5	1000	400	1600	200	10	300	4	31.01	43.63
6	1000	400	1600	400	8	600	2	38.52	45.44
7	1000	800	800	200	10	600	2	32.73	39.67
8	1000	800	800	400	8	300	4	33.26	43.58

All flotation tests were conducted without desliming. Although recovery and grade were generally better 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 some advantages, particularly in oxide ore flotation, further optimization—potentially through reagent combinations or surface modification strategies—is necessary to achieve satisfactory results.

3.3. Mixed Collectors

3.3.1. Without Desliming

To better understand the flotation behavior of zinc oxide ore with mixed cationic and anionic collectors and reduce the number of full-scale experiments, a preliminary series of tests was conducted using a Taguchi L12 orthogonal array design. This design included 11 process variables, each evaluated at two levels. The selected parameters encompassed pH, reagent dosages, conditioning times, and flotation durations, with their roles in the flotation process summarized in Table 5.

Table 5. Key Factors in the Taguchi L12 Design with 11 Two-Level Factors.

N.	Factors	Unit	Low level	High level
1	pH	-	9	11
2	Sodium Silicate Concentration 1	ppm	500	1000
3	Starch	ppm	400	800
4	Na_2S concentration 1	ppm	1500	3000
5	Conditioning time	min.	5	10
6	Xanthate concentration 1	ppm	300	600
7	Flotation time	min.	3	6
8	Sodium silicate concentration 2	ppm	2000	4000
9	Na_2S concentration 2	ppm	800	1600
10	Armac C concentration	ppm	100	200
11	Xanthate concentration 2	ppm	200	400

Twelve experimental runs were performed based on the L12 matrix, with each test repeated twice to enhance statistical reliability and enable calculation of signal-to-noise (S/N) ratios. The flotation process was conducted in two sequential stages. In the first stage, starch and sodium silicate were introduced into the pulp and mixed thoroughly, followed by sodium sulfide addition and pH adjustment. Xanthate was then added and conditioned before flotation. In the second stage, following froth removal, additional sodium sulfide was added and pH adjusted before sequential addition of Armac C and xanthate. Airflow was initiated two minutes later to commence the second flotation stage. No frother was used in the second stage. Observations during testing revealed that froth characteristics were highly dependent on Armac C concentration. Interestingly, lower Armac dosages tended to yield better flotation responses, potentially due to reduced surface tension and improved selectivity. The two main response variables were zinc recovery and calcium recovery in the concentrate. Since high calcium content increases acid consumption during downstream leaching, minimizing calcium recovery while maximizing zinc recovery was targeted. The combined concentrates from both flotation stages were analyzed, and the results are presented in Table 6. Analysis of variance (ANOVA) [34] for zinc recovery (Table 7) indicated that flotation time, the dosages of sodium silicate and sodium sulfide in the first stage, Armac C dosage, and pulp pH had significant effects. Calcium recovery ANOVA (Table 8) also revealed notable influences from conditioning time, starch dosage, and xanthate addition, particularly in the first stage. Optimization was carried out using a statistical method, assigning higher importance to zinc recovery than calcium recovery.

Table 6. Experimental Results Using the Taguchi L12 Method for Cationic Collectors without Desliming.

Experiment N.	Zn recovery %		Ca recovery %	
	Response 1	Response 2	Response 1	Response 2
1	39.28	43.51	6.57	8.26
2	52.66	61.18	17.93	19.92
3	53.18	54.97	19.03	24.11
4	63.53	68.44	22.42	20.09
5	55.83	58.57	20.27	21.49
6	57.16	55.14	20.87	23.51
7	63.46	69.73	22.13	27.84
8	53.91	52.38	20.05	19.02
9	46.45	50.27	11.64	18.37
10	52.75	60.12	14.38	15.64
11	58.33	64.26	19.17	23.46
12	66.49	62.49	26.52	25.34

The optimal process conditions included: pH 10.8, sodium silicate (Stage 1: 997 ppm, Stage 2: 4000 ppm), starch 400 ppm, Na_2S (Stage 1: 2193 ppm, Stage 2: 1090 ppm), conditioning time 5 min, xanthate (Stage 1: 434 ppm, Stage 2: 375 ppm), Armac C 100 ppm, and flotation time 6 min. Model predictions under these conditions yielded a zinc recovery of 63.5% and a calcium recovery of 19.1%. Validation tests confirmed the general trend, with zinc recovery ranging from 53.2% to 54.4%, and calcium recovery between 21.8% and 22.7%. The lower-than-expected zinc recovery is likely due to the negative effect of slimes and ultra-fine particles in the feed, which were not removed before flotation.

Table 7. Analysis of Variation (ANOVA) for Zinc Recovery.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob. > F
Model	542.15	6	90.36	9.50	0.013
pH	28.81	1	28.81	3.03	0.142
Sodium Silicate. 1	140.53	1	140.53	14.78	0.012
Na_2S 1	43.61	1	43.61	4.59	0.085
Flotation time	165.21	1	165.21	17.37	0.009
Sodium Silicate. 2	36.56	1	36.56	3.84	0.107
Armac C.	127.43	1	127.43	13.40	0.015
Residual	47.55	5	9.51		
Cor Total	589.69	11			

Table 1. Analysis of Variation (ANOVA) for Calcium Recovery.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	276.44	7	39.49	102.95	0.0002
A-pH	7.59	1	7.59	19.79	0.0113
B-Sodium Silicate. 1	30.54	1	30.54	79.63	0.0009
C-Starch	17.10	1	17.10	44.58	0.0026
D-Na2S 1	28.91	1	28.91	75.36	0.0010
E-Cond. time	17.12	1	17.12	44.64	0.0026
G-Flotation time	83.35	1	83.35	217.28	0.0001
K-Armac C.	91.83	1	91.83	239.39	0.0001
Residual	1.53	4	0.38		
Cor Total	277.97	11			

3.3.2. With Desliming

To improve flotation performance and reduce interference from ultra-fine particles, desliming was carried out by removing particles smaller than 20 µm from the feed before flotation. The flotation tests were then conducted using mixed collectors under the experimental design of a Taguchi L8 ($2^1 \times 3^7$) orthogonal array. This design incorporated eight factors, one at two levels and the rest at three levels, as detailed in Table 9.

Eighteen experiments were conducted based on the L18 matrix, with a randomized test order to minimize systematic error. The factors studied included pulp pH, concentrations of sodium silicate, starch, sodium sulfide, xanthate (at two stages), Armac C dosage, and flotation time. The responses analyzed were zinc recovery, zinc grade in the concentrate, and calcium recovery in the concentrate. The experimental results are summarized in Table 10.

Table 9. Key Factors and Their Levels for Flotation Experiments with Desliming.

N.	Factors	Unit	Level 1	Level 2	Level 3
1	pH	-	9	10	11
2	Sodium silicate concentration	ppm	400	800	1200
3	Starch	ppm	400	700	1000
4	Na_2S concentration	ppm	800	1800	2800
5	Xanthate concentration 1	ppm	250	500	750
6	Flotation time	min	2	4	6
7	Xanthate concentration 2	ppm	200	400	-
8	Armac C concentration	ppm	100	200	300

Table 10. Experimental Responses for Each Flotation Test with Desliming.

Experiment N.	Zn recovery %		Zn grade%		Ca recovery %	
	Response 1	Response 2	Response 1	Response 2	Response 1	Response 2
1	73.80	74.58	31.59	30.29	29.69	20.29
2	74.86	71.09	29.49	28.39	19.29	21.19
3	82.19	80.78	41.08	40.78	13.19	15.28
4	81.94	82.39	34.79	35.58	24.89	14.39
5	76.34	77.58	39.89	38.49	30.59	24.39
6	75.60	71.98	34.79	35.28	19.89	15.98
7	76.16	79.29	34.18	36.69	25.78	22.09
8	76.57	74.68	32.59	33.09	18.08	16.88
9	80.11	80.58	36.59	35.19	28.48	28.49
10	76.19	75.19	41.69	41.18	16.89	15.19
11	71.57	71.79	36.29	32.89	34.19	34.98
12	80.27	79.88	39.98	38.98	24.28	26.59
13	78.64	77.89	40.89	36.58	28.09	21.69
14	83.74	82.58	34.49	38.29	20.09	23.29
15	72.16	72.59	36.18	36.58	27.98	25.89
16	80.13	81.29	39.19	34.39	22.58	26.68
17	82.46	82.69	37.48	36.18	26.29	15.79
18	77.38	77.88	35.69	35.94	20.29	19.88

To evaluate the influence of each parameter on the flotation performance, marginal means and signal-to-noise (S/N) ratio plots were generated for each response. Analysis of variance (ANOVA) for zinc recovery (Table 11) and grade (Table 12), and calcium recovery (Table 13) shows that for zinc grade in the concentrate, Na_2S concentration was the most significant factor ($p = 0.009$), followed by xanthate dosage in the second stage ($p = 0.034$). The overall model was statistically significant ($F = 4.54$, $p = 0.038$), with a good match between predicted and experimental data. Regarding calcium recovery, starch concentration showed a strong effect ($p = 0.010$), with additional contributions from xanthate 1, flotation time, and Armac C ($p < 0.1$). The model was significant ($F = 4.52$, $p = 0.038$), and the predicted vs. actual calcium recovery values confirmed the model's validity.

Overall, desliming significantly improved flotation performance, yielding zinc recoveries above 80% and higher zinc grades, while maintaining acceptable levels of calcium recovery in the concentrate. These results highlight the importance of proper feed preparation and optimization of reagent dosages in the flotation of zinc oxide ores.

Table 11. Analysis of Variation (ANOVA) for Zinc Recovery.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	221.37	12	18.45	7.79	0.017
Xanthate 2			pooled		
pH	28.77	2	14.39	6.08	0.046
Sodium Silicate.			pooled		
Starch	5.42	2	2.71	1.14	0.390
Na2S	25.38	2	12.69	5.36	0.057
Xanthate 1	10.55	2	5.28	2.23	0.203
Flotation time	34.65	2	17.32	7.32	0.033
Armac C	116.59	2	58.30	24.62	0.003
Residual	11.84	5	2.37		
Cor Total	233.21	17			

Table 12. Analysis of Variation (ANOVA) for Zinc Grade.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	2.29E+09	11	2.08E+08	4.54	0.038
Xanthate 2	3.46E+08	1	3.46E+08	7.54	0.034
pH			pooled		
Sodium Silicate.	2.55E+08	2	1.28E+08	2.78	0.140
Starch	2.78E+08	2	1.39E+08	3.03	0.123
Na2S	1.04E+09	2	5.22E+08	11.38	0.009
Xanthate 1	1.3E+08	2	64752429	1.41	0.315
Flotation time			pooled		
Armac C	2.39E+08	2	1.19E+08	2.60	0.154
Residual	2.75E+08	6	45887332		
Cor Total	2.57E+09	17			

Table 13. Analysis of Variation (ANOVA) for Calcium Recovery.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	384.00	11	34.91	4.52	0.038
Xanthate 2	24.27	1	24.27	3.15	0.127
pH			pooled		
Sodium Silicate.			pooled		
Starch	166.42	2	83.21	10.78	0.010
Na2S	11.40	2	5.70	0.74	0.517
Xanthate 1	60.54	2	30.27	3.92	0.081
Flotation time	66.98	2	33.49	4.34	0.068
Armac C	54.39	2	27.20	3.52	0.097
Residual	46.29	6	7.72		
Cor Total	430.29	17			

3.3.3. Optimized Condition

The flotation process was optimized to maximize zinc recovery and grade and minimize calcium recovery in the concentrate. Using design constraints within selected factor ranges and assigning importance levels to each parameter, the software predicted 10 optimal conditions (Table 14), all leading to improved Zn recovery and grade while reducing Ca contamination. Case 1 was identified as the most optimal, with predicted Zn recovery of 84.27%, Zn grade of 41.52%, and Ca recovery of 13.85%. Confidence intervals confirmed the reliability of the predictions. Experimental tests under these optimal conditions confirmed the model's accuracy, although actual recoveries were slightly lower after adjusting for desliming losses. Corrected values accounted for the loss of fine particles, which contained significant amounts of zinc and calcium. After correction, Zn recovery ranged from 64.7% to 74.2%, indicating a trade-off between desliming benefits and overall recovery (Table 15).

Table 14. Ten Predicted Optimal Conditions.

	Xanthate 2	pH	Sodium silicate.	Starch	Na2S	Xanthate 1	Flotation time	Armac C
1	400	11	400	1000	2800	500	4	300
2	400	11	1200	1000	2800	500	4	300
3	400	10	400	1000	2800	500	6	300
4	400	11	400	1000	2800	500	6	300
5	400	10	1200	1000	2800	500	6	300
6	400	11	1200	1000	2800	500	6	300
7	400	10	400	1000	2800	500	4	300
8	400	10	1200	1000	2800	500	4	300
9	400	9	400	1000	2800	500	6	300
10	400	9	1200	1000	2800	500	6	300

Table 2. Ten Predicted Optimal responses and Their Corresponding real Responses.

Number	Predicted			Test Result		
	Zn recovery	Zn grade	Ca recovery	Zn recovery	Zn grade	Ca recovery
1	84.27	41.52	13.85	81.87	38.24	13.09
2	84.27	42.05	13.85	79.30	39.46	14.32
3	84.91	41.52	14.65	77.29	40.16	16.19
4	86.23	41.52	14.65	80.19	41.08	13.64
5	84.91	42.05	14.65	81.43	38.97	14.08
6	86.23	42.05	14.65	80.74	39.37	12.93
7	82.96	41.52	13.85	72.38	40.60	14.57
8	82.96	42.05	13.85	74.85	41.53	15.94
9	83.14	41.52	14.65	81.26	40.03	15.69
10	83.14	42.05	14.65	77.47	42.19	15.38

4. Conclusions

This study demonstrated that the flotation of zinc oxide ores—typically regarded as complex and refractory—can be significantly improved through the synergistic use of mixed collectors and targeted process optimization. Neither potassium amyl xanthate (KAX) nor cocoalkylamine acetate (Armac C) alone provided satisfactory performance, due to their limited interaction with oxide mineral surfaces and poor froth characteristics. However, their combination led to a marked enhancement in both zinc recovery and concentrate grade, confirming the benefits of mixed collector systems for such ores. The incorporation of a desliming stage proved critical, effectively mitigating the adverse effects of ultra-fine particles and enabling better reagent interaction. Experimental designs based on Taguchi orthogonal arrays and ANOVA analysis identified optimal operational parameters, which were validated through flotation tests. Under these optimized conditions, zinc recoveries as high as 84.3% and concentrate grades exceeding 42% were achieved, with minimal calcium contamination—an essential factor for downstream processing efficiency. These findings not only highlight the technical feasibility of using mixed collectors for zinc oxide flotation but also provide a practical framework for processing low-grade, slime-rich ores. The integrated strategy of desliming, reagent synergy, and statistical optimization offers a promising approach for enhancing the economic viability of zinc oxide ore beneficiation, particularly as sulfide resources continue to decline.

Ethical Considerations

The authors avoided data fabrication, falsification, and plagiarism, and any form of misconduct.

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Conflict of Interest

The authors declare no conflict of interest.

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