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Alima Mambetaliyeva, Tansholpan Tussupbekova *, Lyaila Sabirova, Guldana Makasheva, Saparbek Yeleussiz, Madina Barmenshinova * and Sultan Kaliaskar

Department of Metallurgy and Mineral Processing. Non-Profit Joint Stock Company (NJSC) Kazakh National Research Technical University Named K.I. Satbayev. Almaty 050013. Kazakhstan
* Correspondence: tansholpan_87.09@mail.ru; m.barmenshinova@satbayev.university

Abstract

This study examines the impact of regrinding on the interfacial properties of sulfide minerals and the flotation performance of weathered copper-porphyry tailings. The feed material is characterized by a low copper grade (0.17%) and a high proportion of oxidized species (53.84%), which contributes to its inherent chemical stability and poor flotation kinetics. The findings indicate that regrinding serves a dual role: facilitating the liberation of mineral intergrowths and inducing mechanical surface renewal. This renewal is characterized by a significant decrease in the oxidation-reduction potential (ORP) and an intensification of the surface reactivity. Experimental results identify an optimal grinding fineness of 77-81% passing -0.045 mm, yielding a copper recovery of 16.26% in the absence of a sulfidizing agent. The integration of sodium sulfide (400 g/t) with regrinding significantly enhances recovery to 36.37%, driven by the establishment of a reducing environment (ORP ≈ -150 mV) and the chemisorption-mediated activation of mineral surfaces. While ultrafine grinding (90-100% passing -0.045 mm) further increases recovery to 51.47%, it is accompanied by deleterious sliming effects and a subsequent loss of process selectivity. The study confirms that mechanical surface rejuvenation and the optimization of electrochemical conditions are critical for improving the processing efficiency of anthropogenic resources. providing a theoretical framework for establishing rational beneficiation regimes.

Keywords: regrinding; surface renewal; copper tailings; flotation; sulfidization; redox potential; tailings reprocessing

1. Introduction

As high-grade mineral reserves deplete and conventional mining becomes more complex, the industry must pivot toward reclaiming anthropogenic resources. Today. mining operations face a dual challenge: falling ore grades and expanding plant capacities, both of which lead to a massive buildup of tailings. This resource depletion is no longer just a geological concern-it has become a critical technological and environmental bottleneck.

On a global scale, between 8.9 and 14.4 billion tonnes of tailings are generated annually, adding to an estimated 200-280 billion tonnes already in storage [1–3]. While these sites pose environmental risks, they also represent a significant opportunity for secondary recovery [4–8]. International experience proves this is viable. For instance, Amerigo Resources in Chile successfully recovers copper and molybdenum from El Teniente tailings, while DRDGOLD in South Africa has scaled up gold recovery from legacy dumps [9,10].

This issue is particularly pressing for Kazakhstan, where over 1.700 technogenic mineral sites (TMFs) hold roughly 55 billion tonnes of material [11–13]. To date, only 11% of these resources are reprocessed - far below the 70-80% seen in leading mining nations. To address this, Kazakhstan is currently launching 25 projects aimed at extracting copper, gold, and iron from existing tailings.

Sulfide tailings are of particular scientific and practical interest. During long-term storage, sulfide minerals undergo oxidation and passivation, leading to the formation of secondary surface phases that suppress flotation activity. The efficiency of metal recovery from such materials depends on the particle size distribution, the degree of mineral liberation, and most critically, the surface state. While incomplete liberation limits recovery over-grinding can also degrade performance by generating excessive slimes.

In modern reprocessing circuits, regrinding serves a dual purpose: it reduces particle size and cleans the mineral surfaces. Optimizing the grinding regime allows for surface renewal-stripping away oxide films to expose fresh sulfide phases, which significantly boosts floatability [14]. Research indicates that the liberation of valuable components improves with increased grinding time regardless of particle size. However, to achieve maximum selectivity and efficiency, it is often more effective to process narrow size fractions separately.

Ultimately, mineral liberation is dictated by the ore's specific mineralogy and texture [4,5,15–18]. Consequently, the performance of the flotation circuit is a direct result of the ore texture and the target particle size achieved during the grinding or regrinding stage.

In their study, Bakalarz, Duchnowska, and Luszczkiewicz demonstrated that increasing the grinding time of copper sulfide ores improves the liberation of valuable components across all particle sizes. While deep grinding may slightly diminish the flotation performance of fully liberated fines, it remains essential for achieving maximum selectivity. Their findings suggest that to optimize overall efficiency, it is practical to process narrow size fractions separately, as fine and coarse particles have distinct flotation requirements [2].

One of the primary hurdles in tailings reprocessing is their mineralogical complexity. In copper-bearing tailings, valuable metals are often found in refractory forms, specifically as oxidized copper species coating the particle surfaces. To improve recovery, these oxidized minerals must be activated through sulfidization [19–22]. Research by T.B.Oserov, Smailov, et al. indicates that hydrophobicity in oxidized minerals can be achieved by adding sodium sulfide. However, this sulfidization process occurs primarily as a surface-level reaction, forming an extremely thin film. Precisely controlling this reaction requires monitoring the oxidation-reduction potential (ORP). Previous studies on oxidized lead-zinc ores have demonstrated that maintaining a specific ORP level is critical for effective flotation performance.

Regrinding legacy tailings does more than just reduce particle size; it facilitates surface rejuvenation. This process strips away passivating oxide films and exposes fresh sulfide phases, fundamentally altering the physicochemical and flotation properties of the material. Consequently. investigating how regrinding affects the surface state of aged sulfide minerals is a critical task for improving metal recovery rates.

The electrochemical state of the pulp is one of the key factors determining the floatability of sulfide minerals. According to the fundamental concepts of flotation electrochemistry, the pulp potential affects the oxidation and dissolution of mineral particles, the state of reagents in the solution, the interaction of the collector with the mineral surface, as well as galvanic processes within the 'grinding medium – mineral – reagent' system [23]. Therefore, the change in ORP during grinding can be considered an important indicator of alterations in the surface reactivity of minerals.

It was previously shown that regrinding can significantly alter pulp chemistry: fine grinding often leads to more reducing Eh values, a decrease in dissolved oxygen content, and an increase in oxygen demand, which affects subsequent flotation [7,24]. Furthermore. oxidative weathering of copper sulfide ores impairs flotation performance; however, this effect can be partially compensated for through the appropriate selection of grinding conditions and pulp chemistry [25].

The novelty of this work lies not in the application of standard flotation reagents, but in establishing a correlation between regrinding. mechanical surface renewal, ORP changes, sulfidization, and the flotation recovery of copper from long-term oxidized anthropogenic tailings. Unlike previous studies, which focused predominantly on the influence of the grinding medium.

pulp chemistry, or the oxidation of primary sulfide ores, this work examines weathered porphyry copper tailings that have been subjected to atmospheric exposure for over 70 years.

2. Materials and Methods

To address the objectives of this study. a sequential methodology was developed. consisting of several key stages: designing the experimental circuit. regrinding the legacy tailings in both a rotary axis mill and an ultra-fine mill. and performing flotation tests on the resulting pulp. During flotation. strict control was maintained over reagent dosages. pH levels, ORP, and temperature. This structured approach ensures a smooth transition from theoretical analysis to a reproducible laboratory protocol suitable for future scaling and industrial implementation.

The study focused on legacy flotation tailings from porphyry copper ores, sampled from various tailings storage facilities in the Republic of Kazakhstan. The investigated tailings represent weathered anthropogenic material that has accumulated over a period of more than 70 years. The deposition process was continuous, with freshly deposited tailings constantly overlying older layers, which led to the formation of a complex oxidation and weathering structure. Long-term atmospheric exposure facilitated significant alterations on the surface of sulfide minerals and the formation of secondary oxidized copper phases. The bulk chemical and phase compositions were determined via conventional silicate analysis, while copper and trace element concentrations were measured using ICP-MS. Mineralogical analysis was conducted on polished sections in reflected light using an OLYMPUS BX 53 microscope. integrated with a SIMAGIS XS-3CU imaging system and SIAMS Mineral C7 software. Furthermore, the particle size distribution was mapped using a FRITSCH Analyzette 22 laser diffraction analyzer and a CYCLOSIZER LF-11. Phase identification was finalized using a Bruker D2 Phaser diffractometer.

The beneficiation process began with the pre-conditioning of the ground pulp, followed by the addition of flotation reagents (collector and frother). Flotation tests were then carried out using a laboratory-scale flotation machine. The primary equipment used in these experiments included:

- Grinding: An MSHL-7 (7-liter) laboratory ball mill (manufactured by Mekhanobr-tekhnika) was operated at a rotational speed of 75% of the critical speed, utilizing steel balls as the grinding medium.
- Grinding equipment: A NETZSCH PE 075 ultra-fine grinding mill.
- "Flotation: A Vektis 3-liter pneumo-mechanical flotation machine was operated at an impeller speed of 1700 rpm and an air flow rate of 3 L/min;
- Monitoring: Hanna HI3230B and HI1230B electrodes were used to monitor pH, ORP, and temperature.

The core experimental parameters were set as follows:

- Grinding kinetics: Intervals of 0, 3, 5, 10, and 15 minutes for conventional grinding, and 15 and 30 minutes for ultra-fine grinding;
- Rougher flotation: 5 minutes;
- Pulp density: A solids content of 28–30% by weight;
- Flotation sample mass: 1000 g;
- Sample specific gravity: 2.7 g/cm^3;
- Reagent dosages: Sodium sulfide (Na_2S) at 400 g/t; potassium butyl xanthate (PBX) at 50 g/t; and Methyl Isobutyl Carbinol (MIBC) as a frother at 20 g/t;
- During flotation experiments utilizing Na_2S, the pH level was maintained at 7.0–7.5, thereby limiting the generation of gaseous H_2S. All experiments were conducted under standard laboratory ventilation.
- Process Monitoring: pH, ORP, and temperature readings were recorded at three critical stages: immediately after grinding, before collector addition. and after collector addition;
- Water Quality: All tests were conducted using laboratory tap water (Table 1) of standardized chemical composition.

Table 1. Chemical composition of the process (tap) water used in flotation experiments.

Parameter	**Value**
$Na^+ + K^+$	110 mg/L
Ca^{2+}	128 mg/L
Mg^{2+}	41 mg/L
SO_4^{2-}	423 mg/L
HCO_3^-	317 mg/L
Cl^-	18 mg/L
NO_3^-	5.3 mg/L
pH	7.5
Total dissolved solids	885 mg/L

Sample grinding was performed by a wet method in an air atmosphere. Specific control over the dissolved oxygen content and monitoring of the oxidation dynamics of the mineral surface during the fine grinding stage were not provided for, which corresponds to standard conditions for ore preparation prior to flotation.

Flotation concentrates and tailings were weighed and analyzed for copper content to calculate recovery rates. To ensure reliability, all flotation tests were performed in triplicate. with the results averaged for the final analysis. The separation efficiency was quantified using the Hancock-Luyken formula (1), providing a standardized measure of the beneficiation performance.

$$E=(\varepsilon-\gamma)/(100-\alpha) \tag{1}$$

A detailed analysis of the flotation test results across varying levels of the -0.045 mm size fraction, along with the developed copper recovery model, is presented in the 'Results' section.

3. Results

The results of this study are structured as follows: first, the raw material was characterized using a suite of analytical techniques, including optical microscopy and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The initial sample was then ground to the target particle size in a laboratory mill. Following the grinding stage, pulp samples were dried and submitted for mineralogical analysis to evaluate the degree of mineral liberation and visualize particle morphology.

Table 2 summarizes the chemical composition of the primary sample.

Table 2. Chemical composition of the feed sample.

Element	**Content (wt. %)**
Copper	0.17
Silver (Ag). g/t	1.19
Zinc	0.28
Lead	0.09
Iron	5.37
Total Sulfur	1.03
Sulfide Sulfur	1.00
Arsenic	0.015
Antimony	0.003
Cadmium	0.0001
Molybdenum	0.005
Tellurium	0.0003
Silicon dioxide	58.06
Aluminum oxide	17.47
Calcium oxide	4.82

Magnesium oxide	1.34
Potassium oxide	2.89

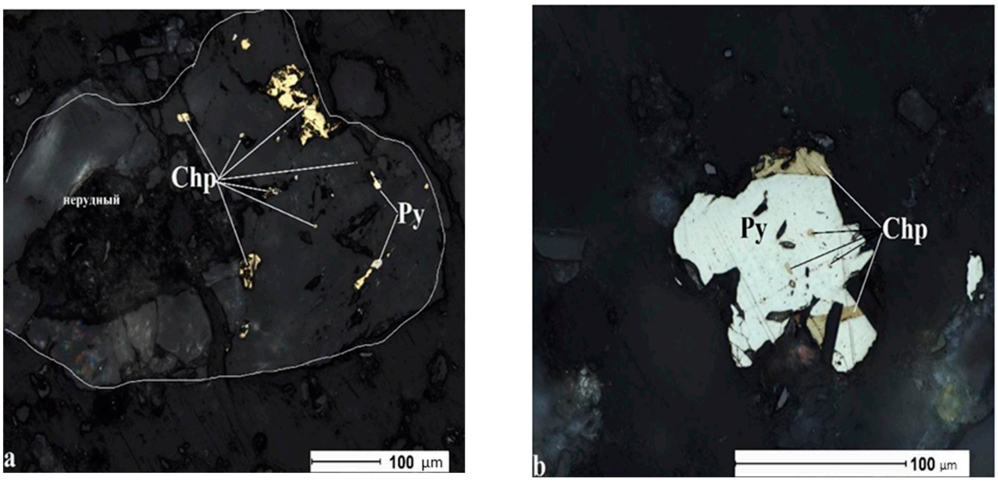
Copper Speciation Analysis

To evaluate the potential for copper recovery, phase analysis was performed to determine the distribution of copper across different chemical forms (Table 3).

Table 3. Copper phase composition of the tailings.

Copper Phase / Mineral Form	**Content, % (absolute)**	**Distribution, % (relative)**
Sulfide Minerals. including.:	0.078	46.16
Secondary sulfides	*0.026*	*15.39*
Primary sulfides	*0.052*	*30.77*
Oxidized Minerals	0.092	53.84
including: Chrysocolla	0.029	17.08
Total Copper	0.170	100.0

The results of the optical mineralogy study of the legacy tailings are presented below. This examination established the mineral composition of both the ore and gangue fractions, grain morphology and size distribution, and the specific characteristics of mineral associations within the anthropogenic processing products. Chalcopyrite is the most abundant copper sulfide in the sample. Its grains are most commonly observed as intergrowths with gangue minerals or in a liberated state. In certain areas, it occurs in association with pyrite (see Figure 1a–c), magnetite (Figure 1a), sphalerite, and bornite. The predominant (average) grain size of chalcopyrite is characterized as ultra-fine (1–10 µm) and fine (10–30 µm), although relatively coarser grains (40–60–120 µm) are occasionally encountered.



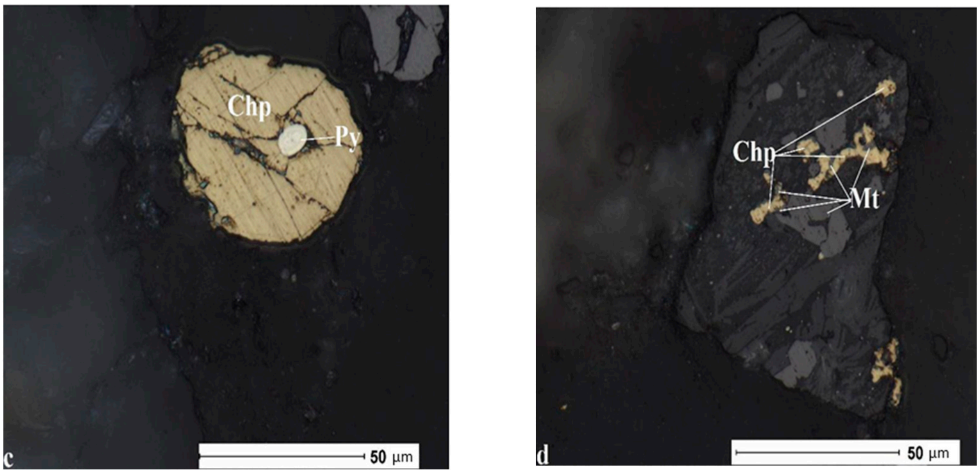


Figure 1. Primary occurrences and mineral associations of chalcopyrite. Abbreviations: Ccp – chalcopyrite, Py – pyrite, Mt - magnetite. Magnification: 500x/1000x. Reflected light, plane-polarized light (PPL).

Bornite. covellite. and chalcocite are observed only as accessory minerals and are extremely rare. The grain size for these minerals typically ranges from less than 1 µm up to 80 µm.

The particle size distribution (PSD) of the legacy tailings sample. categorized by size fractions. is presented in Table 4.

Table 4. Particle size distribution of the initial tailings sample.

Size fraction, µm	Weight, %	Grade, %, g/t*			Distribution, %		
		Cu	Ag*	S	Cu	Ag	S
-500+200	8.15	0.196	1.472	1.11	9.27	10.08	8.80
-200+100	13.24	0.176	1.106	1.02	13.53	12.31	13.14
-100+71	5.19	0.201	1.882	1.15	6.06	8.21	5.81
-71+45	21.76	0.162	1.196	0.92	20.46	21.87	19.48
-45+0	51.66	0.169	1.095	1.05	50.68	47.54	52.77
Feed	100.0	0.17	1.19	1.03	100.0	100.0	100.0

The initial analysis showed that the -0.045+0 mm fraction dominates the sample with a weight recovery of 51.66% while the total content of the finished size class (-0.071 mm) reaches 73.42%. Interestingly, the copper distribution across all size fractions is directly proportional to their weight. This correlation points to a fine-grained and relatively uniform mineralization, suggesting that the valuable components are not implementedd in specific pockets, but are spread throughout the material.

To better understand how these components are distributed within the finest particles, the -0.071+0 mm fraction, including micro-slimes. This detailed analysis was performed using a Cyclosizer with the results summarized in Table 5.

Table 5. Particle size analysis of the -71+0 µm fraction (Cyclosizer data).

Size fraction (µm)	Weight, %	Cu Grade, %	Distribution, %
+71	26.08	0.147	22.55
-71+59.1	13.42	0.156	12.31
-59.1+45.4	9.06	0.163	8.69
-45.4+32.7	13.61	0.103	8.24
-32.7+22.22	4.06	0.156	3.73
-22.22+11.11	6.24	0.115	4.22
-11.11+8.4	0.68	0.078	0.31
-8.4+0	26.85	0.253	39.95

Total (Feed)	100.0	0.17	100.0

The data in Table 5 highlight a significant challenge: the highest copper distribution (39.95%) is concentrated in the finest fraction (-8.4+0 µm). The presence of a substantial amount of these micro-slimes (26.85% of the total mass), coupled with their high metal content. confirms the extremely fine-grained nature of the copper mineralization. From a metallurgical perspective this often hinders flotation due to the detrimental effect of 'slime coating' where ultra-fine particles interfere with the recovery of valuable minerals.

To address this and find the optimal balance for mineral liberation, a series of laboratory experiments were conducted using different grinding times. The resulting particle size distributions for these ground samples are presented in Table 6.

Table 6. Particle size distribution of the samples at varying grinding intervals.

Size (µm)	**Initial (0 min)**						
	Ball Mill (Rotary Axis)					**Ultra-Fine Grinding (UFG)**	
	0	**5**	**10**	**15**	**20**	**10**	**20**
8.4	26.85	32.14	38.59	44.75	47.03	43.97	65.44
11.11	27.53	44.23	47.85	51.04	54.95	50.02	77.49
22.22	33.77	54.81	58.72	64.99	70.21	72.70	93.23
32.7	37.83	58.05	63.67	71.64	79.36	85.90	98.29
45.4	51.44	65.50	69.95	77.16	84.57	96.26	100.00
59.1	60.50	75.05	79.34	83.82	88.71	99.52	100.00
71	73.92	81.26	87.06	94.06	96.30	100.00	100.00

*data represents cumulative percent passing.

A series of experimental studies were conducted to determine how the degree of grinding influences copper recovery. To evaluate the effectiveness of surface activation these experiments were carried out both with the addition of sodium sulfide and in its absence. This comparative approach allows isolation of the impact of chemical activation from physical liberation. The experimental procedure and flowsheets are illustrated in Figure 2.

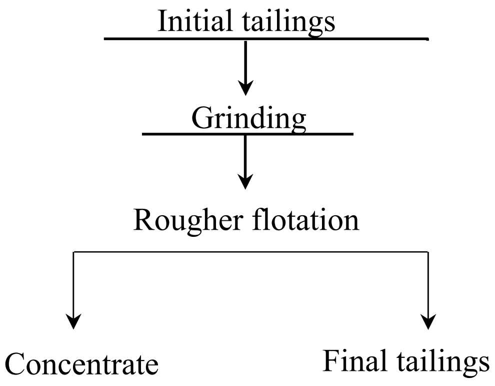


Figure 2. Experimental flowsheet for the flotation of the initial tailings sample.

The metallurgical performance results. detailing the grades and recovery rates of copper. are summarized in Table 7.

Table 7. Copper flotation performance and metallurgical balance.

-0.045 mm content (%)	Na_2S dosage. g/t	Yield. %	Concentrate grade. %	Recovery. % (±SE)	Enrichment Efficiency. %
51 (initial)	0	3.05	0.911	13.74 (±0.55)	10.71
65	0	3.55	0.858	14.93 (±0.88)	11.40
70	0	3.56	0.879	15.05 (±1.01)	11.52
77	0	3.73	0.868	16.26 (±0.92)	12.56
81	0	2.89	1.14	15.56 (±0.67)	12.70
51 (initial)	400	4.18	0.823	17.54 (±0.61)	13.38
65	400	4.28	1.37	29.41 (±0.73)	25.19
70	400	4.11	1.64	33.93 (±0.81)	29.88
77	400	5.27	1.41	36.37 (±1.60)	31.17
81	400	5.52	1.29	35.80 (±1.12)	30.34
90	400	16.98	0.622	50.43 (±0.81)	33.52
100	400	17.28	0.634	51.47(±0.72)	34.26

The data in Table 7 clearly indicate that copper recovery is not solely dependent on the fineness of the grind, but is significantly enhanced by the addition of sodium sulfide. For the as-received tailings (without regrinding) the introduction of Na_2S increased recovery from 13.74% to 17.54% (a net gain of 3.8%). The impact of regrinding becomes far more pronounced when combined with chemical activation. For instance, at -0.045 mm content of 77% copper recovery rose from 16.26% (without Na_2S) to 36.37% (with Na_2S). Furthermore, ultra-fine grinding (UFG) pushed the recovery even higher, reaching 50.43–51.47%. However, it is important to note the Hancock-Luyken enrichment efficiency. which remained within the 33.52-34.26% range. Once the -0.045 mm fraction exceeds 90% the growth in efficiency begins to decelerate. This trend suggests that the process is approaching an optimal technical limit. where further energy expenditure for grinding may no longer yield proportional metallurgical benefits.

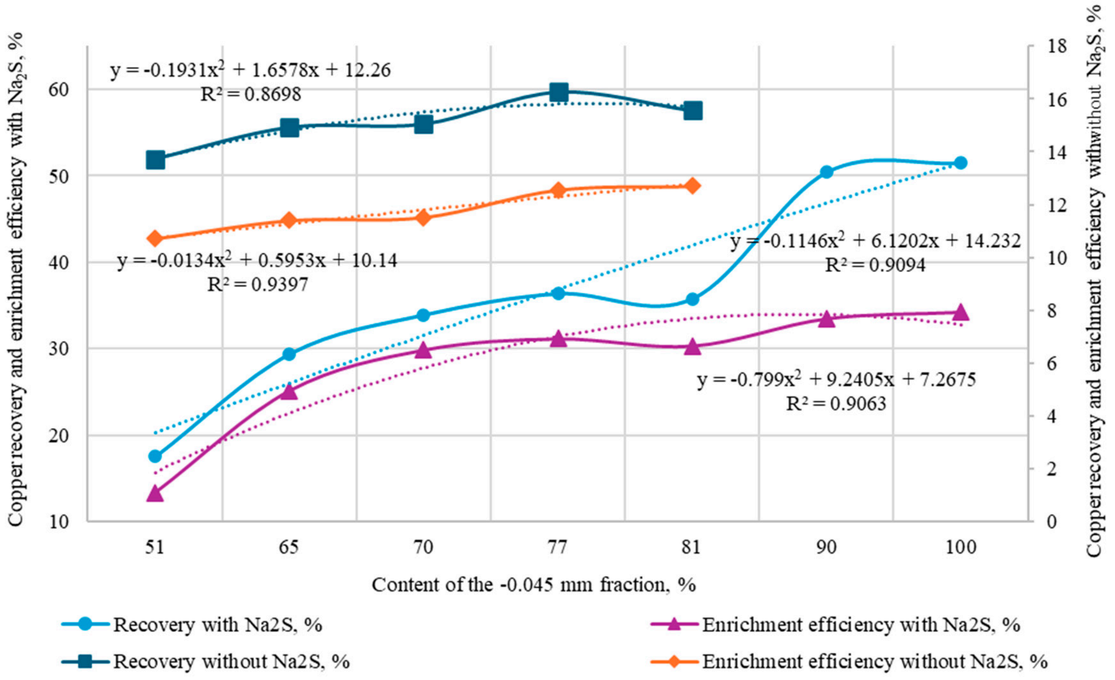


Figure 3. Copper recovery as a function of the -0.045 mm fraction content.

Based on the trends illustrated in Figure 3, several key observations can be made regarding the experiments conducted without the addition of sodium sulfide:

- maximum Recovery Plateau: The highest copper recovery values (ranging from 16.26% to 15.56%) were achieved at a grinding fineness of 77-81% (-0.045 mm). Enrichment Efficiency: The Hancock-Luyken enrichment efficiency at these fineness levels was recorded as 12.56% (for 77% passing) and 12.70% (for 81% passing).
- Marginal Gains: The negligible difference of only 0.14% between these efficiency rates indicates that further grinding beyond 77% - in the absence of chemical activation- does not lead to any significant metallurgical improvement.

The approximation of the experimental data using a second-order polynomial function yielded high coefficients of determination: $R^2 = 0.8698$ and $R^2 = 0.9397$. These values confirm a strong nonlinear relationship between the degree of grinding and copper recovery into the concentrate. Furthermore, the high correlation coefficients validate the reliability of the observed dependencies and ensure the statistical significance of the experimental results.

Following the baseline tests, experiments were conducted with the addition of sodium sulfide (Na_2S) acting as a sulfidizing agent for the oxidized copper minerals. This step was essential, as the sample contains a high proportion of oxidized species 53.84%, including 17.08% chrysocolla. which is notoriously difficult to recover. As shown in Figure 3, the second-order polynomial approximation demonstrates a high degree of fit with $R^2 = 0.9094$, confirming the strong predictability of the recovery trend under sulfidizing conditions.

To better understand the chemical environment during flotation, real-time measurements of pH, qxidation-Reduction Potential (ORP), and temperature were recorded.

The dynamics of these electrochemical parameters are presented in Table 8.

Table 8. The dynamics of these electrochemical parameters.

-0.045 mm Content (%)	pH			ORP			temperature. °C			Note
	After grinding	Before Xanthate	After Xanthate	After grinding	Before Xanthate	After Xanthate	After grinding	Before Xanthate	After Xanthate	
51 (initial)	7.77	7.77	7.8	186	186	182	15.71	15.71	15.71	without Na_2S
65	7.54	7.52	7.56	44	38	38	18.4	18.2	18.1	without Na_2S
70	7.5	7.51	7.48	-3	-8	-10	19.4	19.4	19.4	without Na_2S
77	7.52	7.53	7.54	-37	-41	-50	20.4	20.5	20.5	without Na_2S
81	7.49	7.49	7.52	-58	-69	-140	21	21	21	without Na_2S
51 (initial)	7.54	7.52	8.66	186	186	-150	18.4	18.2	18.1	with Na_2S
65	7.5	7.51	8.62	47	41	-150	19.4	19.4	19.4	with Na_2S
70	7.52	7.53	8.64	-5	-11	-150	20.4	20.5	20.5	with Na_2S
77	7.49	7.49	8.69	-33	-44	-150	21	21	21	with Na_2S
81	7.49	7.49	8.73	-51	-71	-150	21	21	21	with Na_2S
90	7.7	7.7	8.71	146	126	-150	21	21	21	with Na_2S
100	7.6	7.67	8.72	129	112	-150	22	22	21	with Na_2S

The measurements conducted indicate that the degree of grinding directly influences the electrochemical characteristics of the mineral pulp, as the -0.045 mm fraction increased from 65% to 100%, a moderate decrease in pH (from 7.77 to 7.49–7.6) was observed, accompanied by more pronounced shifts in the ORP. The introduction of sodium sulfide triggered a sharp decline in ORP, which stabilized at -150 mV regardless of the grinding fineness. This creates a potent reducing environment conducive to the flotation of oxidized copper species. Simultaneously, the pH values rose to approximately 8.6, a change directly attributed to the alkaline nature of sodium sulfide. These electrochemical conditions facilitate effective surface activation, which is essential for the subsequent adsorption of collectors on the mineral surfaces.

The dependence of ORP changes on the grinding fineness is shown in Figure 4.

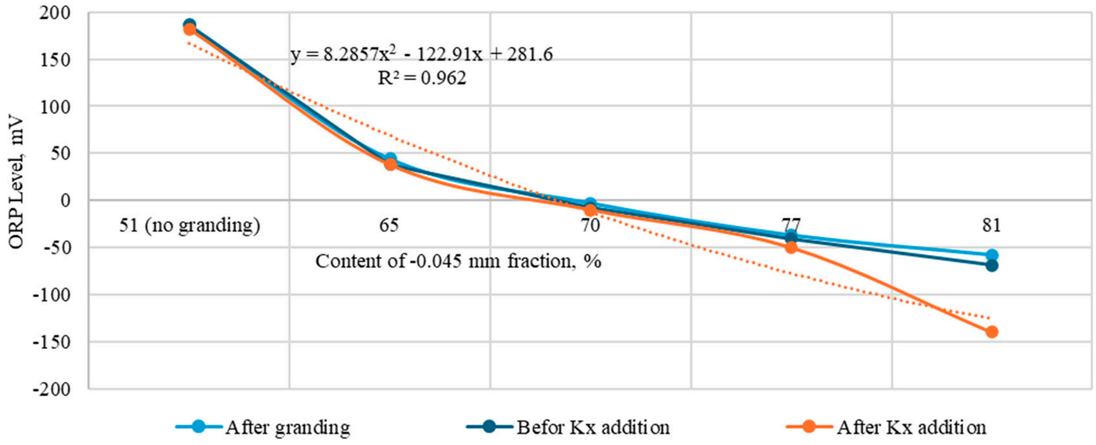


Figure 4. Effect of grinding fineness on redox potential (ORP) changes.

The results presented in Figure 4, indicate that in the absence of Na_2S, the ORP decreases from +44 mV at 65% fineness to -58 mV at 81% fineness. This trend suggests a reduction of the medium as grinding intensifies. which facilitates the removal of slimes and gangue from the copper mineral surfaces.

Laboratory tests were conducted using a conventional flotation circuit (rougher flotation followed by three cleaning stages) until the copper grade and recovery metrics stabilized across seven individual samples.

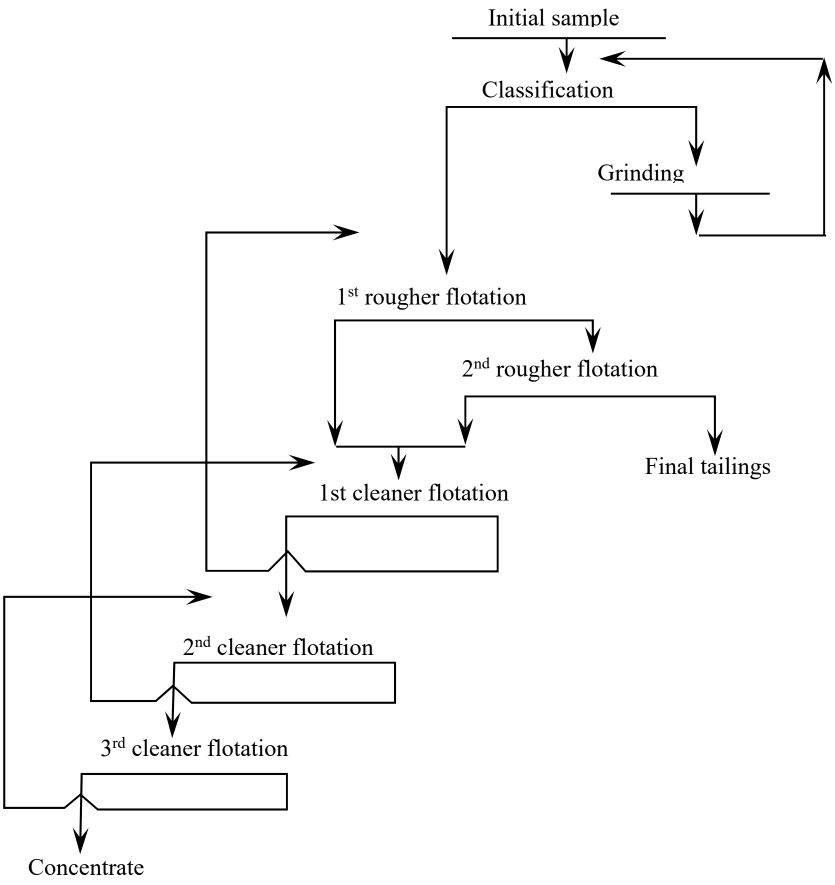


Figure 5. Locked-cycle laboratory experiment flowsheet.

The conditions of the laboratory tests and the corresponding results are presented in Table 9.

Table 9. Results of locked-cycle laboratory tests.

Product	Yield. %	Content. %	Recovery. %	Experimental Conditions
Concentrate	0.87	9.315	47.60	Content of -0.045 mm fraction: 80%; Flotation time: rougher 5+5 min. cleaner 7+3+2 min; Reagent dosage: Na_2S – 400 g/t. Kx – 50+20 g/t. MIBC – 20+5 g/t.
Tailings	99.13	0.09	52.40	
Initial sample	100.0	0.17	100.0	

During the locked-cycle test conducted in accordance with the presented flowsheet and reagent regime, a copper concentrate with a grade of 9.315% was obtained at a recovery of 47.60%.

4. Discussion

A comprehensive investigation of the aged copper ore tailings revealed a complex mineralogical and technological structure, resulting from prolonged storage in the tailings facility. According to the chemical phase analysis (Table 2) more than half of the total copper (53.84%) exists in oxidized forms. including a significant proportion of chrysocolla (17.08%) [16–18]. These characteristics, combined with the extremely low initial metal content (0.17%) account for the inefficiency of direct flotation which yields a recovery of no more than 13.74%.

The obtained results are consistent with contemporary studies demonstrating that the flotation efficiency of copper-bearing materials is determined not only by the reagent regime, but also by mineralogical constraints, surface conditions, and pulp chemistry. Koucham et al. demonstrated that during the processing of low-grade copper tailings, recovery is limited by fine dissemination, encapsulation of copper minerals, and the poor floatability of chrysocolla; notably regrinding was deliberately omitted in their work due to the risks of ultra-fine particle formation, increased reagent consumption, and reduced flotation efficiency. Studies by Greet and Chen et al. indicate that regrinding can significantly alter Eh/ORP, dissolved oxygen, oxygen demand. and the surface properties of sulfide minerals, thereby influencing subsequent flotation. In contrast to these studies the present work considers regrinding as a functional stage for the mechanical renewal of weathered copper-bearing tailing surfaces, while the reduction of the ORP to approximately −150 mV following Na_2S addition is identified as a key condition for activating oxidized copper surfaces prior to xanthate flotation [7,24–26].

The primary factor reducing floatability is the passivation of the sulfide surfaces. Microscopic examinations conducted using an OLYMPUS BX 53 system confirmed the presence of ultra-fine chalcopyrite grains (1–30 μm) often found in intimate associations with non-metallic minerals and magnetite (Figure 1). Prolonged storage within the tailings facility has led to the formation of oxide-hydroxide films on the grain surfaces which inhibit the adsorption of the collector.

To address these surface barriers, a regrinding strategy was implemented to trigger a "mechanical renewal" of the mineral surfaces. Our data show that as the grinding fineness increases to 77% (passing -0.045 mm) copper recovery rises to 16.26%, even in the absence of specific reagents. This clearly supports the hypothesis that mechanical action cleans the surfaces and exposes fresh sulfide minerals. The most telling indicator of this process is the electrochemical potential. We observed a significant shift in the ORP, which dropped from an initial +186 mV to -58 mV at 81% (-0.045 mm) without the addition of sodium sulfide (Table 7). This measurable decline in potential provides direct evidence that the mineral surfaces are being liberated and successfully cleaned of passivating layers [7]. The reduction in ORP should not be considered direct evidence of the complete removal of passivating films. as surface-sensitive techniques. such as XPS or SEM–EDS mapping were not employed in the present work. However, the aggregate data – encompassing the decrease in ORP the enhanced copper recovery following regrinding. the intensified effect of Na_2S and the copper phase composition – indirectly supports the hypothesis of mechanical surface renewal.

The established relationship between regrinding ORP and flotation response is consistent with the findings of Greet [24], which demonstrated that regrinding affects not only mineral liberation but also pulp chemistry. In particular, fine grinding can induce more reducing Eh values low dissolved oxygen content and high oxygen demand significantly impacting subsequent flotation. However, in contrast to those studies. where the primary focus was placed on run-of-mine ores or sulfide concentrates the object of the present study is long-term stored anthropogenic tailings characterized by a high degree of copper mineral oxidation.

The results are also consistent with the findings of Jacques et al. [25], which indicate that the oxidative weathering of copper sulfide ore deteriorates metallurgical performance, whereas properly selected grinding chemistry can partially offset the negative impacts of oxidation. The present work extends this approach to weathered copper-bearing tailings. demonstrating that mechanical surface renewal combined with sulfidization can partially restore the flotation activity of oxidized copper minerals.

The synergistic effect observed when combining regrinding with sulfidization is particularly noteworthy. Introducing Na_2S (400 g/t) alongside regrinding to 77% (-0.045 mm) triggered a sharp jump in copper recovery, reaching 36.37%. We attribute this surge to the high surface energy of the newly liberated mineral faces. These "fresh" surfaces exhibit a superior adsorption capacity for HS^- ions, which facilitates the formation of a stable, sulfide-like layer [16–18]. Furthermore, the stabilization of the ORP at -150 mV (Table 7) upon sulfidizer addition appears to create a favorable electrochemical range. This specific electrochemical environment is essential for the effective attachment (anchoring) of the xanthate collector to the mineral surface.

Thermodynamic modeling of the system further supports the experimental findings. It supports the thermodynamic feasibility that in the initial state without the addition of reagents, copper exists primarily in the form of passivating oxides, such as CuO and Cu_2O. These stable oxide layers effectively block collector access to the mineral core. The corresponding Pourbaix diagram (Potential–pH diagram) illustrated in Figure 6, clearly delineates the stability regions of these phases [20].

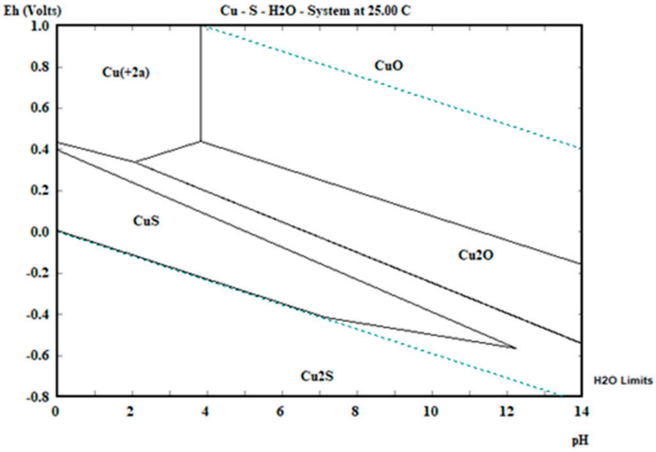


Figure 6. Eh–pH diagram for the Cu-S-H_2O system at 25 °C, calculated using HSC.

Chemistry software, the experimental data point (pH 8.6; Eh -150 mV) falls within the thermodynamic stability region of secondary copper sulfides (CuS, Cu_2S). This alignment supports the thermodynamic feasibility of sulfidization process following the mechanical renewal of the mineral surfaces.

With the mechanical renewal of the surface and the addition of Na_2S, the potential of the system shifts to approximately -150 mV. In the Pourbaix diagram, this region corresponds to the thermodynamic stability of chalcocite (Cu_2S). This transition provides a clear fundamental explanation for the significant jump in copper recovery – from 16.26% (without Na_2S) to 36.37% (with Na_2S) – observed under optimal grinding conditions.

However, an efficiency analysis using the Hancock-Luyken method points to a distinct «technological barrier». As the process shifts toward ultra-fine grinding (90-100% passing -0.045 mm) the separation efficiency reaches a plateau (33.5-34.2%) even as recovery climbs to 51.47%. This phenomenon is clarified by CYCLOSIZER size analysis (Table 5) which reveals a high copper concentration (39.95% distribution) within the micro-slimes of the -8.4 μm fraction. Excessive sliming during ultra-fine comminution leads to increased unproductive reagent consumption and diminished selectivity. Consequently, these findings define the rational grinding limit within the range of 77-81% passing -0.045 mm.

The proposed approach aligns with global trends in the processing [1,2,6,9] of low-grade anthropogenic materials (such as projects by Amerigo Resources and DRDGOLD) and positions Kazakhstan's legacy tailings as a promising resource within the circular economy model [5]. By transforming industrial waste into a viable source of copper this strategy addresses both economic recovery and environmental sustainability.

5. Conclusions

1. Regrinding of weathered copper-bearing tailings improves the flotation response due to additional mineral liberation and the probable mechanical renewal of the mineral surfaces.
2. At a particle size of 77% passing -0.045 mm, copper recovery reaches 16.26% without Na_2S and increases to 36.37% upon the addition of 400 g/t of Na_2S.
3. Ultra-fine grinding enhances recovery up to 51.47%, but is accompanied by the formation of micro-slimes (ultra-fine slimes) and a plateauing of the separation efficiency.
4. The rational operating range constitutes 77-81% passing the -0.045 mm fraction under controlled sulfidization conditions.
5. Weathered tailings can be considered a viable secondary source of copper.
6. The reprocessing of these tailings can mitigate the environmental footprint associated with tailing storage facilities (TSFs).

As a continuation of this study, future research will investigate ultrasonic treatment as a method for mineral surface activation and evaluate its impact on the selective flotation of anthropogenic raw materials.

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