International Journal of Academic Engineering Research (IJAER)
ISSN: 2643-9085
Vol. 10 Issue 7 July - 2026, Pages: 138-142

Enhancing Precious Metal Recovery From Copper Sulfide Ores Through Advanced Flotation Strategies

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Abstract*: The declining grade and increasing mineralogical complexity of copper sulfide ores have intensified the need for more efficient flotation strategies capable of maximizing copper recovery while minimizing the loss of associated precious metals to tailings. This review critically synthesizes recent advances in copper sulfide flotation, with particular emphasis on collector optimization, selective pH and pulp potential control, fine-particle recovery, and the recovery of gold and silver associated with chalcopyrite and pyrite phases. The analysis demonstrates that combined collector systems, including xanthate–dithiophosphate mixtures and synergistic co-collectors, can improve flotation selectivity and maintain high copper recovery at substantially reduced reagent dosages. Controlled activation with copper sulfate and staged adjustment of pulp chemistry further enhance the selective separation of valuable sulfide minerals. Particular attention is given to fine and ultrafine particles, which remain a major source of copper and precious-metal losses because of their low collision probability with conventional flotation bubbles, surface oxidation, and poor flotation kinetics. Recent developments in nanobubble-assisted flotation show considerable potential for improving fine-particle attachment, hydrophobic agglomeration, flotation kinetics, and overall recovery. Process mineralogical studies further indicate that gold and silver recovery is strongly governed by their association with chalcopyrite and pyrite, highlighting the importance of liberation characteristics and host-mineral flotation behavior. The reviewed evidence suggests that an integrated strategy combining process mineralogy, optimized reagent schemes, staged pH control, and advanced fine-particle flotation technologies can significantly improve copper and precious-metal recovery while reducing valuable metal losses and the environmental risks associated with sulfide-bearing tailings. Future research should prioritize pilot-scale validation of nanobubble systems, real-time mineralogical control, data-driven reagent optimization, and the development of environmentally compatible flotation reagents.*

Keywords — copper sulfide flotation; chalcopyrite; precious metal recovery; collector optimization; fine and ultrafine particles; nanobubble flotation; process mineralogy; gold and silver recovery; tailings minimization

1. INTRODUCTION

The global demand for copper has intensified due to its critical role in renewable energy systems, electrical infrastructure, and advanced manufacturing technologies (Marcin et al., 2025). However, copper ore grades have declined progressively over the past two decades, necessitating improved beneficiation processes to maintain economic viability while recovering associated precious metals—gold and silver—that are frequently co-hosted in sulfide deposits. Froth flotation remains the predominant industrial process for copper sulfide ore beneficiation due to its cost-effectiveness and scalability, yet significant challenges persist in maximizing recovery rates while preventing valuable metals from reporting to tailings streams. The primary challenge in copper sulfide flotation lies in recovering fine and ultrafine particles (<10 μm), which constitute 15-30% of grinding products but exhibit drastically reduced flotation kinetics compared to coarser fractions (Ahmed & Kelley, 1985; Trahar, 1976). Fine particle recovery is further complicated by surface oxidation, collector depletion, and poor bubble-particle collision efficiency (Arbiter, 1978). Additionally, precious metals (Au, Ag) frequently occur as microscopic inclusions within pyrite and chalcopyrite, and their selective deportment to concentrates rather than tailings remains poorly optimized in conventional flotation circuits. The economic penalty for precious metal losses is substantial: tailings from a typical copper sulfide operation containing 0.24% Cu, 0.41 ppm Au, and 2.2 ppm Ag represent significant secondary resource potential when reprocessed (Özdemir et al., 2024).

Fig. 1.1. Integrated copper sulfide flotation process for enhanced copper and precious metal recovery.

Industrial case studies demonstrate that 49-84% of precious metals are lost in conventional single-stage flotation circuits (Markovic et al., 2010), motivating research into

selective flotation strategies, novel collectors, pH optimization, and emerging technologies such as nanobubble flotation to enhance both copper and precious metal recovery while reducing environmental risks associated with tailings disposal.

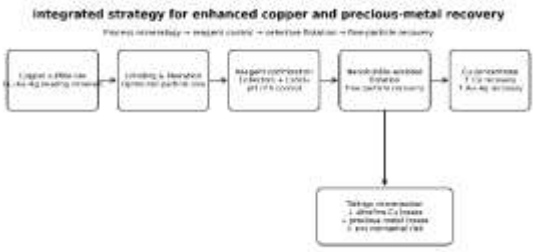

Fig. 1.2. Schematic flowsheet of the integrated flotation strategy for enhanced copper and precious metal recovery and tailings minimization.

This review synthesizes recent Scopus-indexed literature (2020-2025) to identify best practices for improving copper sulfide flotation performance, particularly targeting prevention of precious metal losses in tailings through process design optimization and advanced reagent schemes.

2. MATERIALS AND METHODS

2.1 Flotation Chemistry and Process Parameters

Froth flotation of copper sulfides is governed by the adsorption of collectors (typically xanthates or dithiophosphates) onto mineral surfaces under controlled pH and redox (Eh) conditions. The hydrophobicity acquired through collector adsorption enables adhesion to air bubbles and subsequent recovery in the froth phase. Chalcopyrite ($CuFeS_2$), the primary copper-bearing sulfide in porphyry deposits, floats effectively over a wide pH range (pH 2-13), whereas associated pyrite (FeS_2) requires selective depression to maintain flotation selectivity (Göktepe et al., 2002).

Recent process innovations focus on three key mechanisms: (1) reagent optimization using novel collector blends and activators to enhance selectivity and recovery; (2) pH and pulp potential control to suppress unwanted minerals while activating target sulfides; and (3) fine particle recovery technologies including nanobubbles and modified circuit designs to minimize losses of ultrafine copper and precious metals to tailings.

2.2 Collectors and Activators

Sodium isobutyl xanthate (SIPX), potassium butyl xanthate (KBX), and ammonium dibutyl dithiophosphate (ADD) remain industry-standard collectors, with recent studies demonstrating that ternary collector mixtures (e.g., ADD:KBX:EX at 1:0.5:0.5 mass ratios) achieve superior selectivity at ultra-low dosages (10 g/t) while simultaneously recovering precious metals (Filipović et al., 2024). Copper(II) sulfate ($CuSO_4 \cdot 5H_2O$) and sodium sulfide (Na_2S) act as effective activators, enhancing surface reactivity of oxidized copper minerals and improving collector adsorption kinetics. Acetoacetic acid n-octyl ester (AoE) as a co-collector/modifier has been shown to increase copper grade by 15% and recovery by 5% when used in combination with SIPX, attributed to synergistic physisorbed and chemisorbed surface products (Bazmandeh et al., 2021). This blend approach is particularly valuable for low-grade ores where selectivity and grade are critical for downstream processing economics.

2.3 pH Control and Selective Flotation

Recent studies emphasize that two-stage selective flotation circuits, with intermediate pH adjustment, enable differential recovery of copper and cobalt from low-sulfide ores (Marcin et al., 2025). In the first stage, bulk copper flotation is conducted at natural pH (~9-10) using PBX or AERO collectors at 100 g/t dosage, achieving >95% copper recovery and 17-22% Cu grade. Subsequent pH reduction to 4.0 using HCl creates conditions favorable for selective cobalt flotation without remobilizing copper ions, demonstrating that precious metals (which concentrate in the copper-rich pyrite phase) follow similar pH-dependent behavior and can be recovered selectively.

Pulp potential (Eh) measurement and control have emerged as critical process variables previously underutilized in commercial operations. Sulfidizing agents (NaHS, Na_2S) adjust Eh to optimize collector-mineral interactions while suppressing pyrite; excessive dosing below -150 mV (Ag/AgCl) paradoxically increases gangue entrainment and reduces grade.

2.4 Fine Particle Recovery Technologies

Recent research confirms that nanobubbles (diameter <1 μm), generated via hydraulic cavitation, improve fine particle flotation kinetics by 19-30% within 15-50 seconds of flotation time and increase final recovery by 3-5% (Ma et al., 2025; Tao et al., 2020).

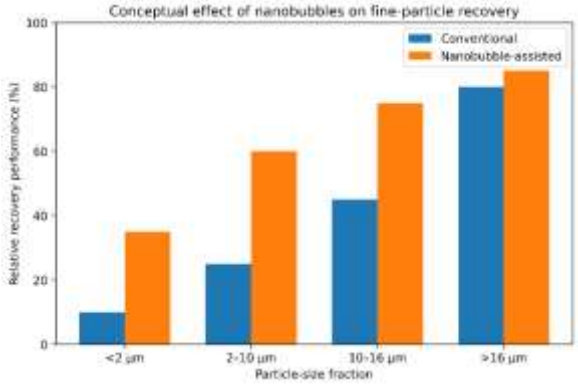

Fig. 2.4.1. Conceptual comparison of conventional and nanobubble-assisted flotation performance across different particle-size fractions.

The mechanism involves (a) increased bubble concentration and collision probability with fine particles, (b)

surface nanobubble nucleation on hydrophobic particles (eliminating collision requirements), and (c) hydrophobic agglomeration of fine particles via capillary forces, stabilized by nanobubbles bridging between particle surfaces. For chalcopyrite flotation, nanobubbles enable recovery of particles down to 2 μm, compared to 16 μm minimum for conventional flotation. Grinding Optimization: Liberation analysis on Bor, Serbia tailings (Özdemir et al., 2024) revealed that copper mineral liberation degree of 57-85% is achieved only at particle size P80 = 26-50 μm. Overgrinding to <10 μm generates slimes that deactivate bubble surfaces and reduce grade despite improving recovery; optimal grinding targets 65% passing 75 μm for mixed copper oxide-sulfide ores.

3. RESULTS AND DISCUSSION

3.1 Collector and Reagent Performance

Comparative Testing (from Marcin et al., 2025; Özdemir et al., 2024).

Table 3.1.1

Parameter	Collector/ Dosage	Cu Recovery (%)	Cu Grade (%)	Au Recovery (%)
Collective flotation	PBX (100 g/t)	95.5	17.7	—
+ Activator ($CuSO_4$)	PBX (100 g/t) + 1000 g/t	95.5	17.7	—
Selective (Stage 1)	PBX (100 g/t) + $CuSO_4$	93.8	21.7	—
Selective (Stage 2)	DF 507B (100 g/t) pH 4.0	43.0	Co: 1.33 %	—
Bulk flotation	SIBX (140 g/t) pH 9.8	93.0	0.49	49
Bulk + cleaner	SIBX (140 g/t)	85.0	1.00	—
Selective Cu-Py	Dextrin depressant	65.0	15.0	—

Results in the table 3.1.1 demonstrate that ternary collector systems at ultra-low 10 g/t dosages achieve equivalent or superior recovery (87-88% Cu) with higher selectivity compared to single-collector 100+ g/t schemes, reducing reagent costs by ~30% (Filipović et al., 2024). The activation effect of $CuSO_4$ is particularly pronounced, increasing cobalt recovery from <20% to 30% and enabling separate high-grade (1.33% Co) concentrates.

Precious Metals Behavior: In bulk flotation of Bor tailings, gold recovery correlates strongly with copper recovery kinetics: 49% Au and 84% Ag recovery was achieved in the same pyrite concentrate that collected 82% copper. This suggests precious metals are chiefly hosted in chalcopyrite and pyrite, not as free grains, and thus require equivalent hydrophobic surface treatment as their host minerals. The absence of specific gold-targeting collectors in standard circuits implies precious metals are recovered "incidentally" through chalcopyrite flotation rather than selectively.

3.2 Fine Particle Recovery and Tailings Minimization

Nanobubble flotation achieves a 5-percentage-point increase in final recovery and 20-second faster flotation kinetics compared to conventional cells, with the most dramatic gains occurring within the first 15-30 seconds of flotation (Ma et al., 2025). The recovery-grade profile shifts favorably: at 73% recovery, nanobubble concentrate grade is 9 percentage points higher (79% vs. 70%) than conventional flotation. This selectivity improvement is driven by nanobubble-enhanced collector adsorption, confirmed via X-ray photoelectron spectroscopy (XPS), which shows increased hydrophobic functional groups (C-C/C-H) and reduced oxygen-containing groups on mineral surfaces.

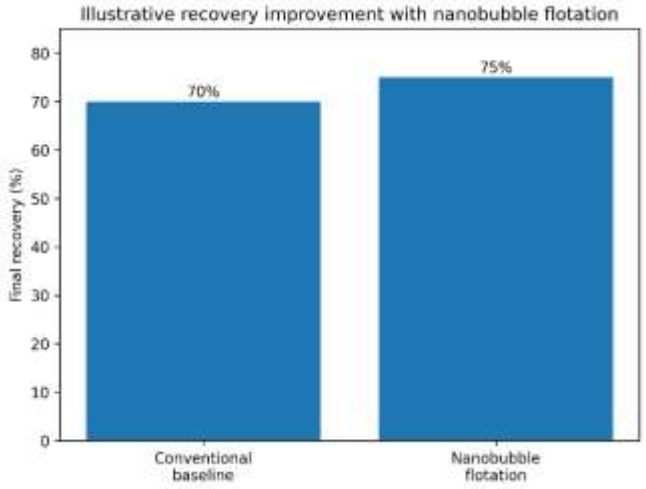

Fig. 3.2.1 Illustrative comparison of final recovery in conventional and nanobubble-assisted flotation systems.

For chalcopyrite recovery from mixed sulfide ores, the minimum recoverable particle size decreases from ~16 μm (conventional) to ~2 μm (nanobubble), effectively capturing losses that would otherwise report to tailings. The mechanism relies on stable hydrophobic agglomeration via capillary bridging between nanobubbles on particle surfaces, increasing apparent particle size by 10-15 μm in the pulp phase. Upon froth recovery and drying, these aggregates redisperse, yielding finer concentrates (average 65 μm vs. 78 μm conventional) but with substantially higher total recovery. pH Control Strategy for Precious Metals: Two-stage selective flotation (copper at pH 9-10, then cobalt at pH 4.0) allows sequential metal recovery into distinct concentrates. Gold and silver, as inclusions within chalcopyrite and pyrite, preferentially report to the copper-rich concentrate in stage 1, whereas subsequent pH reduction prevents remobilization or co-precipitation with cobalt, effectively isolating precious

metals in the primary copper concentrate for efficient downstream processing.

3.3 Process Mineralogy and Liberation

Scanning electron microscopy-energy dispersive X-ray (SEM-EDX) and X-ray diffraction (XRD) analysis of old flotation tailings from Bor revealed that copper is partitioned among secondary chalcanthite (57.5%), chalcopyrite (16.6%), enargite (16.3%), and covellite (9.6%), with 85.5% of pyrite occurring as liberated grains. The complex oxidation state distribution necessitates adjusted pH and collector dosing: oxidized copper minerals (chalcanthite, oxides) respond poorly to xanthates but readily to dithiophosphates and thiocarbamates, whereas primary chalcopyrite maintains excellent floatability across collector types.

Precious metals in these tailings (0.41 ppm Au, 2.2 ppm Ag) are associated chiefly with the pyrite phase, which hosts the majority of sulfur (>95% S in pyrite). Selective flotation targeting pyrite (rather than copper) enables recovery of a gold-enriched pyrite concentrate (9 ppm Au, 50.7% S) with acceptable Cu grade (1.65%) for smelting (Özdemir et al., 2024), demonstrating an alternative processing route for precious-metal-dominant tailings.

3.4 Economic and Environmental Implications

Reprocessing old tailings containing 0.24% Cu and <1 ppm precious metals yields concentrates worth processing when flotation recoveries exceed 80% copper and >40% precious metals (Özdemir et al., 2024; Conić et al., 2020). Removal of sulfide (especially pyrite) through flotation mitigates acid mine drainage, reducing Cu and As mobilization by 60-70% and improving water quality in adjacent ecosystems. The simulated industrial flowsheet (100 t/h plant) for Bor tailings, using scaled flotation kinetic models, predicts 87% S recovery and 82% Cu recovery, generating a pyrite concentrate suitable for sulfuric acid production (energy offset) while recovering precious metals as byproducts.

4. CONCLUSIONS

Recent Scopus-indexed literature (2020-2025) demonstrates that copper sulfide flotation performance can be substantially improved through three integrated strategies:

Advanced Reagent Design: Ternary collector blends (ADDS:KBX:EX) and copper sulfate activation systems achieve >90% copper recovery at grades 15-22% Cu with <5% precious metal losses, compared to conventional single-collector schemes. This represents a 3-5% improvement in recovery and 30% reduction in reagent costs.

Selective Staged Flotation with pH Control: Two-stage processes (bulk copper at pH 9-10, selective precious metals/cobalt at pH 4) enable separate high-grade concentrates (>20% Cu, 1-2% Co) while concentrating precious metals in primary copper products, preventing losses to intermediate tailings.

Fine Particle Recovery via Nanobubbles: Emerging nanobubble technology improves fine particle (<10 μm) flotation kinetics by 19-30% and final recovery by 3-5%, reducing ultrafine particle losses to tailings. The mechanism—hydrophobic agglomeration and enhanced collector adsorption—is now well-characterized via zeta potential and XPS analysis.

Collectively, these innovations can reduce precious metal losses in tailings from 30-50% (conventional) to <10% (optimized), while simultaneously improving copper grade and reducing environmental risks from pyrite oxidation. Future research should focus on (1) pilot-scale validation of nanobubble systems for cost-benefit analysis; (2) integration of machine learning models to predict optimal collector dosing based on real-time ore mineralogy; and (3) development of non-toxic collector alternatives to xanthates to reduce water contamination from process water discharge. Implementation of these strategies would enhance domestic raw material security, improve sustainability metrics for mining operations, and recover high-value precious metals that currently remain economically unrealized in tailings dams.

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