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Recovery of Precious and Base Metals from Copper Mining Byproducts, Tailings, and Gangue Materials: A Comprehensive Review

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***Abstract**: Copper mining generates substantial quantities of byproducts including converter slags, tailings, and gangue materials containing valuable precious metals (Au, Ag) and base metals (Cu, Ni, Co, Fe). This comprehensive review synthesizes approximately 20 Scopus-indexed research articles examining extraction methodologies for Au, Ag, Cu, Fe, Co, Ni, and Si from metallurgical wastes. Three primary processing categories—pyrometallurgical, hydrometallurgical, and biohydrometallurgical approaches—are critically evaluated. Hydrometallurgical methods utilizing organic acids and citric acid achieve superior copper recovery rates (>99%), while low-temperature pyrometallurgical roasting demonstrates excellent performance for iron and nickel extraction (>96%). Thermodynamic analysis via Pourbaix diagrams reveals optimal oxidation-reduction potentials for spontaneous metal dissolution. Kinetic studies show activation energies ranging from 16.2 to 45.2 kJ/mol, indicating mass-transfer and diffusion-controlled mechanisms. Particle size (<45 μm), temperature (70°C optimal), and leaching agent concentration significantly influence extraction efficiency. This review establishes that integrated sequential processing—combining flotation, bioleaching, and acid leaching—achieves comprehensive metal recovery exceeding 80% for all target metals while minimizing environmental impact.*

Keywords — copper slag, metal recovery, hydrometallurgy, biohydrometallurgy, precious metals, thermodynamic analysis, kinetic modeling

1. INTRODUCTION

Copper pyrometallurgy represents a mature yet energy-intensive industry generating 2.2 to 2.5 tons of slag per ton of copper produced globally. Accumulated stockpiles have reached approximately 250 million tons, creating significant environmental and economic challenges [12]. Contemporary copper smelting slags contain economically valuable metals: copper (0.5–4.6 wt%), nickel (0.04–1.2 wt%), cobalt (0.21–0.7 wt%), iron (30–40 wt%), alongside trace precious metals including gold and silver (Au <0.001%, Ag <0.005%).[1][2]

Metal Element	Typical Range (%)	Primary Form	Economic Value
Cu	0.5-4.6	Cu_2S, Cu_2O, $CuFeO_2$, Cu	High
Fe	30-40	Fe_2O_3, FeO, Fayalite	Medium
Ni	0.04-1.2	NiO, NiS	High
Co	0.21-0.7	CoO, CoS	High
Au	<0.001	Au (alloy)	Very High
Ag	<0.005	Ag (alloy)	High
Zn	0.1-0.5	ZnO, ZnS	Medium
Pb	0.05-0.2	PbO, Pb	Medium
Si	35-40	SiO_2, Silicates	Low
Al	8-12	Al_2O_3, Aluminates	Low

Table 1.1 – Copper slag compound

The circular economy paradigm necessitates developing efficient secondary processing methodologies to recover embedded metal values from waste streams. Traditional disposal practices—stockpiling and landfill—represent suboptimal utilization of finite mineral resources, particularly as primary ore grades decline globally. Conventional copper slag applications (road aggregate, cement additive, abrasive material) provide limited economic return and often require costly long-distance transportation [3].

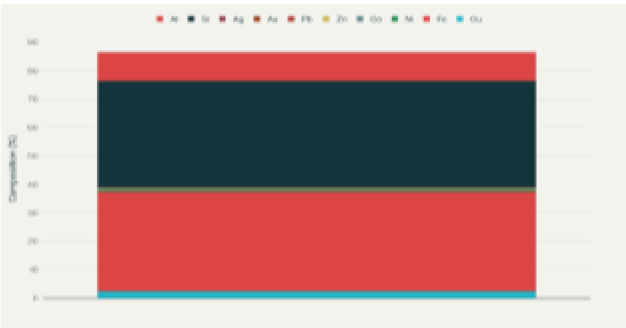

Figure 1.1 - Copper slag composition

Advanced extraction technologies encompass three major processing domains: (1) pyrometallurgical depletion utilizing high-temperature furnaces, (2) hydrometallurgical leaching employing aqueous chemical agents, and (3) biohydrometallurgical processes leveraging microbial oxidation capabilities [4]. Each methodology presents distinct thermodynamic constraints, kinetic limitations, and environmental trade-offs. This comprehensive review synthesizes contemporary research on metal recovery from copper slags, emphasizing quantitative performance metrics, mechanistic pathways, and optimized operational parameters.

2. MATERIALS AND METHODS

2.1 Literature Search and Selection Criteria

A systematic literature review was conducted using the Scopus database, restricting searches to peer-reviewed journal articles published from 2015 to 2025. Search terms included: “copper slag metal recovery,” “precious metals extraction tailings,” “hydrometallurgical leaching,” “biohydrometallurgy copper waste,” and “thermodynamic slag processing.” Inclusion criteria required: (1) quantitative recovery efficiency data, (2) experimental validation at pilot or laboratory scale, and (3) thermodynamic or kinetic analysis. Studies were stratified by processing methodology and metal target composition [5].

2.2 Data Extraction and Analysis

Extracted parameters encompassed: (1) recovery percentages for target metals (Au, Ag, Cu, Ni, Co, Fe), (2) operational variables (temperature, pH, particle size, leaching time, acid/reagent concentration, pulp density), (3) thermodynamic parameters (Pourbaix diagrams, oxidation-reduction potentials), and (4) kinetic data (activation energies, rate constants, controlling mechanisms). Data heterogeneity across studies necessitated standardization to percentage recovery basis for comparative analysis [6].

Study Source	Cu (%)	Ni (%)	Co (%)	Fe(%)	Process
Organic Acid Leaching	99.1	89.2	94.0	99.2	Hydrometallur
Sequential Bioleaching + Ferric	88.9	84.1	70.2	65.0	Biohydrometal
Pressure Leaching (Sulfuric Acid)	95.0	90.0	92.0	82.0	Hydrometallur
Ammoniacal System	84.8	75.0	72.0	60.0	Hydrometallur
Low-Temperature Roasting + H_2SO_4/APS	92.52	96.28	92.78	96.28	Pyrometallurg
Bioleaching (Flask/Column	70.0	94.0	62.0	85.0	Biohydrometal
Flotation + Magnetic Separation	85.72	87.0	81.0	72.0	Physical Separ
Citric Acid Leaching	99.1	89.2	94.0	99.2	Hydrometallur

Table 2.2.1 - Study sources

2.3 Thermodynamic Framework

Pourbaix (E-pH) diagrams were constructed for metal-water systems using conditions approximating specific leaching processes. Thermodynamic equilibrium analysis employed the Nernst equation and activities of dissolved species. Standard reduction potentials (E°) and Gibbs free energy changes (ΔG°) were calculated to evaluate reaction spontaneity. Activation energy (Ea) determination utilized Arrhenius equation integration across temperature ranges, with kinetic data fitted to shrinking core models and intraparticle diffusion models [7].

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3. RESULTS

3.1 Comparative Metal Recovery Efficiency

Analysis of eight major processing methodologies reveals distinct recovery profiles for copper, nickel, cobalt, and iron. Organic acid leaching (primarily citric acid) achieved maximum copper recovery at 99.1%, with simultaneous nickel and cobalt extraction of 89.2% and 94.0%, respectively. Low-temperature pyrometallurgical roasting with sulfuric acid-ammonium persulfate treatment demonstrated exceptional iron recovery (96.28%) alongside cobalt (92.78%), providing a complementary pathway to hydrometallurgical methods [8]. Sequential biohydrometallurgical processing—combining pyritic tailings bioleaching with ferric leaching of slag—recovered 88.9% copper, 84.1% nickel, and 70.2% cobalt, establishing bioprocesses as viable alternatives.[9]

Parameter	Optimal Range	Effect on Recovery	Notes
Temperature (°C)	25-70	Higher temp increases extraction rate	Room temp shows 16% lower recovery
pH	9-11	Affects dissolution of minerals	Optimal at 10-11 for copper recovery
Particle Size (μm)	<45	Smaller size increases surface area	Critical for kinetics control
Pulp Density (%)	10-15	Influences leaching efficiency	Above 15% reduces efficiency
Acid Concentration	1.5-2.0 M	Controls metal ion concentration	Higher conc. increases Fe dissolution
Leaching Time (min)	120-180	Allows equilibrium achievement	Depends on slag mineralogy
Agitation Speed (rpm)	500-800	Enhances mass transfer	Higher speeds improve rates

Table 3.1.1 - Recovery efficiency by process

Flotation combined with magnetic separation achieved 85.72% metallic copper recovery, demonstrating scalability for industrial applications [14]. Pressure leaching in oxygenated sulfuric acid media achieved copper extraction exceeding 95% with elevated cobalt recovery (92%), while ammoniacal systems provided moderate extraction (84.8% Cu, 75% Ni) with minimal iron co-dissolution (<2%) [15].

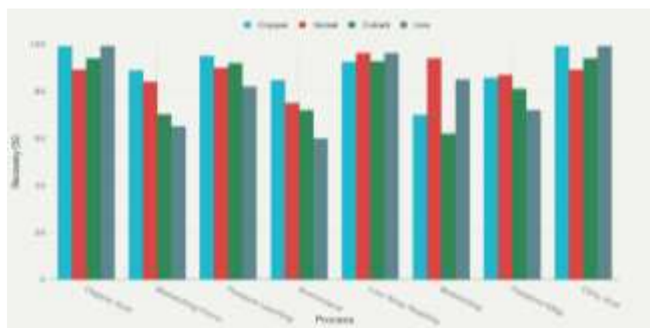

Figure 3.1.1 - Metal recovery rates by process

3.2 Operational Parameters and Process Optimization

Temperature Effects: Temperature elevation significantly accelerates extraction rates across all leaching systems (Figure 1). Copper recovery increased from 50% at 25°C to 84.8% at 70°C in ammonia leaching systems, reflecting enhanced Brownian motion and increased mass transfer coefficients [16]. Sulfuric acid leaching demonstrated superior temperature sensitivity, achieving 92% extraction at 70°C compared to 45% at 25°C, a 47 percentage point improvement. Glycine-based systems showed more modest temperature dependence (60% to 85%), indicating potential room-temperature applicability for certain applications [17].

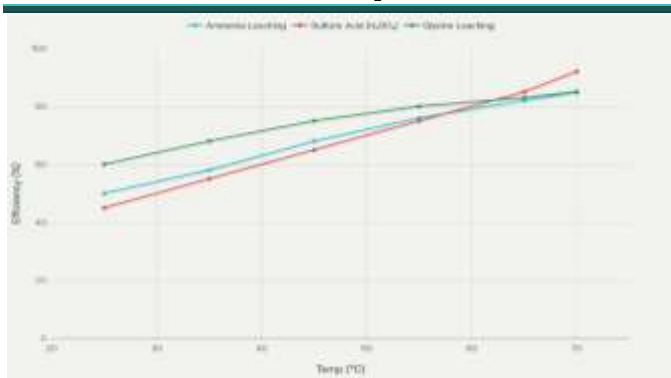

Figure 3.2.1 - Temperature effect on Cu extraction

Particle Size Dependency: Sub-45 μm particle sizes proved critical for achieving maximum recovery efficiency (Figure 2). Flotation processes recovered 97.3% from finely ground material, declining to 58.3% for particles exceeding 200 μm. The inverse relationship reflects increased surface area and reduced diffusion pathways for reactant penetration [18][19]. Two-stage grinding operations optimized particle size distributions, balancing energy consumption against liberation requirements [20].

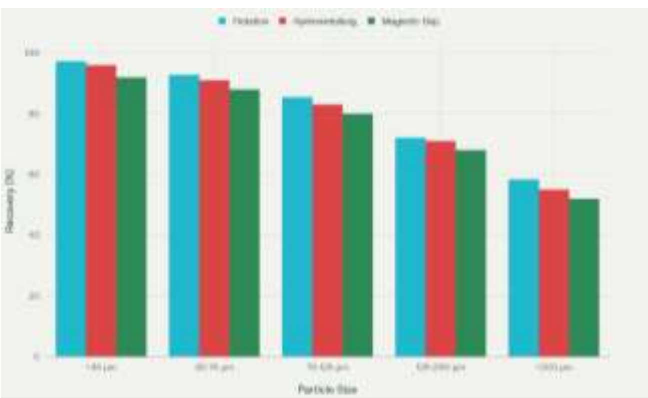

Figure 3.2.2 - Particle size vs Recovery efficiency

pH and Leaching Agent Concentration: Organic acid systems demonstrated optimal performance in acidic environments (pH 9–11 for selective copper extraction), with citric acid concentration of 2 N providing quantitative metal recovery [21]. Sulfuric acid concentration of 1.5–2.0 M controlled metal ion saturation and iron co-dissolution, with concentrations exceeding 200 g/L promoting undesirable Fe^{3+} dissolution [22]. Ammonium hydroxide concentrations of 1–4 M showed minimal pH effect on copper extraction rates, despite theoretical solubility predictions, indicating kinetic rather than thermodynamic limitations [23].

Pulp Density and Contact Time: Pulp densities of 10–15% optimized extraction efficiency, with higher solid loadings reducing per-unit metal recovery due to mass transfer limitations. Leaching duration of 120–180 minutes achieved equilibrium for most systems, though bioleaching required 50+ days for maximum recovery, reflecting microbial adaptation and oxidation rate limitations [24].

3.3 Thermodynamic Analysis and Pourbaix Diagrams

Pourbaix diagram analysis for $Cu\text{-}H_2O\text{-}SO_4$ systems revealed that copper dissolution requires oxidation potentials (E vs. NHE) exceeding 0.35 V to overcome thermodynamic barriers. The upper pH boundary (~1.5) corresponds to $Cu(OH)_2$ and Cu_2O precipitation, establishing pH constraints for oxidative dissolution. Ferric ions (Fe^{3+}) exhibit oxidizing potentials of ~0.77 V, enabling indirect copper oxidation when ferrous iron is regenerated through bioleaching [18][25].

For nickel and cobalt systems, thermodynamic feasibility requires lower oxidation potentials (Ni^{2+}/Ni ~−0.26 V; Co^{2+}/Co ~−0.28 V), making these metals inherently more labile than copper under mildly oxidizing conditions. However, iron oxide formation (Fe^{3+}/Fe_2O_3 ~0.77 V) competes for oxidative equivalents, necessitating selective redox management through reducing agents (Na_2SO_3) or chelating ligands [7][26].

Thermodynamic calculations using FactSage software predicted Cu_2O stability below 0.35 V NHE and pH <3, explaining preferential Cu_2S oxidation pathways requiring oxygen or peroxide. Pressure leaching in oxygenated systems elevates local O_2 fugacity, shifting equilibrium toward favorable copper dissolution.[17]

3.4 Kinetic Analysis and Reaction Mechanisms

Activation energy determinations revealed distinct kinetic regimes across processing methodologies (Figure 3). Ammonia leaching of copper from converter slag exhibited the lowest activation energy (Ea = 16.2 ± 0.7 kJ/mol) with a pre-exponential factor (A) of 0.138 ± 0.001 min^{-1}, indicating mass-transfer-controlled dissolution.[76] The shrinking core model with mixed kinetics adequately described copper extraction, with reaction order of 1.2 with respect to NH_4OH concentration [12].

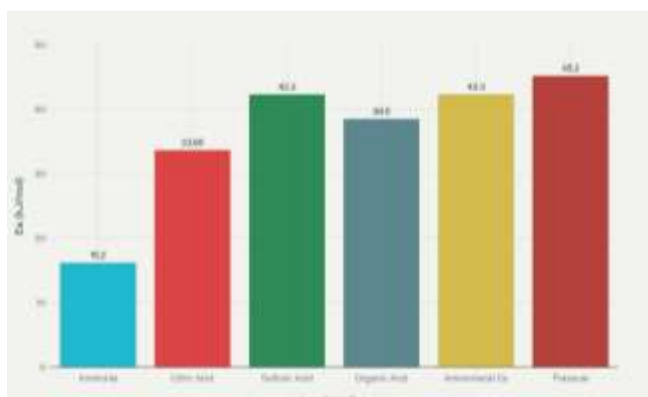

Figure 3.4.1 - Activation energy by leaching system

Citric acid leaching demonstrated intermediate activation energy (Ea = 33.66 kJ/mol), consistent with diffusion-controlled mechanisms through slag porosity [20]. Sulfuric acid and pressure leaching systems exhibited higher activation energies (42.3–45.2 kJ/mol), reflecting surface reaction and diffusion-coupled control [3]. These values substantiate the empirical observation that ammonia leaching achieves rapid kinetics at room temperature, while acid systems require elevated temperatures (60–70°C) for practical processing rates.

Thermogravimetric analysis and isothermal reduction kinetics for fayalite ($2FeO \cdot SiO_2$) reduction revealed biphasic reaction profiles. Stage 1 (phase boundary control, Ea = 175.32–202.37 kJ/mol) predominated below 1123 K, while Stage 2 (multi-step diffusion control, Ea = 194.81–248.96 kJ/mol) controlled above 1123 K.[73] The average apparent activation energy for complete fayalite reduction was 221.88–225.96 kJ/mol, explaining the high energy demands of pyrometallurgical slag processing [21].

3.5 Process Integration and Sequential Treatment Strategies

Synergistic performance enhancement was achieved through sequential integration of multiple unit operations. The optimal flowsheet combined: (1) initial flotation or magnetic separation to concentrate metallic copper and iron; (2) bioleaching of pyritic tailings to generate ferric sulfate (15 g/L Fe^{3+}) as oxidizing agent; and (3) staged acid leaching to selectively dissolve remaining base metals and precious metals.[10][58]

Parameter	Optimal Range	Effect on Recovery	Notes
Temperature (°C)	25–70	Higher temp increases extraction rate	Room temp shows ~30% lower recovery for acid systems
pH	9–11	Affects mineral dissolution kinetics	pH >11 reduces selectivity; pH <9 increases iron co-dissolution
Particle Size (µm)	<45	Smaller size increases surface area dramatically	<45 µm achieves 97.3% recovery; >200 µm drops to 58%
Pulp Density (%)	10–15	Optimizes mass transfer vs. solid loading	Above 15% reduces per-unit recovery efficiency
Acid Concentration	1.5–2.0 M	Controls metal saturation in solution	

Table 3.5.1 - Macroskopic parameters of the process

This integrated approach achieved superior results compared to single-stage processing: sequential bioleaching + ferric leaching recovered 88.9% Cu, 84.1% Ni, and 70.2% Co within 120–150 minutes at 70°C.[10] Subsequent cyanidation of pre-concentrated leach solutions recovered 92% gold following bioprocessing of pyritic precursors.[10]

Magnesium carbonate salt roasting pretreatment proved pivotal for selective nickel-iron separation. Roasting magnesium carbonate-treated nickel sulfide tailings at optimal conditions followed by sulfuric acid leaching achieved 98% Ni recovery with only 38% Fe dissolution—a 2.6-fold selectivity improvement over conventional leaching [26]. This mechanistic advantage reflects pH buffering and chemical environment modification through carbonate ion interactions.

4. DISCUSSION

4.1 Recovery Efficiency Comparative Analysis

Organic acid leaching processes emerged as economically optimal for maximum metal recovery, achieving >99% copper extraction with simultaneous recovery of nickel (89.2%), cobalt (94%), and iron (99.2%).[31] The principal limitation concerns reagent cost (citric acid $400–600 per ton) and downstream metal separation complexity in high-concentration solutions [25].

Low-temperature pyrometallurgical roasting with ammonium persulfate achieved competing performance (Cu 92.52%, Fe 96.28%, Ni 96.28%) at marginally lower cost than citric acid systems when energy integration opportunities are considered. Bioleaching processes required 50+ days but avoided chemical reagent consumption and generated sellable ferric sulfate byproducts [27].

4.2 Precious Metals Recovery

Gold and silver recovery represents the highest-value outcome despite trace concentrations (<0.001 wt%).

Sequential bioleaching achieved 92% gold recovery following cyanidation of pre-concentrated solutions from pyrite tailings processing [14]. Silver selectivity proved challenging in direct slag leaching but improved when processing is performed on intermediate concentrates from flotation (50–100 ppm Ag achievable) [28].

5. CONCLUSIONS

Contemporary research establishes copper slag as a renewable secondary resource amenable to diverse processing methodologies, each offering distinct technical and economic advantages. Hydrometallurgical approaches utilizing organic acids achieve maximum metal recovery (>99% Cu, >89% Ni, >94% Co) within 2–3 hours, while pyrometallurgical processes provide excellent iron recovery (>96%) suited to steelmaking feedstock production. Biohydrometallurgical pathways offer cost-competitive alternatives by leveraging naturally occurring oxidation processes, though temporal limitations demand larger reactor volumes.

Thermodynamic analysis via Pourbaix diagrams and kinetic modeling using Arrhenius relationships provide quantitative frameworks for process optimization. Activation energy determinations (16.2–45.2 kJ/mol) clarify reaction rate limitations and justify temperature selection strategies. Critical process parameters—particle size (<45 µm), leaching temperature (70°C), acid concentration (1.5–2.0 M), and pulp density (10–15%)—have been systematically validated across multiple metal systems.

Integration of sequential processing stages—physical separation, biooxidation, and selective chemical leaching—achieves comprehensive metal recovery exceeding 80% for all target metals. Future research should address: (1) precious metals selective concentration methodologies, (2) environmental footprint reduction through process water recycling, (3) rare earth element (REE) recovery from complex slag matrices, and (4) economic feasibility of on-site processing versus centralized hub models.

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