

Article

Efficient Copper Extraction from a Refractory Slag-Flotation Copper Sulfide Concentrate via Atmospheric Oxygen-Enriched Leaching

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Abstract

The accumulation of low-grade, refractory copper sulfide concentrates from secondary resources, such as smelting slag-flotation products, represents a growing challenge in the copper industry. This study develops and validates an atmospheric oxygen-enriched leaching process that requires neither grinding nor high pressure, targeting a typical slag-flotation copper sulfide concentrate. Systematic mineralogical analysis shows that copper is 95% in secondary sulfides, with quartz, chlorite, and muscovite as major gangue. Batch leaching optimization identifies the following conditions: H₂SO₄ 250 g/L, temperature 90 °C, leaching time 8–12 h, pulp density 30–33% solids, and oxygen-enriched air (80–90% O₂) at a flow rate ensuring sufficient oxygen mass transfer. Under these conditions, copper extraction reaches 97–99% without grinding. Continuous pilot-scale trials (over 500 kg dry feed) compare a five-stage mechanically agitated tank train and a four-stage tower reactor. The tank train achieves a stable copper extraction of 97.1% with a residue grade of 0.53% Cu at 8 h residence time and acid consumption of 857 kg/t concentrate, significantly outperforming the tower reactor. Reducing oxygen purity from 100% to 90% has no measurable effect on extraction, while 80% O₂ gives only a 2% loss. The process eliminates grinding, operates at ambient pressure, and uses widely available reactor technology, offering a potentially low-capital and technically robust solution for recovering copper from such refractory secondary sulfide concentrates.

Keywords: copper sulfide concentrate; slag flotation; atmospheric leaching; pilot scale; hydrometallurgy

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1. Introduction

Copper is an irreplaceable industrial metal, with global demand steadily driven by infrastructure development, electrification, and the transition to low-carbon energy systems. More than 80% of the world's copper is produced from sulfide ores, among which chalcopyrite (CuFeS₂) is the most abundant, but secondary copper sulfides such as chalcocite (Cu₂S), covellite (CuS), and digenite (Cu₉S₅) also contribute significantly to copper production, particularly in supergene enrichment zones [1,2]. As high-grade, easily accessible sulfide deposits are being depleted, the mining and metallurgical industries are increasingly forced to deal with low-grade ores, complex polymetallic associations, and large volumes of secondary materials such as flotation tailings and smelting slag-flotation

concentrates [3–6]. These materials often contain copper at economically attractive levels (typically 5–15% Cu) but are considered refractory because their copper minerals are finely intergrown with gangue, partially oxidized, or present as secondary sulfides that behave differently from primary chalcopyrite under conventional leaching conditions [7,8].

The hydrometallurgical processing of copper sulfides has been extensively studied as an alternative to smelting, especially for small-scale or remote deposits, for ores with high impurity contents, and for secondary materials. Atmospheric acid leaching is the simplest and most cost-effective route, but it suffers from slow kinetics and incomplete copper extraction for most sulfide minerals [9,10]. The poor leachability arises from the formation of a passivating layer, which is often elemental sulfur or a metal-deficient polysulfide film on the particle surface; this blocks further contact between the oxidant and the unreacted core [11–13]. For chalcopyrite, the passivation problem is particularly severe, and even under highly oxidizing conditions, copper extraction rarely exceeds 30–40% in simple sulfate media without external energy input. Secondary copper sulfides (digenite, covellite, and chalcocite) are generally more reactive than chalcopyrite because they are less prone to strong passivation, yet their atmospheric leaching still proceeds slowly unless the redox potential is sufficiently raised and oxygen transfer is efficient [14,15].

To overcome these kinetic barriers, numerous enhancement strategies have been developed. Pressure oxidative leaching (POX) operates at elevated temperatures (150–220 °C) and oxygen overpressures (0.5–1.5 MPa), achieving high copper extraction (>95%) from even refractory chalcopyrite concentrates within a few hours [16–19]. However, POX requires expensive autoclaves made of titanium-lined or other corrosion-resistant alloys, sophisticated pressure control systems, and skilled maintenance. These factors make POX economically prohibitive for many operations, particularly in regions where technical support and spare parts are not readily available. Bioleaching offers a low-temperature, atmospheric alternative by using acidophilic iron- and sulfur-oxidizing bacteria to catalyze sulfide oxidation [20–22]. Although bioleaching has been successfully applied to secondary copper sulfides and some chalcopyrite ores, its kinetics are slow (residence times of days to weeks), and the process can be sensitive to temperature fluctuations, high chloride levels, and the presence of certain organic compounds. Chemical additives such as ferric ions, chloride, or silver have been shown to accelerate dissolution [23,24]. Ferric sulfate provides an oxidant for sulfide minerals, while chloride promotes the breakdown of passivating sulfur layers by forming soluble polysulfide complexes. Nevertheless, adding concentrated chloride solutions is often avoided because it can severely corrode equipment and contaminate the downstream solvent extraction and electrowinning circuits.

Beyond the challenges of primary ores, a growing class of secondary copper resources has emerged from the flotation of smelting slags. In many copper smelters and integrated mining–metallurgical complexes, the slag from the converting or smelting step is subjected to grinding and flotation to recover entrained copper. The resulting “slag-flotation copper concentrate” typically contains 8–15% Cu, the remainder being gangue minerals such as fayalite, quartz, and glassy silicates. The copper occurs mainly as fine-grained secondary sulfides (digenite, covellite, and bornite) that precipitated during slow cooling of the slag, often intergrown with or encapsulated by silicate phases. Although these materials are chemically more reactive than primary chalcopyrite, they still require an efficient oxidizing environment to achieve high recovery. Conventional atmospheric leaching with air and moderate sulfuric acid gives only mediocre copper extraction (typically 40–60%), limited by poor oxygen mass transfer and incomplete exposure of the sulfide phase. Grinding to a very fine particle size improves liberation but adds substantial

cost and may cause practical problems such as increased slurry viscosity and filter cake moisture.

Recent research from Europe has demonstrated the feasibility of atmospheric oxidative leaching for copper sulfide flotation concentrates. Chmielewski [25] reported that a copper sulfide concentrate from the Lubin Concentrator (Poland) could achieve 95% copper extraction within 5–7 h at 90 °C using oxygenated sulfuric acid solutions containing ferric ions. Borowski et al. [26] further extended this approach to recover cobalt and nickel from the same concentrate. In Finland, Outotec OYJ has developed a patented atmospheric leaching process in which ferric iron is continuously regenerated by oxygen in a closed reactor, enabling efficient copper dissolution from sulfide ores without high-pressure equipment [27]. In the United States, several patents have been granted for atmospheric oxidative leaching of copper sulfide concentrates, particularly for treating arsenical copper sulfides [28–30]. These processes typically employ acidic iron sulfate solutions under an oxygen atmosphere to dissolve copper while managing arsenic precipitation. Meanwhile, in Tokyo, Japan, Nippon Mining & Metals Co., Ltd. has developed a patented atmospheric leaching process for recovering copper from nickel–copper matte containing precious metals, which utilizes existing copper smelting equipment without requiring special high-pressure apparatus [31]. This approach demonstrates the industrial viability of atmospheric oxidative leaching for copper-bearing sulfide materials without the need for costly autoclave systems. In addition, researchers at Kyushu University have explored the use of silver ions to enhance the atmospheric leaching of arsenic-bearing copper sulfides in acidic solutions, showing that catalytic additives can effectively promote the breakdown of passivating sulfur layers on mineral surfaces [32]. Despite these advances, most studies have focused on primary sulfide concentrates, and systematic investigations on atmospheric oxygen-enriched leaching of secondary sulfide concentrates derived from smelting slag flotation remain limited. Comprehensive reviews on the hydrometallurgical treatment of copper sulfide concentrates have highlighted the persistent challenge of elemental sulfur passivation, which hinders complete dissolution under atmospheric conditions [33,34]. Various strategies have been proposed to mitigate this issue, including the use of chloride media, catalytic amounts of silver ions, and elevated oxygen partial pressures. However, the industrial application of atmospheric leaching for secondary copper sulfide materials—particularly those with complex gangue associations and fine mineral intergrowths—has not been thoroughly evaluated. The present study addresses this gap by systematically investigating the atmospheric oxygen-enriched leaching of a refractory slag-flotation copper sulfide concentrate, with emphasis on process optimization and continuous pilot-scale validation.

Therefore, there is a clear need for a simple, atmospheric, low-CAPEX, and robust leaching process that can be applied to such refractory slag-flotation copper sulfide concentrates without requiring fine grinding or high-pressure equipment. The process should exploit the relatively high reactivity of secondary copper sulfides while ensuring efficient oxygen delivery and good solids suspension. Enriched oxygen (rather than pure oxygen or air) represents a promising middle ground: it can significantly increase the oxygen partial pressure and driving force for the oxidation reactions without the full cost of cryogenic pure oxygen, and it can be generated on-site by vacuum pressure swing adsorption technology. Yet, very few studies have systematically evaluated the use of oxygen-enriched air (80–95% O₂) for atmospheric leaching of such specific materials [35,36], and even fewer have carried out continuous pilot-scale campaigns to validate the process and compare reactor configurations.

In this work, we present a comprehensive study of atmospheric oxygen-enriched leaching applied to a typical refractory copper sulfide concentrate obtained from flotation of smelting slag. The specific objectives are as follows: 1. characterize the mineralogy and

copper deportment of the concentrate, identifying the phases that control leachability; 2. determine, through batch experiments, the optimum values of key parameters: initial sulfuric acid concentration, temperature, leaching time, pulp density, gas flow rate, and oxygen concentration; 3. test whether fine grinding is necessary; 4. scale up the process in continuous pilot-scale trials, comparing two reactor designs: a conventional five-stage stirred-tank cascade and a four-stage tower reactor, under realistic slurry conditions; 5. evaluate the possibility of synergistic leaching with a secondary roasting residue and quantify the trade-off between oxygen purity and copper recovery.

Our results demonstrate that under optimized conditions (90 °C, 250 g/L H₂SO₄, 80–90% O₂, 8 h residence time, and no grinding), copper extraction exceeds 97% in a simple stirred-tank cascade. The tower reactor is less efficient. The use of 90% O₂ gives essentially the same extraction as pure oxygen, whereas 80% O₂ yields only a small decrease. The proposed process is technically straightforward, uses existing equipment types, and can be implemented with low capital expenditure. This study provides a complete engineering basis from mineralogy to continuous pilot-scale demonstration for recovering copper from a currently underutilized intermediate product, turning an environmental and economic burden into a valuable copper resource.

Before presenting the experimental approach, it is useful to clarify why this material is considered “refractory” in the context of conventional processing. In this study, the slag-flotation copper sulfide concentrate is termed “refractory” for two main reasons. First, from a mineralogical perspective, although more than 95% of the copper occurs as secondary copper sulfides (digenite, covellite, and bornite), these copper minerals are finely intergrown with gangue phases such as quartz, chlorite, and muscovite, with grain sizes typically in the range of 10–30 µm, and a substantial portion is locked within the gangue matrix. This texture makes it difficult to achieve effective liberation by conventional re-grinding and re-flotation, thus necessitating a chemical leaching route for copper recovery. Second, from a leaching behavior perspective, conventional atmospheric acid leaching using air yields a copper extraction of less than 40%. The underlying reason is the low oxygen partial pressure in air, which limits both the dissolved oxygen concentration and the oxygen mass-transfer rate in the aqueous solution, thereby failing to provide sufficient oxidizing power for the dissolution of sulfide minerals. Consequently, the kinetics are sluggish, and copper extraction remains incomplete. Therefore, an enhanced leaching method—such as the oxygen-enriched atmospheric process proposed in this work—is essential for the economic recovery of copper from this type of secondary sulfide concentrate.

2. Materials and Methods

2.1. Materials

The refractory copper sulfide concentrate used in this study was obtained from the flotation circuit of a copper smelter’s slag processing unit. The material was collected from a large stockpile, homogenized by repeated cone-and-quartering, and air-dried. The as-received moisture content was 2.2 wt%. The concentrate had a true density of 2.42 g/cm³. Particle size analysis (laser diffraction, Hydro 2000MU, Malvern Instruments Ltd., Worcestershire, UK) gave D₅₀ = 60.2 µm and D₉₀ = 158.5 µm. For comparison, a portion was ground in a laboratory ball mill to D₅₀ = 28.9 µm. Unless otherwise stated, the as-received material was used without further grinding.

A roasting residue (a by-product from processing a high-grade copper sulfide concentrate) was also used in synergistic leaching experiments. Its composition is given in Table S1. All chemicals (98% H₂SO₄, NaOH) were of analytical or industrial grade and were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Oxygen-

enriched air was prepared by blending industrial-grade oxygen (99.5%) with compressed air using mass flow controllers.

2.2. Analytical Methods

Chemical analysis of solids and solutions was performed by inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima 8300, PerkinElmer, Inc., Waltham, MA, USA) after microwave-assisted acid digestion. Free acid in leach liquors was determined by titration with standard NaOH using phenolphthalein. Oxidation-reduction potential (ORP) was measured with a Pt electrode against an Ag/AgCl reference, and pH was measured with a glass electrode. Mineralogical characterization included X-ray diffraction (XRD, PANalytical X'Pert Pro with Cu K α radiation, PANalytical B.V., Almelo, The Netherlands), scanning electron microscopy (SEM, Zeiss EVO 50, Carl Zeiss AG, Oberkochen, Germany) with energy-dispersive X-ray spectroscopy (EDS), and optical microscopy. Copper phase analysis was carried out by selective sequential leaching. Quantitative mineral liberation analysis (MLA) was performed on a FEI Quanta 600 (FEI Company, Hillsboro, OR, USA).

2.3. Batch Leaching Experiments

Batch leaching tests (Nanjing Ruinike Technology Development Co., Ltd., Nanjing, China) were conducted in a 1 L three-neck round-bottom flask equipped with a mechanical stirrer (600 rpm), a water-cooled condenser, a thermocouple, and a gas sparger (porous glass frit or stainless-steel tube). In a typical run, a known amount of concentrate (dry basis) was mixed with deionized water and concentrated H₂SO₄ to obtain the desired initial acid concentration (100–300 g/L) and pulp density (16.7–33.3% solids, corresponding to liquid-to-solid ratios of 5:1 to 2:1). The slurry was heated to the target temperature (80–96 °C) under stirring. Once the temperature stabilized, gas (air, oxygen, or oxygen-enriched mixture) was introduced at a controlled flow rate (0.3–1.2 L/min). Leaching time was recorded from the moment of gas introduction. At predetermined intervals, small slurry samples ($\approx$ 5 mL) were withdrawn, filtered, and the filtrate was analyzed for Cu, Fe, and free acid. At the end of the test, the entire slurry was filtered, and the residue was washed with acidified water (pH 2.0), dried at 105 °C, weighed, and analyzed for Cu, Fe, S, and Co. Copper extraction was calculated from the residue mass and its copper content (residue-based calculation). All batch experiments were performed in duplicate; average values are reported.

Metals contained in the leach residue and leaching liquor were analyzed, and the metal leaching percentage was calculated using Equation (1) [37,38]:

$$x = \frac{W_C}{W_C + W_R} \times 100\% \quad (1)$$

where x is the leaching percentage in %, W_C is the mass of the metal element in the solution in grams (g), and W_R is the mass of the metal element in the residue in grams (g).

2.4. Continuous Pilot-Scale Setup

The transition from batch laboratory experiments to continuous pilot-scale trials was deliberately designed to mimic industrial practice. In industrial copper hydrometallurgy, continuous operation is almost universally adopted owing to its higher throughput, better process stability, and lower labor intensity. A single continuous stirred-tank reactor, however, suffers from back-mixing, which results in a residence time distribution that lowers the average conversion compared with a batch reactor at the same nominal residence time. Therefore, a cascade of stirred tanks is necessary to approximate plug-flow behavior and to achieve the high conversion levels observed in batch tests. The stepwise approach

adopted here—batch tests for rapid chemical screening followed by continuous cascade trials for engineering validation—is a standard and well-established strategy in hydro-metallurgical process development. This strategy ensures that the chemical conditions identified at the laboratory scale are reliably translated to continuous operation under realistic slurry conditions.

To evaluate the industrial applicability of the atmospheric oxygen-enriched leaching process, two continuous pilot-scale reactor configurations were constructed and operated on site.

The choice of these two configurations was deliberate and aimed at providing a side-by-side engineering comparison. The conventional five-stage mechanically agitated tank train represents an established and reliable technology widely used in the hydrometallurgical industry. In contrast, the four-stage tower reactor is a more novel design that has been successfully applied in the chemical industry, where it offers advantages such as higher gas utilization, reduced floor space, and potentially lower capital investment due to its compact structure. However, its performance in metallurgical leaching applications, particularly for high-density mineral slurries, has not been systematically evaluated. Therefore, by testing both configurations under identical feed and operating conditions, we aimed to generate valuable engineering data that can guide future industrial reactor selection and design. This comparative approach also helps to identify potential limitations of the tower reactor, such as gas–liquid mixing efficiency and solids suspension, which may not be evident from chemical-scale experiments alone.

Configuration A: Five-stage mechanically agitated tank train. Five polypropylene tanks (each with a 50 L effective volume) were connected in series. Each tank was fitted with a three-blade axial-flow impeller (diameter 140 mm, speed 466 rpm), an electric heating coil, and a gas sparger (multi-hole stainless steel tube). Oxygen-enriched air (nominally 90% O₂, prepared on-site by blending) was supplied to each tank at 0.72 L/min per tank (total 3.6 L/min). The temperature was maintained at 90 °C.

Configuration B: Four-stage tower reactor. The tower had an effective volume of 72 L with four compartments separated by perforated plates. Each compartment contained a turbine impeller (diameter 155 mm, speed 400 rpm). Gas was sparged into the bottom of each compartment at 1 L/min per stage (total 4 L/min). The same oxygen-enriched air was used.

The feed slurry was prepared by mixing the as-received concentrate with process water to a pulp density of 27.5% solids. It was continuously agitated in a holding tank and delivered by a peristaltic pump to a surge tank with overflow and then to the first stage of the reactor. Concentrated H₂SO₄ was added by a separate metering pump. The total residence time was varied between 8 and 12 h by adjusting the feed rate. Continuous runs lasted for 8–12 days for each configuration. Samples were taken every 4 h from the outlet of the last stage. The solids and liquids were separated by vacuum filtration and analyzed as described above.

Figure 1 gives schematic diagrams of the three leaching experimental setups.

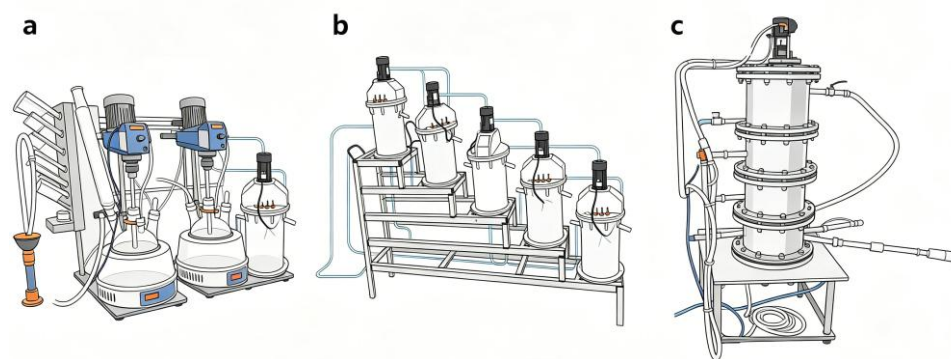


Figure 1. Leaching experimental setups: (a) batch leaching apparatus (round-bottom flask with condenser, stirrer, gas sparger); (b) five-stage stirred-tank cascade; (c) four-stage tower reactor.

3. Results and Discussion

3.1. Mineralogical Characterization of the Concentrate

The chemical composition of the concentrate is given in Table 1. Copper content averaged 10.65%, with relatively low iron (3.2%) and sulfur (3.79%) but high silicon (23.9%) and aluminum (5.85%), indicating abundant quartz and phyllosilicate gangue.

Table 1. Major element composition (wt%).

Element	Cu	Co	Fe	Mn	Ca	Mg	Al	Si	S
Content (wt.%)	10.65	0.031	3.20	0.006	0.721	3.65	5.85	23.93	3.79

Copper phase analysis (Table 2) shows that 95.4% of the copper is present as secondary copper sulfides (digenite, covellite, and bornite). Primary sulfides (chalcopyrite) account for only 0.8%, and oxides (chrysocolla) for 0.34%. This composition is typical for a slag-flotation concentrate, where copper has been recrystallized as secondary phases during slow cooling of the slag.

Table 2. Copper phase distribution.

Phase	Soluble Cu	Oxide Cu	Secondary Sulfide Cu	Primary Sulfide Cu	Other	Total Cu
Content (%)	<0.005	0.03	8.31	0.07	0.30	8.71
Distribution (%)	–	0.34	95.41	0.80	3.44	100

SEM-EDS examination (Figure 2) reveals that most copper sulfide grains are intergrown with silicates or partially locked inside gangue; only a small fraction is fully liberated. Grain sizes range from 10 to 30 μm . This texture explains why leaching must rely on solution penetration along grain boundaries rather than on complete liberation.

Modal mineralogy (Table S2) confirms digenite (5.48%) and covellite (5.03%) as the main copper minerals, with bornite (1.56%) as a minor phase. Gangue consists predominantly of quartz (49.9%), chlorite (19.6%), and muscovite (11.6%).

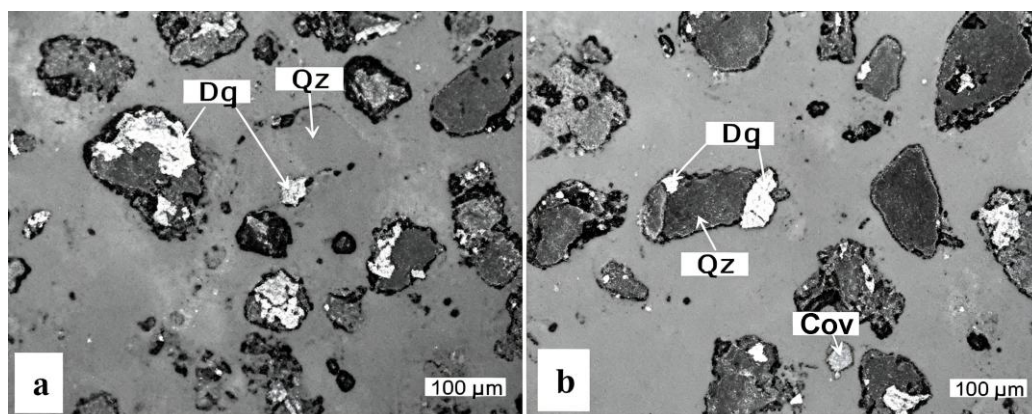


Figure 2. Backscattered electron SEM images of the slag-flotation copper sulfide concentrate showing the textural relationship between copper sulfides and gangue minerals. (a) Digenite (Dg) intergrown with quartz (Qz) and muscovite (Ms); (b) covellite (Cov) partially locked in chlorite (Chl).

3.2. Batch Leaching Optimization

During the atmospheric oxygen-enriched leaching process, the effects of operating parameters, including temperature, initial sulfuric acid concentration, leaching time, gas flow rate/oxygen concentration, and pulp density, on copper extraction were systematically investigated. A one-factor-at-a-time (OFAT) method was employed to identify the optimal operating conditions. The OFAT approach was deliberately chosen for this initial screening study for several reasons. First, it is straightforward to implement and interpret, allowing for rapid identification of the individual effect of each parameter and its approximate optimum range. This is particularly important when dealing with a material of variable composition and when the response surface is not well characterized beforehand. Second, OFAT provides clear cause-and-effect relationships that are easy to communicate and verify in subsequent pilot trials. We acknowledge that a multivariate design of experiments, such as response-surface methodology (RSM), would be better suited for quantifying interactions between parameters (e.g., temperature $\times$ acid concentration or residence time $\times$ gas flow rate). However, such an approach requires a well-defined experimental domain and a larger number of experiments, which were beyond the scope of this initial investigation. Accordingly, we recommend RSM as a logical next step for future work to refine the process and to optimize the interplay between key variables under industrial conditions.

The values of each parameter were selected based on our preliminary batch experiments as well as industrial practice and are listed as follows: for temperature, it ranges from 80 to 96 °C; for initial H_2SO_4 concentration, it ranges from 100 to 300 g/L; for leaching time, it ranges from 4 to 12 h; for gas flow rate, it ranges from 0.3 to 1.2 L/min (air or oxygen-enriched air with oxygen concentration from 21% to 100%); and for pulp density, it ranges from 16.7% to 33.3% solids (corresponding to liquid-to-solid ratios of 5:1 to 2:1). The optimal conditions were found to be 90 °C, 250 g/L H_2SO_4 , 8–12 h, 0.6–1.0 L/min of 80–90% O_2 , and 30–33% solids. Interactions among these factors and their combined effects on copper extraction may be of interest to researchers in future studies, particularly when scaling up the process or treating concentrates of different mineralogical compositions.

3.2.1. Effect of Sulfuric Acid Concentration

Figure 3 shows the effect of initial H_2SO_4 on copper extraction (95 °C, 8 h, air 1 L/min). At 100 g/L, extraction was only 66.7%. Raising the acid to 250 g/L increased extraction to 88.6%, but further increase to 300 g/L caused a slight decline to 85.6%. The initial improve-

ment is attributed to higher proton activity and a more positive redox potential, which accelerate the dissolution of secondary sulfides. The decline at very high acid may result from increased viscosity reducing oxygen mass transfer and from rapid sulfur precipitation forming a passivating layer on unreacted particles. Thus, 250 g/L was chosen as the optimum initial acid concentration.

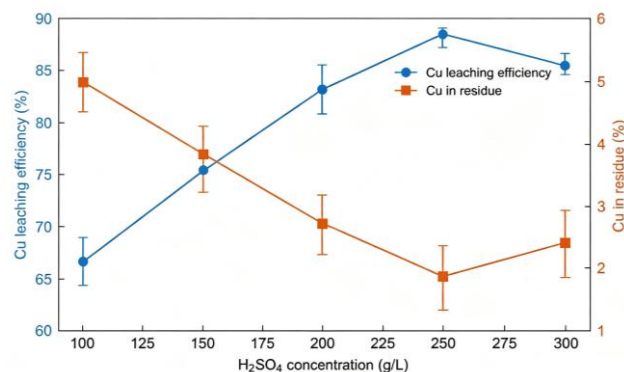


Figure 3. Effect of initial sulfuric acid concentration on copper extraction and residue copper grade. Batch leaching conditions: 95 °C, 8 h, liquid-to-solid ratio 5:1, air flow 1 L/min. The optimum acid concentration is 250 g/L, giving 88.6% Cu extraction; higher acid (300 g/L) slightly reduces extraction due to increased viscosity and possible sulfur passivation.

3.2.2. Effect of Temperature

Figure 4 presents the temperature dependence (250 g/L H₂SO₄, 8 h, air 1 L/min). Copper extraction increased from 85.0% at 80 °C to 93.9% at 93 °C and then dropped to 86.0% at 96 °C. The increase is consistent with an activation energy of approximately 45 kJ/mol (estimated from the 80–93 °C range), indicating chemically controlled kinetics rather than pure diffusion. The decrease above 93 °C is mainly due to the lower solubility of oxygen in hot sulfate solutions, which becomes the limiting factor.

Based on the above results, the highest copper extraction (93.9%) was achieved at 93 °C, which is, therefore, identified as the single optimum temperature from the batch leaching tests. The slightly lower extraction observed at 90 °C (88.9%) compared with that at 85 °C (91.3%) is attributed to experimental scatter, as the overall trend from 80 °C to 93 °C shows a clear increase consistent with chemically controlled kinetics.

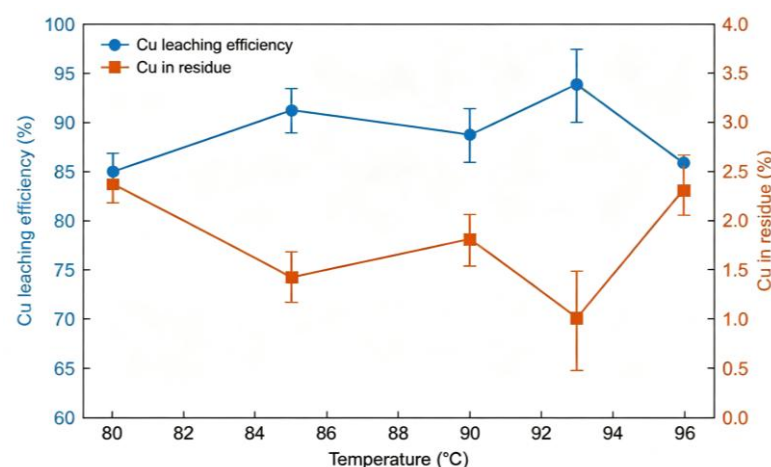


Figure 4. Effect of temperature on copper extraction and residue copper grade. Conditions: 250 g/L H₂SO₄, 8 h, liquid-to-solid ratio 5:1, air flow 1 L/min.

3.2.3. Effect of Residence Time and Gas Flow Rate

Figure 5 illustrates the leaching progress at 90 °C, 250 g/L H₂SO₄, and 1 L/min air. Extraction rose from 71.6% at 4 h to 94.9% at 12 h. A residence time of 8–12 h is considered appropriate. Increasing the air flow rate from 0.3 to 0.6 L/min improved extraction by about 10 percentage points, but a further increase to 1.2 L/min gave a slight decrease (Figure 6a), likely due to bubble coalescence and reduced gas–liquid contact. When pure oxygen replaced air (Figure 6b), extraction jumped to 97–99% even at a low flow rate (0.4 L/min), clearly demonstrating that oxygen partial pressure is the dominant factor.

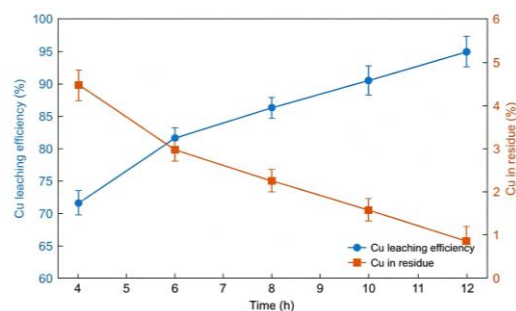


Figure 5. Effect of leaching time on copper extraction and residue copper grade. Conditions: 90 °C, 250 g/L H₂SO₄, liquid-to-solid ratio 5:1, air flow 1 L/min. Extraction rises from 71.6% at 4 h to 94.9% at 12 h. A residence time of 8–12 h is suitable for continuous operation.

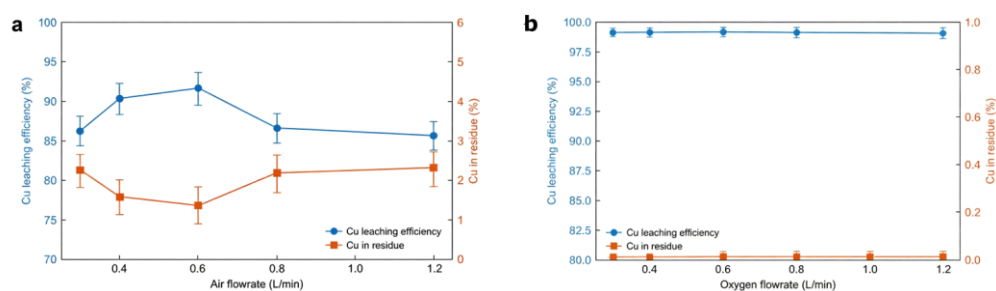


Figure 6. Effect of gas flow rate on copper extraction using (a) air and (b) pure oxygen. Conditions: 90 °C, 250 g/L H₂SO₄, liquid-to-solid ratio 5:1, 8 h. For air, the optimum flow rate is 0.6 L/min (91.8% extraction). Pure oxygen gives much higher extraction (97–99%) even at 0.4 L/min, highlighting the importance of oxygen partial pressure.

A further increase to 1.2 L/min gave a slight decrease. This decline is attributed to bubble coalescence and reduced gas–liquid contact at excessively high gas flow rates. It is well established in the gas–liquid mixing literature that, beyond a critical superficial gas velocity, the gas holdup may continue to increase, but the specific interfacial area decreases because smaller bubbles coalesce into larger ones, which rise faster and have lower mass-transfer coefficients [39,40]. This phenomenon has been observed in various stirred vessel geometries, including those with axial and radial impellers, and is particularly pronounced in slurry systems where fine solid particles can further promote coalescence by acting as bubble-bridging agents. Although we did not perform direct measurements of bubble size distribution in this study, the observed decrease in copper extraction at the highest gas flow rate is consistent with this well-documented mechanism. Therefore, an optimal gas flow rate exists that balances oxygen supply and effective gas–liquid dispersion. For the present system, a gas flow rate of 0.6 L/min (air) or 0.4 L/min (oxygen) was found to be sufficient to achieve high extraction without entering the coalescence-dominated regime.

Although batch experiments showed that extending the leaching time from 8 h to 12 h increased copper extraction from 86.4% to 94.9%, a nominal residence time of 8 h was selected as the starting point for the continuous pilot trials. This decision was based on the expectation that continuous reactors, particularly a well-mixed cascade, often achieve higher conversion than a batch reactor at the same nominal residence time, owing to more efficient utilization of the reaction volume and continuous removal of reaction products. This expectation was later confirmed by the continuous trials, in which the five-stage tank train at 8 h residence time achieved a stable copper extraction of 97.1%, comparable to the 12 h batch result. Regarding the interaction between residence time and gas flow rate, it is acknowledged that a longer residence time may reduce the sensitivity of extraction to gas flow rate, as the reaction has more time to progress even under suboptimal oxygen supply. A quantitative assessment of such interactions is suggested for future work using a response-surface methodology.

3.2.4. Effect of Grinding

A comparison between the as-received coarse feed ($D_{90} = 158 \mu\text{m}$) and the ground feed ($D_{90} = 135 \mu\text{m}$) showed only a marginal difference in copper extraction (Table S3). For example, with air leaching at 90 °C, coarse feed gave 88.4% extraction, while ground feed gave 92.7%. With oxygen, both exceeded 98%. This indicates that fine grinding is not necessary for this material, presumably because the secondary sulfides are already sufficiently accessible via intergranular pores and microfractures. The elimination of grinding is a major economic advantage.

3.2.5. Effect of Oxygen Concentration

The oxygen concentration in the sparging gas was varied from 21% to 100% (Figure 7). At 21% O_2 , copper extraction after 10 h was 85.4%. At 80% O_2 , it reached 94.8%; at 90% O_2 , 97.0%; and at 100% O_2 , 97.2%. The difference between 90% and 100% is negligible, and even 80% O_2 provides a substantial enhancement over air. Therefore, oxygen-enriched air at 80–90% O_2 is recommended as the most cost-effective oxidant.

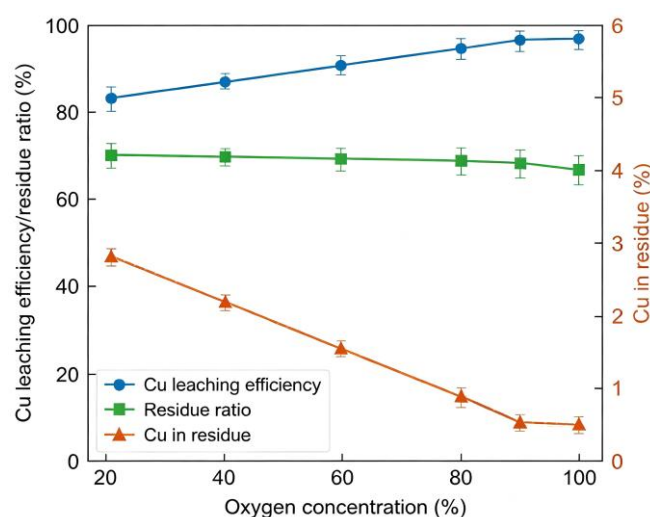


Figure 7. Effect of oxygen concentration in the sparging gas on copper extraction and residue copper grade. Conditions: 90 °C, 260 g/L H_2SO_4 , 10 h, 28.5% solids. Increasing O_2 from 21% to 80% raises extraction from 85.4% to 94.8%; further increase to 90% gives 97.0%, while 100% O_2 yields 97.2% (no significant improvement). Oxygen-enriched air at 80–90% O_2 is recommended for optimal cost-performance.

3.2.6. Silicate Gel Formation and Its Effect on Solid–Liquid Separation

In addition to the leaching chemistry discussed above, the behavior of gangue minerals under acidic conditions also deserves attention, as it can significantly affect downstream solid–liquid separation. In the present slag-flotation copper sulfide concentrate, the gangue minerals are mainly quartz ($\approx 49.9\%$), chlorite ($\approx 19.6\%$), and muscovite ($\approx 11.6\%$) (Table S2). Under the aggressive leaching conditions applied in this study (temperature $\geq 90\text{ }^{\circ}\text{C}$, initial $\text{H}_2\text{SO}_4 \geq 250\text{ g/L}$), the layered silicate minerals, particularly chlorite and muscovite, undergo partial decomposition, releasing silicic acid (H_4SiO_4) into the solution. When the concentration of silicic acid exceeds its solubility limit, polycondensation reactions occur between silicic acid molecules, leading to the formation of amorphous silica gel ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). This phenomenon has been well documented in the acid leaching of siliceous sulfide ores and slag-flotation concentrates [41–43].

The presence of silica gel can impose notable negative effects on subsequent solid–liquid separation operations. During filtration, gelatinous particles tend to block filter cloth pores, resulting in a marked decrease in filtration rate, increased moisture content of the filter cake, and in severe cases, complete failure of filtration. In our batch experiments, when the acid concentration exceeded 250 g/L or the temperature rose above $93\text{ }^{\circ}\text{C}$, we indeed observed extended filtration times and higher cake moisture, which are consistent with gel formation.

To mitigate these adverse effects in industrial practice, the following measures can be considered: (1) strict control of the final acid concentration to avoid excessive silicate decomposition; (2) addition of suitable flocculants (e.g., anionic polyacrylamide) to the leach slurry before filtration to promote agglomeration and settling of fine particles and gel species, thereby improving filterability; and (3) if gelation becomes critical, pre-neutralization or dilution of the slurry to reduce silicic acid supersaturation and suppress gel formation. In our continuous pilot trials, by maintaining the residual acid in the range of $140\text{--}160\text{ g/L}$ and applying an appropriate flocculant, solid–liquid separation proceeded without major obstacles and did not impede the continuous operation.

3.3. Continuous Pilot-Scale Results

3.3.1. Five-Stage Stirred-Tank Train

The five-stage train was operated for 8 days at a feed rate giving 8 h total residence time (dry concentrate 1.51 kg/h , 27.5% solids). The average copper extraction was 97.1% , and the residue copper content averaged 0.53% (range $0.22\text{--}1.08\%$) over the 8-day continuous run (Figure 8). The acid consumption was 857 kg per ton of concentrate. The ORP in the discharge slurry was around 440 mV (vs. Ag/AgCl), and the free acid concentration was 146 g/L on average. Extending the residence time to 10 h increased extraction only marginally (to 96.9% , within experimental error). Hence, 8 h is sufficient.

Although $93\text{ }^{\circ}\text{C}$ was identified as the optimal temperature in batch tests, a temperature of $90\text{ }^{\circ}\text{C}$ was selected for the continuous pilot trials as a practical engineering compromise. This choice provides a safety margin for temperature control in the industrial-scale equipment, reduces steam consumption, and is less aggressive towards the polypropylene reactor material over extended operation periods. This trade-off between maximum extraction and operational robustness is common in process scale-up and is explicitly considered in the present study. Sampling from each tank (Figure 9a) revealed that the first tank already achieved 92% copper extraction; the subsequent four tanks increased extraction to 98.6% . This shows that the reaction is fast and that the first stage is the most critical. In industrial practice, the number of stages might be reduced to three or four, and oxygen supply can be tapered along the cascade.

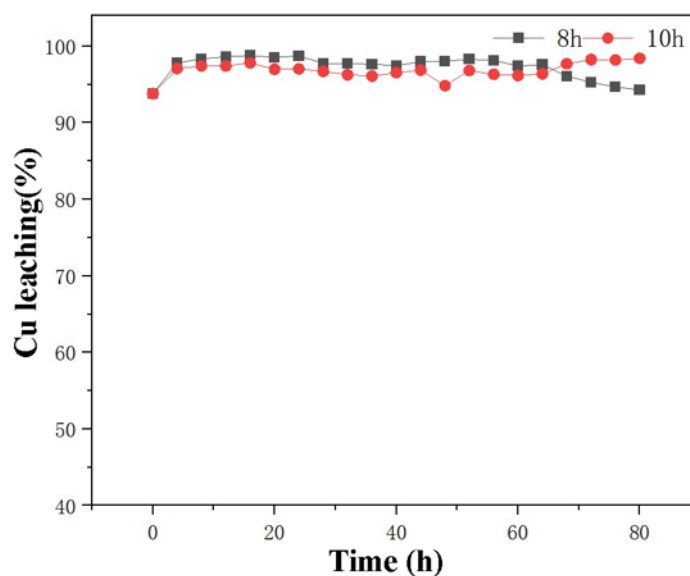


Figure 8. Continuous pilot-scale performance of the five-stage mechanically agitated stirred-tank reactor. (a) Copper extraction and residue copper grade as a function of operating time at 8 h total residence time; (b) oxidation-reduction potential (ORP) and free acid concentration in the discharge slurry. Average extraction = 97.1%, residue Cu = 0.53%. Conditions: 90 °C, 27.5% solids, 90% O₂-enriched air (0.72 L/min per tank), initial H₂SO₄ 250 g/L, dry feed rate 1.51 kg/h.

It should be noted that achieving 92% extraction in the first tank does not imply that the subsequent stages are redundant. Rather, this is a characteristic behavior of a cascade of continuous stirred-tank reactors: the majority of the reaction occurs rapidly in the initial stage, while the later stages serve to push the conversion from 92% to 98.6%, representing a significant incremental recovery of copper. Optimizing the first tank alone—for example, by increasing its volume, oxygen supply, or agitation intensity—would be less efficient than adding a few additional stages, which is a standard industrial practice to approach complete conversion. This design is, therefore, not a sign of process inefficiency but a deliberate engineering choice to achieve high overall recovery with a practical and scalable reactor configuration.

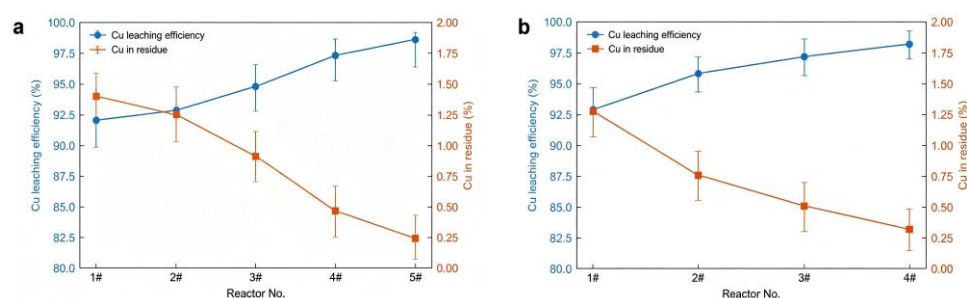


Figure 9. Comparison of copper extraction and residue copper grade across individual stages for (a) the five-stage stirred-tank cascade (10 h residence time) and (b) the four-stage tower reactor (12 h residence time).

3.3.2. Four-Stage Tower Reactor

The tower reactor was tested at 8, 10, and 12 h residence times. At 8 h, copper extraction averaged only 92.5% (residue Cu 1.49%). At 10 h, extraction increased to 95.6% (residue 0.73%). Even at 12 h, extraction reached only 97.1% (residue 0.63%), which is no better than the five-stage train at 8 h. The tower's inferior performance is attributed to poorer gas–liquid mixing and a higher tendency for bubble coalescence due to the compartment

design. Consequently, the conventional stirred-tank cascade is the preferred reactor configuration.

The performance of the tower reactor at individual stages at 12 h residence time is presented in Figure 9b. Copper extraction increased progressively from approximately 92.96% in the first stage to 95.82% in the second, 97.2% in the third, and finally reached 98.24% in the fourth stage. The corresponding residue copper grades decreased from about 1.28% in the first stage to 0.76% in the second, 0.51% in the third, and 0.32% in the fourth. This stepwise improvement confirms that the leaching reaction proceeds gradually through the tower, but the extent of reaction in each individual stage is lower than that observed in the conventional stirred-tank cascade (Figure 9a), where the first tank alone achieved 92% extraction. The slower progress is attributed to less efficient gas–liquid mixing and a greater tendency for bubble coalescence in the compartment design, which reduce oxygen mass transfer.

The choice of four stages was dictated by the available equipment (a standard commercial design supplied by the manufacturer) and site space constraints at the pilot facility. The primary objective of this study was not to optimize the number of stages for the tower reactor, but rather to compare the overall performance of this specific tower configuration with that of the conventional five-stage stirred-tank cascade under identical conditions. Consequently, the conventional stirred-tank cascade is the preferred reactor configuration for this application.

3.3.3. Synergistic Leaching with Roasting Residue

When the slag-flotation concentrate was mixed 1:1 with the roasting residue (5.01% Cu) and leached under the same conditions (five-stage, 10 h, 90 °C, 90% O₂), copper extraction dropped to 91.6% (Figure 10). Although the ORP was slightly higher (463 mV) because of ferric iron release from the residue, the refractory nature of the roasting residue (copper present as chrysocolla and copper ferrite) and its higher acid consumption outweighed any benefit. Therefore, separate processing is recommended.

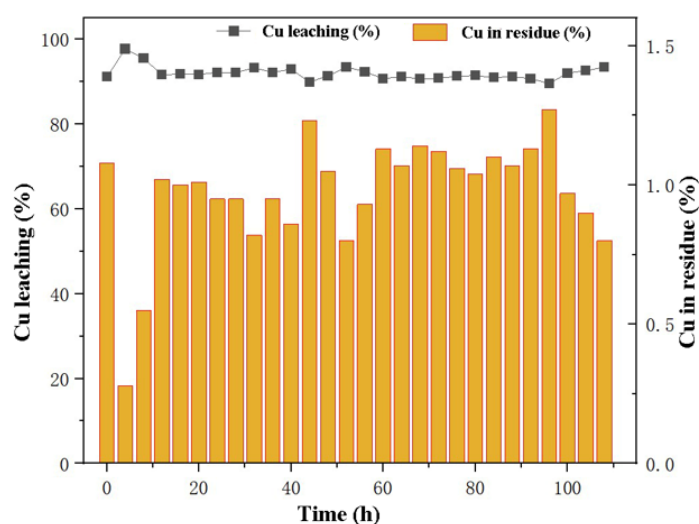


Figure 10. Continuous pilot-scale results for synergistic leaching of a 1:1 mixture of slag-flotation concentrate and roasting residue. Conditions: five-stage reactor, 90 °C, 10 h residence time, 90% O₂. Average copper extraction is 91.6%, significantly lower than that achieved for slag concentrate alone (97.1%), due to the more refractory copper phases (chrysocolla, copper ferrite) in the roasting residue.

4. Conclusions

The slag-flotation copper sulfide concentrate is characterized by 10.6% Cu, with 95% of the copper occurring as secondary sulfides (digenite, covellite, and bornite) intergrown with quartz, chlorite, and muscovite. The grain size is 10–30 μm , and liberation is incomplete, but the material can be leached without fine grinding.

Batch leaching under atmospheric conditions established the optimal parameters: H_2SO_4 250 g/L, temperature 90–93 $^\circ\text{C}$, leaching time 8–12 h, pulp density 30–33% solids, and oxygen-enriched air (80–90% O_2) at a flow rate ensuring sufficient oxygen mass transfer. Under these conditions, copper extraction reaches 97–99% without grinding.

Continuous pilot-scale validation over >500 kg of feed demonstrates that a five-stage mechanically agitated tank train (50 L per stage) consistently yields 97.1% copper extraction at 8 h total residence time, with a residue grade of 0.53% Cu and an acid consumption of 857 kg/t concentrate. The four-stage tower reactor is less efficient, requiring 12 h to achieve the same extraction.

The oxygen concentration can be reduced from 100% to 90% with no measurable loss in copper extraction (97.0% vs. 97.2%). Even 80% O_2 gives 94.8% extraction, only 2% lower than 90% O_2 . This flexibility significantly reduces operating costs by allowing the use of VPSA-generated enriched air instead of pure oxygen.

Synergistic leaching with a roasting residue (containing 5% Cu) is not beneficial; the two materials should be processed separately to avoid lower copper recovery and higher acid consumption.

The claim that the proposed process offers low capital expenditure is qualitatively supported by several inherent features of the flowsheet. First, the process accepts the concentrate without fine grinding, eliminating the significant capital and operating costs associated with comminution. Second, the leaching operation is conducted at atmospheric pressure, avoiding the need for expensive autoclaves and associated high-pressure safety systems that are required in pressure oxidative leaching. Third, the process uses conventional mechanically agitated stirred tanks, which are standard equipment in the metallurgical industry and are considerably less capital-intensive than specialized high-pressure reactors. Fourth, the process achieves high copper extraction using 80–90% oxygen-enriched air generated by VPSA technology, which is substantially cheaper than pure oxygen. These qualitative considerations indicate that the process is economically attractive.

The developed process—atmospheric oxygen-enriched leaching in a simple stirred-tank cascade without grinding—offers an economically attractive and technically robust solution for recovering copper from refractory slag-flotation copper sulfide concentrates. It can be implemented with low capital investment using standard equipment, turning an environmental liability into a valuable resource.

Building on the findings of this study, several promising directions for future research and development can be identified. First, a detailed techno-economic assessment should be carried out to quantify the capital and operating costs of the proposed process. This assessment should compare the use of air, 80–90% oxygen-enriched air, and pure oxygen, evaluating the trade-offs between oxygen purity, copper recovery, and overall cost. Additionally, the economic benefits of eliminating the grinding step and avoiding high-pressure equipment should be quantified against the costs of oxygen generation and reagent consumption. Such an analysis would provide a solid basis for industrial decision-making and investment justification. Second, further optimization of reactor design and gas distribution is warranted. Computational fluid dynamics (CFD) modeling could be employed to simulate gas–liquid–solid flow patterns, bubble size distribution, and oxygen mass transfer in both the stirred-tank cascade and the tower reactor, thereby guiding geometric improvements and scale-up strategies. Third, the applicability of the atmospheric oxygen-enriched leaching process to other secondary copper materials—such as flotation

tailings, oxidized residues, and low-grade dump ores—should be explored. Given the growing importance of secondary resource recovery in the circular economy, extending this process to a broader range of feedstocks would enhance its industrial relevance and environmental benefits.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/met16070788/s1>, Table S1: Chemical composition of the roasting residue used in synergistic leaching experiments (wt%); Table S2: Modal mineralogy (wt%); Table S3: Comparison of copper extraction between the as-received coarse feed ($D_{90} = 158.5 \mu\text{m}$) and the fine-ground feed ($D_{90} = 135.5 \mu\text{m}$) under selected leaching conditions.

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Conflicts of Interest: Authors Qifan Zhou, Hao Ma and Haibei Wang were employed by the company BGRIMM Technology Group. The remaining author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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