

Recovery of valuable metals from copper slags as secondary resources: Selected laboratory-scale case studies

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Abstract: Pyrometallurgical extraction of metallic copper from copper concentrates generates several by-products, among which copper slag constitutes one of the most voluminous solid residues. These slags are generally composed of iron oxides, silica, calcium oxide, alumina, and varying amounts of unrecovered copper. Despite their common disposal by stockpiling or use as landfill material, copper slags may still host appreciable quantities of valuable metals occurring as entrapped metallic particles, sulphide phases, or oxidized compounds. For this reason, different recovery routes have been investigated and applied, including mineral processing methods as well as pyro-, hydro-, and combined pyro-hydrometallurgical treatments. Among these approaches, flotation is particularly important in copper slag beneficiation and is already integrated into several industrial smelting circuits. This review examines the characteristics of smelting, converting, refining, and ancient copper slags formed during pyrometallurgical copper production, together with the main strategies proposed for recovering metals from these secondary resources. Selected examples from laboratory-scale studies carried out on various industrial copper slags from Turkey are also presented. In addition, the environmental implications of copper slag management and the sustainability aspects of slag treatment are considered.

Keywords: copper slags, flotation, pyrometallurgy, hydrometallurgy, slag treatment

1. Introduction

Slags are among the most common by-products generated in metallurgical operations and are generally grouped, according to their source and physicochemical properties, into ferrous, non-ferrous, and incineration slags (Shen & Forssberg, 2003). Their annual production reaches very large quantities worldwide, and certain slag types may contain potentially harmful elements, including heavy metals. If these elements are released into the environment, they may cause serious ecological and public-health concerns. Traditional management of slags has mostly relied on landfilling or stockpiling. However, such practices require extensive disposal areas, lead to the permanent loss of recoverable metal values, and may create environmental problems, particularly through the contamination of surface and groundwater. For these reasons, metal recovery from slags and the conversion of these residues into useful secondary resources have become increasingly important from both environmental and resource-efficiency perspectives.

In the pyrometallurgical production of metallic copper from concentrates, several secondary materials, such as slags, dusts, and fumes, are formed. Many of these by-products contain not only residual copper but also other valuable metals. In modern copper smelting, flash smelting has largely replaced reverberatory furnace technology because of its process advantages and industrial efficiency. Nevertheless, flash furnace slags may still carry substantial copper losses, which makes additional treatment steps

necessary. These commonly include electric furnace slag cleaning, converting, and fire-refining operations (Traulsen et al., 1981; Jones and Deneys, 1998). In some smelters, converter slag is returned to the flash furnace, which can increase the matte grade (Antonioni et al., 1981). In other operations, flash furnace slags containing 1.6-2% Cu and converter slags containing 5-7% Cu are treated in electric arc furnaces in the presence of coke as a reductant, decreasing the final copper content of the slag to about 0.5-0.8% (Kim, 1982; Suzuki et al., 1982). The Ausmelt top-entry submerged lance process has also been applied for the recovery of Cu, Ni, and Co from copper slags (Hughes, 2000; Vernon and Burks, 1997).

In conventional copper production, flotation concentrates are subjected successively to smelting, converting, and fire refining to obtain copper anodes. Each of these stages generates copper-bearing slags, which are regarded as one of the important residue streams of the copper industry. Figure 1 shows the points at which copper slags are produced during pyrometallurgical copper extraction. Since these materials may contain appreciable concentrations of valuable metals, they can be considered potential secondary resources rather than simple wastes. A variety of treatment methods have therefore been developed or proposed for metal recovery from slags. These include physical and mineral processing techniques, such as crushing, grinding, magnetic separation, eddy current separation, and flotation, as well as pyrometallurgical, hydrometallurgical, and combined pyro-hydrometallurgical routes. Through these approaches, metals including Fe, Cr, Cu, Al, Pb, Zn, Co, Ni, Nb, Ta, Au, and Ag may be recovered from different slag systems (Arslan and Bulut, 2025).

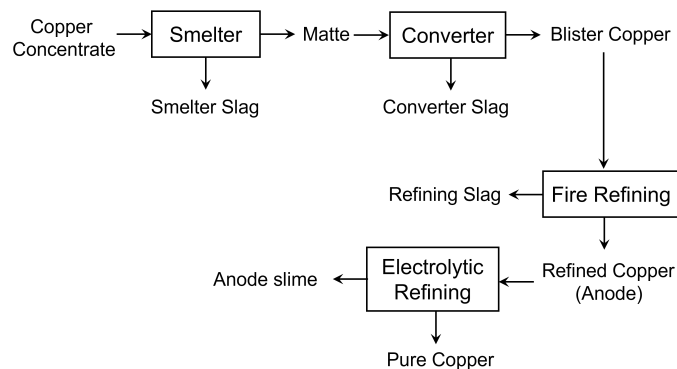


Fig. 1. Slags produced during the various stages of pyrometallurgical copper production

The chemical and mineralogical characteristics of copper slags may vary considerably from one smelter to another because of differences in ore mineralogy, concentrate composition, flux additions, furnace design, and process conditions. In particular, the type of concentrate and fluxes used, together with furnace type and cooling regime during and after smelting or converting, strongly affects slag composition and phase assemblage (Phiri et al, 2021). From a process selection perspective, copper in slags may broadly be classified into two occurrence modes. The first comprises mechanically entrained matte or metallic droplets and discrete copper-bearing sulfide particles, which may become recoverable through controlled cooling, grinding, classification, and flotation. The second comprises chemically dissolved or structurally associated copper occurring in oxide, ferrite/spinel, silicate, or glassy phases. Copper slags are typically enriched in iron, silicon, and alumina, while fayalite and magnetite are commonly reported as the principal mineral phases (Akella et al., 1978; Chen and Zhang, 2025). In many cases, the copper grade of these slags may exceed that of currently mined primary copper ores, which further highlights their importance as secondary sources of valuable metals. In this context, the present paper reviews studies dealing with the recovery of metallic values from ancient copper slags and from copper smelting, converting, and refining slags.

2. Ancient copper slags

Copper is recognized as the earliest metal extracted by smelting, with evidence of production dating back nearly seven millennia in the ancient Near East. For many pre-industrial societies, our understanding of

copper metallurgy relies mainly on the examination of metallurgical residues, especially copper slags, recovered from archaeological contexts. Such slags are generally composed of oxide phases, including iron and manganese oxides, together with olivine-type minerals such as fayalite and/or pyroxenes distributed within a partly glassy polymetallic matrix. Their phase assemblage and texture provide direct information on the raw materials charged into the furnace and on the thermal and chemical conditions prevailing during ancient smelting operations (Bourgarit, 2019).

Potysz et al. (2016) evaluated historical and modern copper slags comparatively and showed that slags formed under less controlled ancient smelting conditions tend to be highly heterogeneous and display greater metal release during pH-dependent leaching. Because of their irregular mineralogy and reactive glass-fayalite matrices, these materials may behave as complex anthropogenic ores. Modern slags, on the other hand, commonly show more consistent fayalite-spinel assemblages and lower metal mobility, which reflects better control of metallurgical parameters and improved environmental stability. Thus, historical slags are generally more reactive and more difficult to process, whereas modern slags usually exhibit more predictable behavior during treatment and reprocessing.

The ancient copper slags from the Küre region in northern Türkiye constitute one of the representative examples of fayalitic residues generated by historical copper smelting. These materials contain notable quantities of copper, cobalt, iron, and several minor metals, mainly trapped within olivine-rich matrices and spinel phases (Bulut, 2006). Because of their metal content and the large tonnages accumulated over long periods, Küre slags have been the subject of continuing interest as potential secondary resources and as candidates for integrated recovery flowsheets. During the last three decades, these slags have been investigated through a wide range of technological routes. The main developments are presented below in chronological sequence.

In Türkiye, other archaeological copper-smelting localities outside the Küre district include Arslantepe in Malatya, Dereköy in Thrace, Murgul in Artvin, Norşuntepe, and several Early Bronze Age settlements in the Tokat region (Kaptan, 1990; Hauptmann et al., 2022; Kurt, 2025). Studies on these sites have mainly addressed archaeometallurgical and geochemical questions, including furnace construction, ore sources, slag mineralogy, and the production of early copper-arsenic alloys. In contrast, metal-recovery-oriented investigations have remained very limited. So far, comprehensive reprocessing studies based on flotation, leaching, sulfidation, or integrated flowsheet design have not been reported for these historical slag deposits.

International research, however, indicates that ancient copper slags may be considered promising secondary metal resources. Potysz & Kierczak (2019) showed that historical slags from Poland could be treated by acid leaching and bioleaching, suggesting an economically attractive recovery potential. In Namibia, Dzinomwa et al. (2023) used detailed mineralogical characterization to support the development of possible Cu-Co extraction strategies. Similarly, the feasibility of reprocessing historical slag deposits at the Rönnskär smelter in Sweden was evaluated from a cost-benefit perspective (Ettlinger, 2020). Taken together, these studies demonstrate that ancient slags can be regarded as anthropogenic ore deposits. Further studies have also confirmed that chemical and biological leaching can be effective for metal extraction from historical slags, with amorphous slags showing the highest dissolution efficiencies and economic potential (Potysz & Kierczak, 2019). Within this framework, studies on Küre slags represent the only detailed reprocessing-oriented investigations reported from Türkiye and therefore address an important gap by illustrating how historical metallurgical residues can be valorized using modern processing approaches.

The first systematic study on Küre slag was carried out by Topkaya (1990), who investigated its carbothermic reduction for the production of an Fe-Cu-Co alloy. In experiments performed with 4% coke at 1400°C for one hour, cobalt and copper recoveries reached 97.7% and 86.7%, respectively. These results demonstrated that valuable metals present in the slag could be effectively collected in a metallic phase by reduction. Following this study, Açma et al. (1992) and Sesigür et al. (1995) conducted smelting experiments in submerged electric arc furnaces. The metal-rich products obtained from these experiments were

subsequently leached with sulfuric acid and further processed to recover copper, cobalt, and iron-bearing products.

Açma et al. (1997) further advanced this approach by reducing fayalitic slag in a DC arc furnace using coke or graphite as reductants. The process yielded Fe-rich alloys containing approximately 3.8% Cu and 3.3% Co. Through repeated leaching steps, selective recovery of cobalt was achieved, together with the production of magnetic $\gamma\text{-Fe}_2\text{O}_3$. Later studies extended this concept toward more complete process schemes combining reduction, granulation, leaching, precipitation, and oxidation-reduction stages.

Yücel et al. (1992) investigated the effect of open and closed DC arc furnace operation and found that closed furnace conditions markedly improved metal recovery. Under optimum temperatures of 1430-1480°C, recoveries of 95.7% Co and 90% Cu were obtained. Derin et al. (2003) subsequently proposed a comprehensive flowsheet that included carbothermic reduction, leaching, precipitation, sulfidation roasting, and the production of metallic and compound products, together with abrasive materials derived from the reduced slag.

Bulut et al. (2007) developed combined pyrometallurgical-hydrometallurgical treatment routes based on pyrite roasting and flotation. In this study, 77% Cu recovery and Co dissolution values as high as 87% were achieved. More recently, Tegin and Ziyadanoğulları (2018) reported that H_2S -assisted sulfidizing flotation was highly effective for Küre slag, producing recoveries of 98.27% Cu and 68.07% Co.

The most recent hydrometallurgical work was reported by Seyrankaya and Canbazoglu (2021), who applied oxidative pressure leaching to Küre slag. Their results showed recoveries of 92.85% Cu, 96.82% Co, and 93.44% Zn, while iron dissolution remained exceptionally low at only 0.3%. This study can be regarded as the most advanced hydrometallurgical investigation of Küre slag reported to date.

Overall, investigations on Küre ancient copper slags have evolved from initial carbothermic reduction experiments to more advanced pyrometallurgical-hydrometallurgical, flotation-based, and integrated processing routes. The increasing attention given to environmental acceptability, mineralogical control, selective metal recovery, and product diversification demonstrates the strong potential of Küre slag as a secondary resource. These studies also point to important opportunities for developing near-zero-waste valorization strategies for historical metallurgical residues.

3. Copper smelting slags

Smelting and converting slags generated in copper plants may contain substantial quantities of recoverable metals, and their treatment is therefore important from both economic and resource-efficiency perspectives. A considerable number of studies have addressed this issue using physical separation, hydrometallurgical, pyrometallurgical, and combined process routes. Arslan & Arslan (2002), for example, examined the recovery of Cu, Co, and Zn from copper slag by a pyro-hydrometallurgical process proposed as an alternative to conventional flotation.

Akhmedov (2024) investigated the leaching behavior of Cu, Fe, and Zn from copper slags in sulfuric acid under controlled experimental conditions. The best results were obtained using 2.5 mol/dm³ H_2SO_4 at 90°C for 120 min, where Cu recovery reached up to 95%, and Fe recovery was approximately 90%. The study showed that increasing acid concentration and temperature, together with decreasing particle size below 100 μm , markedly improved metal dissolution.

Başkurt et al. (2022) studied a copper slag containing 0.9% Cu and applied flotation as an initial concentration step. A concentrate assaying 22.7% Cu was obtained with approximately 40% copper recovery. Because direct leaching with H_2SO_4 caused silica-gel formation, HCl was selected as the leaching medium. Under the conditions of 25 g/dm³ H_2O_2 , 20-25% solids, and 300 g/dm³ HCl, Cu and Ce extractions reached 70-80% within 2 h.

Silica gel formation is a common difficulty during sulfuric acid leaching of copper slags, mainly because of the amorphous character of the slag matrix. This phenomenon may seriously impair filtration and also cause crud formation during solvent extraction. Banza, Gock, & Kongolo (2002) addressed this problem by using hydrogen peroxide as an additive. In their study, peroxide-assisted H_2SO_4 leaching of a <100 μm slag

sample from Lubumbashi, DRC, containing 1.4% Cu, 0.7% Co, 8.9% Zn, and 20.9% Fe(II), produced gel-free pregnant solutions. Copper was subsequently extracted with LIX 984 dissolved in Shellsol D70, followed by the collective extraction of Co and Zn using D2EHPA and selective scrubbing. The overall process yielded separate solutions with recoveries of 80% Cu, 90% Co, and 90% Zn, which were suitable for further treatment by electrowinning or salt precipitation.

Wang et al. (2024) developed a two-stage process, consisting of evaporation followed by water washing, for the selective recovery of Fe and Zn from copper slag. Under optimum evaporation conditions of 3 mol/dm³ H₂SO₄, 60 min, 120°C, and a liquid/solid ratio of 4, followed by water washing at a liquid/solid ratio of 5, leaching efficiencies of 99.94% Fe and 97.40% Zn were achieved, whereas Si dissolution remained as low as 0.15%. During the process, silica gel was converted into aggregated amorphous silica, thereby suppressing silicon dissolution. The treated slag was transformed into iron red, electrolytic zinc, and geopolymer products.

Yang et al. (2010) proposed a selective hydrometallurgical route carried out under atmospheric pressure using sulfuric acid in the presence of sodium chlorate as an oxidant. Subsequent neutralization with Ca(OH)₂ improved the filtration behavior of the precipitate. Metal recoveries reached 98% Co, 97% Zn, and 89% Cu, while the dissolution of Si and Fe was limited to only 3.2% and 0.02%, respectively. Owing to its simple operating principle and favorable economy, this process was considered promising for industrial application.

Nadirov & Mussapyrova (2019) assessed the H₂SO₄-K₂Cr₂O₇ system for leaching Cu, Zn, and Fe from copper smelter slag. The presence of dichromate increased copper recovery to 68% under the conditions of 0.5 mol/dm³ K₂Cr₂O₇ + 1 mol/dm³ H₂SO₄, 15 g/dm³ solids, 120 min, and 298 K. However, zinc and iron recoveries decreased, which was attributed to the selective adsorption of dichromate species. Approximately 70% of the copper was extracted in the first stage, leaving a residue that could be further processed for zinc recovery.

Herreros et al. (1998) investigated chlorine leaching of reverberatory and flash furnace slags by evaluating the effects of stirring rate, temperature, initial Cl₂ and Cl⁻ concentrations, particle size, and reagent addition sequence. Copper extraction was in the range of 75-80%, whereas iron extraction remained around 5%. Characterization of the slags showed that copper was present mainly as metallic copper, chalcocite, bornite, and minor silicate-associated phases, while iron occurred predominantly in the vitreous phase, fayalite, and magnetite.

Alam et al. (2025) examined the sodium sulfate-assisted breakdown of complex copper slag compounds. With 20% Na₂SO₄ addition, a decomposition rate of 89% was obtained. The optimum conditions for fayalite decomposition were reported as 900°C and 90 min. Subsequent sulfuric acid leaching resulted in recoveries of 97% Cu, 96% Fe, and 93% Zn. By comparison, untreated samples yielded much lower recoveries of 61% Cu, 59% Fe, and 65% Zn. The proposed method also helped prevent silica-gel formation during leaching.

Huang et al. (2023) proposed a selective complexation leaching process for copper recovery from smelting slag using an alkaline glycine solution. The effects of several parameters, including initial pH, particle size, stirring speed, liquid/solid ratio, temperature, and glycine concentration, were examined. Under optimum leaching conditions, copper extraction reached 86.40%, whereas the dissolution of other valuable metal elements remained very limited. The study indicated that glycine can act as an efficient and selective leaching agent for copper extraction from smelting slags, offering a potentially greener recovery route.

Mao et al. (2021) developed a two-step treatment method combining oxidative desulfurization and smelting reduction. In this process, waste cathode carbon was used both as a reductant and as a fluxing agent, thereby decreasing the melting temperature of the slag. Under optimum conditions, consisting of 60 min air oxidation followed by smelting with 14.4 wt% waste cathode carbon and 25 wt% CaO for 180 min at 1450°C under an Ar atmosphere, recovery rates of 96% Cu and 95% Fe were obtained. More than 90% of the fluorides originating from the cathode carbon were transferred to the final slag, while the Fe-Cu alloy contained only 0.03 wt% S.

Heo et al. (2016) investigated a novel aluminothermic smelting reduction process for the treatment of waste copper slag, aiming at both iron recovery and hazardous-element removal. The effect of aluminum addition on the reduction of iron oxide at 1773 K was studied with particular attention to changes in the thermophysical properties of the slag. FeO and Al_2O_3 contents varied sharply during the first 5 min of reaction and then approached stable values. The highest iron recovery was achieved at an Al/FeO ratio of 0.53. Spinel and olivine phases were found to precipitate during the process. The ASR method was also effective in removing hazardous elements, including As, Bi, Pb, and Sb, from end-of-life copper slag.

Phiri et al. (2025) studied the low-temperature carbothermic reduction of copper slag using charcoal and borax, followed by sulfuric acid leaching. Mineralogical characterization indicated that the slag consisted mainly of fayalite and magnetite. During reduction, magnetite was transformed stepwise through $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$, whereas fayalite decomposition was catalyzed at 300°C and reduction to metal occurred at 545°C. The optimum treatment consisted of 20% borax and 10% charcoal, 90 min reduction at 850°C, and subsequent leaching for 90 min in 2 M H_2SO_4 . Under these conditions, Cu, Co, and Fe extractions were 77.33%, 83.35%, and 86.53%, respectively, confirming the importance of carbothermic reduction as a pretreatment step for efficient downstream metal recovery.

Copper recovery from smelting slags by flotation is often difficult because copper matte and copper-bearing particles are commonly very fine. Recent work has shown that $\text{Pb}^{2+}/\text{NH}_4^+$ activation during sulfidization flotation promotes the formation of sulfide species on copper oxide surfaces, thereby increasing hydrophobicity and improving flotation recovery (Wang et al., 2025). Wang et al. (2023) also reported that slow cooling in the presence of boron oxide improved flotation performance. Boron oxide entered the silicate network as BO_3 triangular units, which lowered the melting point of the slag and increased the liquid-phase fraction. Holding the slag at 1300°C for 1.5 h, followed by cooling to 850°C at 2°C/min, produced a concentrate containing 47.91% Cu with 77.71% recovery. Compared with slag treated without boron oxide, the recovery and concentrate grade increased by 6.34% and 27.14%, respectively.

Xia et al. (2022) proposed the use of gypsum residue as a sulfur source in the sulfidation treatment of copper smelting slag. After treatment, the copper content in non-sulfide phases decreased below 0.08 wt%, and the average size of sulfide particles reached 37–40 μm , which is suitable for flotation. TCLP (Toxicity Characteristic Leaching Procedure) tests also showed that the treated materials had improved environmental stability. Wang et al. (2024) further investigated reduction-sulfurizing smelting using waste gypsum and waste coke. Their work considered the effects of additive dosage, smelting temperature, matte migration and settling behavior, and the separation of matte droplets by low-temperature super-gravity treatment. Heavy-metal leaching behavior was also evaluated in order to develop a more environmentally compatible recovery route.

Du et al. (2022) proposed a deep-reduction process using rubber seed oil as a reductant for iron recovery from copper slag. Under optimum roasting conditions, Fe recovery reached 91.85%, and the recovered product contained 95.66% Fe. The secondary residue generated after treatment could be reused as a raw material for glass-ceramic production, thereby supporting cleaner and more complete utilization of copper slag.

Wang et al. (2024) applied a green treatment method combining reduction-sulfurizing smelting with low-temperature super-gravity separation to clean copper slag and recover metals. In this process, matte droplets were efficiently separated from the cleaned slag under super-gravity conditions at 1200°C within 3 min. The copper recovery ratio reached 99.56%, while the copper grades of the matte phase and cleaned slag were 85.84 wt% and 0.08 wt%, respectively.

Tümen and Bailey (1990) investigated the roasting of smelting slags with pyrite followed by leaching. Roasting at 550°C for 1 h with a pyrite/slag ratio of 0.25 allowed more than 95% of the copper to be recovered. In contrast, only limited amounts of cobalt, nickel, and zinc were extracted, while approximately 2% of the iron in the slag dissolved into the leach solution. Increasing the roasting temperature reduced iron contamination, but also decreased copper recovery. Aeration was suggested as a suitable approach for lowering iron contamination in the leach solutions.

The use of Ausmelt's top-submerged lance technology for recovering copper, nickel, and cobalt from smelting and converting slags has been demonstrated both at pilot-plant scale and in several commercial operations (Hughes, 2000). This process provides a relatively low-cost treatment option, particularly in cases where the main economic value is associated with cobalt recovery.

4. Copper converter slags

Anand et al. (1983) developed a pressure-leaching approach for copper converter slag using dilute sulfuric acid to extract valuable metals while suppressing iron dissolution through oxidation and hydrolysis. The effects of leaching time, pulp density, particle size, acid concentration, and oxygen partial pressure were systematically examined. Under the optimized conditions, approximately 90% of copper and more than 95% of both nickel and cobalt were brought into solution, whereas iron dissolution was restricted to only 0.8%.

Altundoğan et al. (2004) studied the leaching behavior of Cu, Co, Zn, and Fe from copper converter slag in an oxidative medium containing potassium dichromate and sulfuric acid. Their results indicated that dichromate strongly affected the dissolution behavior of the metals. Copper extraction was particularly favorable in this lixiviant, mainly because high Cu dissolution was accompanied by a relatively low Fe concentration in solution. Increasing the dichromate concentration improved copper extraction; however, it considerably reduced the dissolution of Co, Zn, and Fe.

Beşe (2007) investigated copper dissolution from converter slag in sulfuric acid–ferric sulfate solutions, both in the presence and absence of ultrasound. The main parameters examined were reaction temperature, acid concentration, ferric sulfate concentration, and leaching time. The optimum conditions for copper dissolution were determined as 65°C, 0.2 mol/dm³ acid concentration, 0.15 mol/dm³ ferric sulfate concentration, and 180 min reaction time. Under these conditions, ultrasound-assisted leaching yielded extraction efficiencies of 89.28% Cu, 51.32% Zn, 69.87% Co, and 13.73% Fe. Without ultrasound, the corresponding values decreased to 80.41%, 48.28%, 64.52%, and 12.16%, respectively. These findings show that ultrasound promotes the dissolution of Cu, Zn, Co, and Fe from converter slag.

The recovery of copper, cobalt, nickel, and zinc from copper converter slag by ferric sulfate roasting followed by leaching has also been investigated (Altundoğan and Tümen, 1997; Arslanoğlu et al., 2022). In this process, the slag was first roasted with ferric sulfate and then leached with water to dissolve the metal values. At a roasting temperature of 500°C, a roasting time of 120 min, and a ferric sulfate/slag ratio of 1, recoveries of approximately 93% Cu, 38% Co, 13% Ni, and 59% Zn were obtained. Increasing the ferric sulfate/slag ratio improved the extraction of Cu and Zn, whereas Co and Ni recoveries remained unsatisfactory. The use of H₂SO₄ during leaching was reported to markedly enhance overall metal extraction.

Khalid et al. (2019) proposed a hydrometallurgical route for copper recovery from converter slag rich in copper. Mineralogical characterization showed that the main copper-bearing phases were cuprite, delafossite, and metallic copper. The influence of particle size, temperature, acid concentration, agitation intensity, leaching time, and oxidizing conditions was evaluated. Nearly complete copper extraction was achieved under the optimum conditions of 40°C, 2 mol/dm³ H₂SO₄, 60 min leaching time, 0.26 kW/m³ mixing power, and 2000 cm³/min oxygen flow. XRD analysis of the leach residue confirmed the absence of copper-bearing phases after treatment. The study also showed that temperatures at or below 40°C strongly affected Cu and Fe extraction, whereas temperatures above 40°C promoted the dissolution of Ni and Zn. Under the optimized conditions, acid consumption was 23.7 mol H₂SO₄ per kg Cu.

Anand et al. (1980) examined the extraction of copper, nickel, and cobalt from converter and smelter slags using ferric chloride leaching. The converter slag from Ghatsila, India, contained 4.03% Cu, 1.99% Ni, and 0.48% Co, while the smelter slag contained 1.76% Cu, 0.23% Ni, and 0.19% Co. The effects of stirring, leaching duration, temperature, ferric chloride concentration, solid/liquid ratio, and particle size were investigated. Under optimum conditions, 92% Cu, 28% Ni, and 24% Co were extracted from converter slag. For smelter slag, the corresponding recoveries were 54% Cu, 71% Ni, and 44% Co.

In a subsequent study, Anand et al. (1981) attempted to achieve more complete dissolution of metal values by combining reduction roasting with ferric chloride leaching. The variables considered included ferric chloride concentration, leaching time, roasting time, roasting temperature, and type of reducing agent. At temperatures above 750°C, copper recovery decreased, whereas nickel and cobalt recoveries increased. The decrease in copper extraction was attributed to the formation of copper ferrite, as confirmed by leaching tests on synthetic mixtures and XRD analyses. When solid reductants were used above 850°C, nickel recovery decreased slightly, while cobalt recovery remained almost unchanged. Under the optimum conditions, involving slag reduction at 850°C with 10 wt% furnace oil followed by ferric chloride leaching, recoveries of 80% Cu, 95% Ni, and 80% Co were achieved.

Sukla et al. (1986) studied the roasting of copper converter slag with ammonium sulfate and sulfuric acid in order to sulfate copper, nickel, and cobalt and subsequently leach these metals as soluble sulfates with water. For ammonium sulfate roasting, the effects of temperature between 200 and 600°C, roasting time between 15 and 120 min, and ammonium sulfate addition between 0.5 and 2.5 times the stoichiometric amount were investigated. Under atmospheric conditions, using 2.5 times the stoichiometric ammonium sulfate requirement, recoveries of 85% Cu, 81% Ni, and 85% Co were obtained. Similar experiments were also performed with sulfuric acid. In this case, the variables included sulfuric acid addition between 0.25 and 2 times the stoichiometric requirement, roasting temperature between 100 and 300°C, and roasting time between 15 and 120 min. Under optimum conditions, namely roasting at 150°C for 60 min with the stoichiometric amount of H₂SO₄, recoveries of 95% Cu, 90% Ni, and 99% Co were achieved. However, iron contamination was high, reaching 60-80%. Most of the iron in the leach liquor could be removed by precipitation using ammonia liquor and lime. A two-stage sulfuric acid roasting treatment, first at 150°C and then at 650°C, reduced the iron content of the sulfation product to about 3% without causing a major decrease in the recovery of the other metals.

Dimitrijević et al. (2016) investigated the recovery of Cu and Fe from reverberatory furnace slag by sulfuric acid roasting at 150-800°C, followed by leaching with distilled water at 50°C. After sulfation roasting at 600°C and subsequent water leaching, 79% Cu and 6% Fe were extracted. The dissolution of both Cu and Fe was completed within a few minutes and was not significantly affected by leaching temperature.

5. Copper refining slags

Considerable copper losses may occur during fire refining, and the slags generated in copper refining furnaces can contain 1-13% Cu when process variables and other factors affecting copper retention are not properly controlled (Soroush, 1992). Soroush (1992) carried out experimental studies on copper recovery from Sarkuysan fire-refining slags. The results were evaluated to determine the optimum conditions for reducing copper losses and identifying operating parameters that minimize the amount of copper remaining in the slag.

Yıldız et al. (2000) investigated copper recovery from Sarkuysan refining slags by a pyro-hydrometallurgical route based on sodium sulfate roasting followed by sulfuric acid leaching. However, the process resulted in only 65% Cu recovery. In a later study on the same slag material, Arslan et al. (2002) applied size reduction, flotation, and leaching tests to improve the recovery of Cu and Sn. Their results showed that both metals could be efficiently recovered from copper refining slags, demonstrating the potential of these residues for successful recycling.

Tang et al. (2022) proposed a combined treatment involving waste-acid leaching followed by CaO roasting for the recovery of copper and other valuable metals from slags generated in a copper fire-anode furnace. During the first leaching stage, the effects of temperature, leaching time, liquid/solid ratio, and airflow rate on the dissolution of Cu, Fe, and As were examined. At 90°C, a liquid/solid ratio of 9:1, a leaching duration of 4 h, and an airflow rate of 200 cm³/min, leaching efficiencies of 85.32% Cu, 68.41% Fe, and 44.97% As were achieved. The leached slag was then roasted with CaO at 800°C for 4 h using a CaO/slag ratio of 5:1. Subsequent waste-acid leaching of the roasted material increased the Cu leaching rate to 87.05%. Overall recoveries reached 98.10% Cu, 69.60% Fe, and 50.48% As.

Anode furnace slags may contain significant amounts of copper, nickel, tin, lead, and zinc. For this reason, they are commonly recycled to earlier stages of the process, particularly to Peirce-Smith converters. However, because converter feeds already contain high copper levels, excessive recycling of anode furnace slag may reduce process capacity and efficiency, while also promoting impurity build-up in the circuit. To overcome this limitation, Felkl et al. (2024) investigated the separate treatment of anode furnace slags by ferrothermic reduction. Their findings showed that this approach could produce a copper-rich metallic phase and help interrupt impurity accumulation in secondary copper processing. When the iron reductant addition was increased to 150% of the stoichiometric requirement, corresponding to 39.0 g Fe per 100 g slag, the copper content of the secondary slag decreased to 1.12 wt%. However, the iron content of the metallic phase increased to 25.97 wt%, which is undesirable and would require an additional slagging step. With 100% stoichiometric iron addition, equivalent to 26.0 g Fe per 100 g slag, a metallic phase weighing 58.10 g was obtained with 9.07 wt% Fe, while the copper content of the secondary slag was reduced to 1.43 wt%.

Ma et al. (2024) evaluated jatropha oil (JO), a non-edible vegetable oil and potential renewable reductant, for iron recovery from copper slag (CS) through deep reduction. The slag used in their experiments was obtained from a copper refinery in Yunnan and contained 45.24 wt% Fe and 26.60 wt% SiO₂. After drying, the material consisted of gray-black solid particles, 95 wt% of which were smaller than 0.2 mm. The optimum reduction conditions were determined as 3 wt% JO, 1250°C, and 45 min. Under these conditions, the reduced product contained 94.58% Fe, with an iron recovery of 84.97%. The study presented an innovative and more environmentally compatible route for recovering iron from iron-rich furnace slags.

6. Examples from laboratory-scale studies

6.1. Ancient copper slags

Ancient copper slags constitute an important secondary source of valuable metals, particularly copper (Cu) and cobalt (Co). A representative example is provided by the fayalitic slags of the Küre region in Türkiye, which contain approximately 1.24% Cu and 0.53% Co and have been investigated for metal recovery (Bulut et al., 2007). In that study, a combined flotation-roasting-leaching flowsheet was developed in order to maximize the recovery of both metals. The proposed process consisted of crushing, grinding, flotation, roasting of the flotation tailings with pyrite, and subsequent leaching and filtration, as illustrated in Fig. 2.

Flotation was mainly applied for copper recovery. Under optimum conditions, namely pH around 7, particle size below 100 µm, Na₂S as the sulfidizing agent, and xanthate-type collectors, a copper concentrate assaying approximately 10-11% Cu was produced with a recovery of about 77%. In contrast, cobalt responded only weakly to flotation. Nearly 90% of the cobalt remained in the flotation tailings because it was mainly associated with non-flotable mineral phases such as silicates and spinel-type structures. To recover cobalt, the flotation tailings were therefore subjected to pyrite roasting followed by leaching. During roasting, cobalt-bearing phases were converted into more soluble forms, which enabled efficient extraction in the subsequent leaching stage. The leaching experiments showed that cobalt dissolution could reach approximately 85-87% under optimum conditions, namely a roasting temperature of 500°C, a roasting time of 1 h, and a pyrite/slag ratio of 3:1, as shown in Fig. 3.

The flowsheet presented in Fig. 2 demonstrates a clear separation between the recovery routes for copper and cobalt. Copper was recovered in the flotation concentrate, whereas cobalt was extracted from the flotation tailings through roasting followed by water leaching. This staged treatment route allows efficient utilization of the slag by targeting metals present in different mineralogical forms. In addition, the final leach residue, containing approximately 60% Fe, was found to be suitable for use in the iron and steel industry, thereby supporting a near-zero-waste processing strategy.

6.2. Copper smelting and converter slags

Arslan & Arslan (2002) investigated the recovery of Cu, Co, and Zn from copper slags obtained from the Black Sea region of Türkiye by a pyro-hydrometallurgical route proposed as an alternative to flotation. The slag sample used in the experimental study contained 2.64% Cu, 0.095% Co, 0.67% Zn, 47.2% Fe, 0.13% Pb,

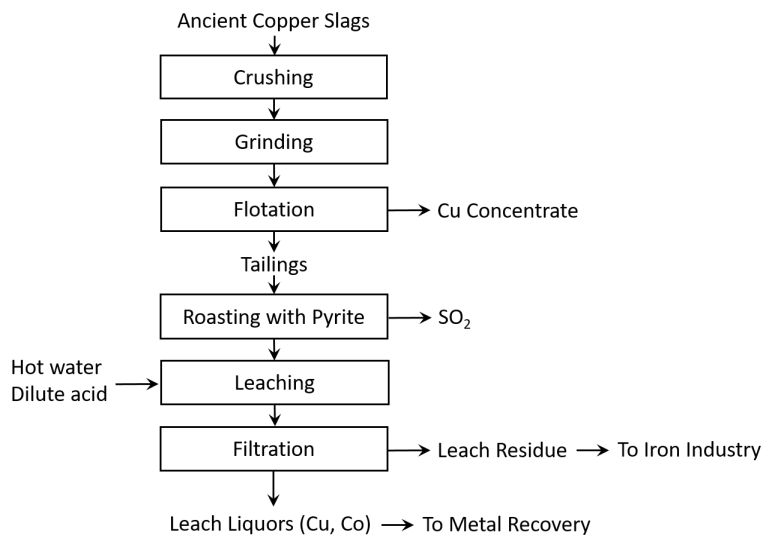


Fig. 2. Proposed flowsheet for the evaluation of Küre ancient copper slag (Bulut et al., 2007)

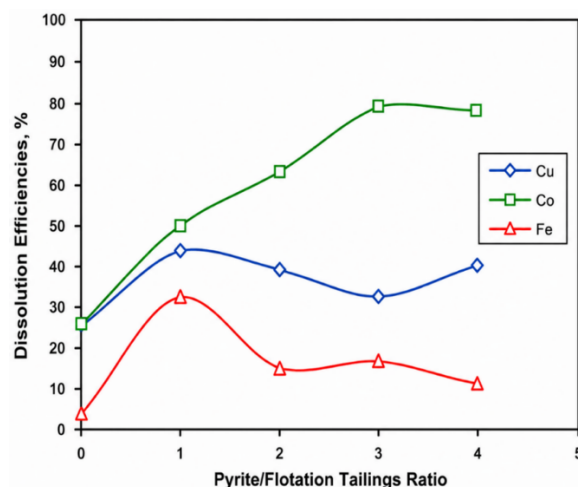


Fig. 3. Effect of pyrite/flotation tailings ratio on metal dissolution at a roasting temperature of 500°C (Bulut et al., 2007)

0.004% Cd, 0.065% Ni, 8.5% Si, and 1.3% S. Microscopic examination and XRD analysis showed that copper was present mainly as bornite, ferrites, and minor metallic copper, whereas zinc, cobalt, and nickel occurred predominantly in silicate and ferrite phases. Iron was mainly associated with a fayalite-type matrix. A mixture of flash-smelting and converter slags supplied by the Black Sea Copper Works, Türkiye, was treated by acid roasting followed either by direct hot-water leaching or by thermal decomposition prior to hot-water leaching, as illustrated in Fig. 4.

Roasting the copper slag mixture with sulfuric acid resulted in the sulfation of slag constituents, in agreement with theoretical expectations. In the leaching tests, the effects of roasting time, acid/slag ratio, roasting temperature, and thermal decomposition before leaching on metal dissolution were examined. Acid roasting followed by hot water leaching showed that the highest overall metal recoveries were obtained at 150°C. At higher roasting temperatures, the sulfation of Co and Zn decreased. After roasting for 2 h at 150°C with an acid/slag ratio of 3/1, the recoveries were 88% Cu, 87% Co, 93% Zn, and 83% Fe, as shown in Table 1. Increasing the acid roasting temperature and duration did not improve the dissolution of Co and Zn, whereas Cu dissolution increased markedly. Extending the acid roasting time to 4 h raised

Cu extraction to 95%. Higher roasting temperatures also promoted the formation of copper sulfate. Complete copper dissolution was achieved by roasting at 250°C for 3 h using an acid/slag ratio of 2/1, as presented in Table 2.

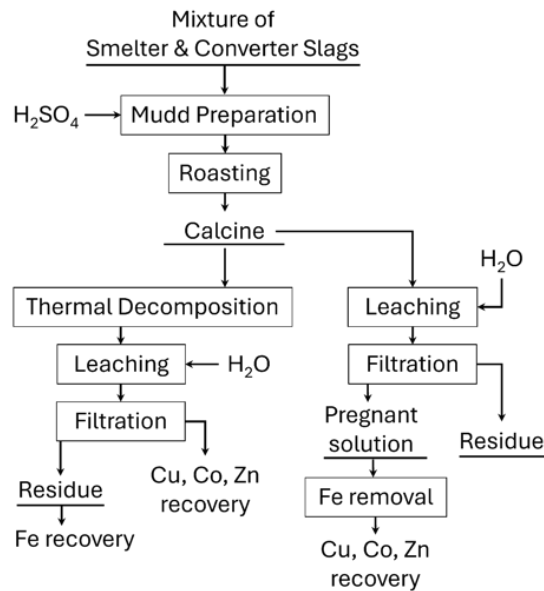


Fig. 4. Recovery of Cu, Co, and Zn from copper smelting and converter slags: acid roasting followed either by direct hot-water leaching (right side) or by thermal decomposition prior to hot-water leaching (left side)

Table 1. Effect of leaching time after acid roasting (at 150°C and a 3/1 acid/slag ratio) on metal leaching recoveries

Time (hours)	Metal Leaching Recoveries (%)			
	Cu	Co	Zn	Fe
0.5	68.64	79.75	83.6	72.90
1	74.13	81.44	82.4	73.86
2	87.80	87.04	92.6	83.51
3	87.63	80.30	84.5	86.07
4	95.43	79.73	93.7	81.31

Table 2. Effect of acid/slag ratio (A/S) on Cu leaching efficiency with the time of roasting at 250°C

Time (hours)	Cu Leaching Recoveries (%) at different A/S ratios			
	1/1	1.5/1	2/1	3/1
0.5	87.01	95.02	92.62	94.02
1	87.44	88.41	96.27	96.68
2	87.44	96.62	94.22	99.42
3	90.94	94.27	100	96.68
4	87.67	93.41	94.22	97.14

Thermal decomposition after acid roasting reduced metal dissolution to some extent. However, after thermal decomposition at 650°C for 2 h, Fe dissolution decreased to almost zero, as shown in Table 3. Although thermal decomposition before water leaching caused slight decreases in the extraction of the valuable metals, it was considered advantageous because the absence of iron dissolution eliminated the need for a separate iron-removal step from the leach solution. Under these conditions, 79% Cu, 66% Co, and 40% Zn were dissolved.

Table 3. Effect of thermal decomposition on metal leaching efficiencies with time at 650°C

Time (hrs)	Metal Leaching Recoveries (%)			
	Cu	Co	Zn	Fe
0.5	91.84	59.70	50.73	18.8
1	85.18	67.68	46.57	3.2
2	78.40	66.21	40.11	--
3	31.78	39.30	35.40	--
4	10.64	29.35	26.95	--

Earlier studies also investigated roasting treatments using ferric sulfate, pyrite, ammonium sulfate, and sulfuric acid. The main results of these studies are summarized in Table 4. Although high dissolution efficiencies were generally achieved for non-ferrous metals, iron dissolution remained an important drawback in many cases. The present study offers an advantage in this respect, since the incorporation of a thermal decomposition stage effectively suppressed iron dissolution. Low or negligible Fe dissolution is particularly beneficial for subsequent metal recovery from the pregnant leach solutions. Dissolved iron increases the load on downstream purification steps and must usually be removed before the recovery of valuable metals by processes such as solvent extraction and/or electrowinning. As emphasized by Ferron (2011), iron separation is one of the major challenges in hydrometallurgical circuits and may, in some systems, dominate the purification stage. Therefore, minimizing Fe dissolution simplifies solution purification, lowers the risk of co-extraction or product contamination during solvent extraction, and reduces the need for additional iron precipitation or bleed streams. Furthermore, limiting iron dissolution may decrease oxidant consumption, since high dissolved iron concentrations require continuous control of the ferric/ferrous redox balance in solution.

Table 4. Summary of metal recoveries from copper smelter and converter slags with roasting followed by water leaching

Type of Copper Slags	Process Steps	Metal Recovery	Reference
Smelting slags	Roasting with ferric sulfate followed by water leaching	93% Cu, 38% Co, 13% Ni, 59% Zn	Altundoğan and Tümen, 1997
Converter slag	Roasting with ammonium sulphate followed by water leaching	85% Cu, 81% Ni, 85% Co	Sukla et al., 1986
Converter slag	Roasting with sulfuric acid, followed by water leaching	95% Cu, 90% Ni, 99% Co	Sukla et al., 1986
Reverberatory furnace slag	Roasting with sulfuric acid, followed by water leaching	79% Cu, 6% Fe	Dimitrijevic et al., 2016
Smelting slag	Roasting with pyrite followed by leaching	95% Cu, 2% Fe	Tümen and Bailey, 1990
Mixture of flash smelting and converter slag	Roasting with sulfuric acid, followed by hot water leaching	88% Cu, 87% Co, 93% Zn, 83% Fe	Present study
Mixture of flash smelting and converter slag	Roasting with sulfuric acid, followed by thermal decomposition, combined with hot water leaching	79% Cu, 66% Co, 40% Zn, 0% Fe	Present study

6.3. Copper refining slags

Arslan et al. (2002) investigated Sarkuysan copper refining slags by applying size reduction, flotation, and leaching to improve the recovery of Cu and Sn. Chemical analysis indicated that the slag contained

approximately 22% Cu and 2.3% Sn. Microscopic observations showed that some heavy metals, including Pb, Sn, Bi, Sb, and As, were enclosed within metallic copper, especially in acidic slags, whereas others were distributed within the silicate matrix.

Through size reduction, classification, and flotation, a concentrate assaying 49.67% Cu and 1.69% Sn was produced, with recovery efficiencies of 81.12% for Cu and 27% for Sn. The results of the concentration tests are summarized in Table 5. This concentrate was considered suitable for recycling in pyrometallurgical copper production. The remaining Cu and Sn in the flotation tailings were subsequently subjected to HCl leaching.

Table 5. Summary of concentration test results (Arslan et al., 2002)

Size Reduction and Flotation Test Results					
Products	Weight (%)	Cu (%)	Sn (%)	Cu Recovery (%)	Sn Recovery (%)
+2 mm	3.3	44.42	1.84	6.67	2.65
+150 m	4.1	82.70	0.66	15.38	1.33
Flotation Concentrate	26.7	45.49	1.85	55.12	21.68
Middlings	7.1	17.08	2.34	5.49	7.52
Tailings	58.8	6.50	2.57	17.33	66.82
Total	100	22.04	2.26	100	100
Combined Tests Results					
Concentrate	36	49.67	1.69	81.12	27
Tailings	64	6.5	2.58	18.88	73
Total	100	22.04	2.26	100	100

In the leaching experiments, the effects of solvent type, solvent concentration, temperature, and leaching time on the extraction efficiencies of Cu and Sn were examined. Among the solvents tested, namely ferric sulfate, HNO_3 , and HCl, the highest recoveries were obtained with HCl, and the best leaching performance was achieved at an HCl concentration of 150 g/dm³ (Arslan et al., 2002). At this acid concentration, both Cu and Sn leaching efficiencies increased with increasing temperature and leaching time, as presented in Figs. 5 and 6. According to Figs. 5 and 6, Cu and Sn leaching efficiencies after 2 h of leaching at 80°C were 100% and 90.3%, respectively. Sn recovery also reached 100% after 6 h of leaching at 80°C.

Overall, the study demonstrated that copper refining slags can be effectively treated for the recovery of both Cu and Sn, indicating a successful recycling route. The experimental flowsheet proposed for the evaluation of Sarkuysan copper fire-refining slags is shown in Fig. 7.

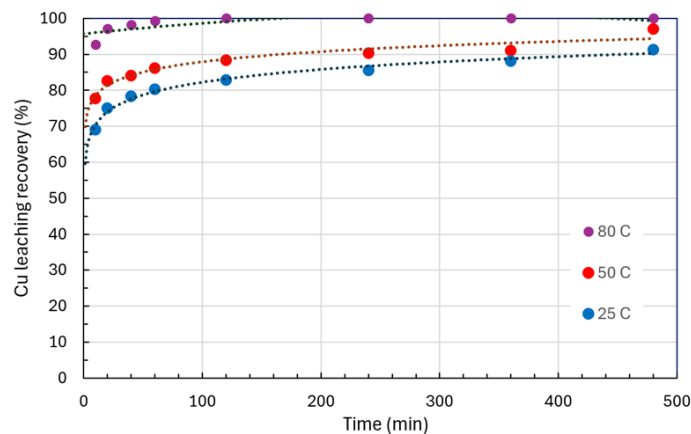


Fig. 5. Effect of temperature on Cu leaching recoveries

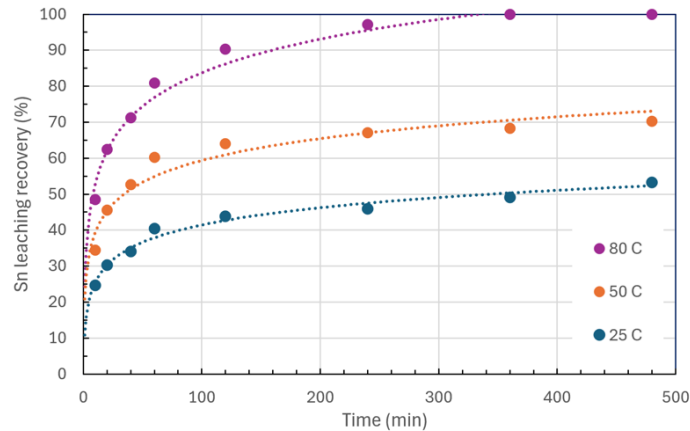


Fig. 6. Effect of temperature on Sn leaching recoveries

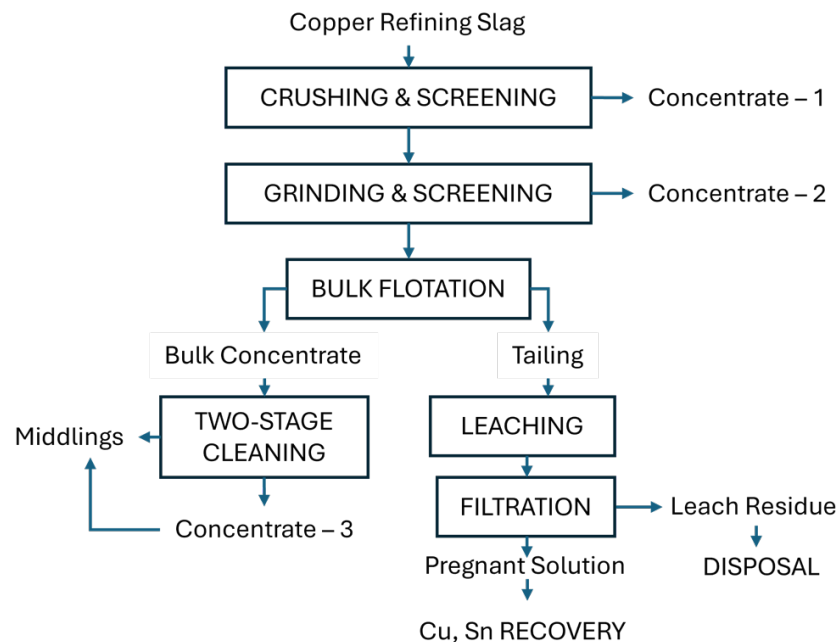


Fig. 7. Proposed flowsheet for the evaluation of Sarkuysan copper fire refining slags (produced from Arslan et al., 2002)

7. Environmental impacts and sustainability of slag treatment

Large amounts of metallurgical slags are produced worldwide each year, but a considerable fraction of these residues is still stockpiled or discarded without effective utilization. Copper slags are of particular concern because they combine environmental risk with considerable resource potential. Due to the presence of hazardous elements and their possible release under leaching conditions, uncontrolled disposal may result in soil contamination as well as pollution of surface and groundwater systems (Adilov et al., 2025; Klaffenbach et al., 2023). Accordingly, recent research increasingly considers copper slag not simply as an industrial waste, but as a secondary raw material that should be managed in accordance with sustainability and circular economy concepts.

The available literature identifies three main approaches for copper slag treatment and valorization: physical beneficiation, pyrometallurgical processing, and hydrometallurgical extraction (Li et al., 2023).

Physical methods, including flotation, magnetic separation, and gravity separation, are generally applied to concentrate valuable phases prior to further processing. Pyrometallurgical routes can be effective for certain slag types; however, their high energy requirements may restrict their economic and industrial applicability. Hydrometallurgical methods provide greater operational flexibility and may be more suitable for low-grade or mineralogically complex slags. Although the technical feasibility of many proposed routes has been demonstrated, detailed economic assessments remain limited, which remains one of the main obstacles to large-scale implementation.

Table 6 compares the main copper slag treatment routes in terms of metal recovery performance, energy requirement, reagent consumption, and environmental impact. As presented in Table 6, flotation is one of the more environmentally compatible options because of its relatively low energy demand and limited reagent consumption, although its applicability is mainly restricted to copper recovery. Pyrite roasting followed by leaching can improve cobalt extraction, but it also requires additional thermal energy and may generate gaseous emissions that must be properly controlled. Direct acid leaching and acid-roasting processes can provide high metal recoveries; however, they often involve considerable chemical consumption and, more importantly, significant iron dissolution, which complicates downstream solution purification.

An important conclusion drawn from Table 6 is that adding a thermal decomposition stage can substantially improve the sustainability of the overall process by suppressing iron dissolution. This reduces the need for additional purification operations before recovering valuable metals from the leach solution. Among the evaluated routes, the integrated flotation-roasting-leaching flowsheet provides the most balanced performance, since it combines selective metal recovery with moderate energy and chemical requirements and allows the possible reuse of iron-rich residues. Such an integrated strategy is therefore consistent with circular economy objectives and supports the development of near-zero-waste approaches for copper slag valorization.

Beyond metal recovery, the direct use of copper slag as a material resource represents another important dimension of sustainable slag management. The studies reviewed indicate that copper slag can be utilized in cement and concrete production, as an iron-correcting additive in clinker manufacturing, as aggregate in road base and asphalt applications, and as a raw material for bricks, artificial stone, glass-ceramics, slag wool, inorganic polymers, catalysts, and thermal energy storage materials (Klaffenbach et al., 2023; Li et al., 2021; Phiri et al., 2021; Priya et al., 2024). These applications can reduce the demand for natural raw materials, limit the need for landfill disposal, and enable the conversion of industrial residues into value-added products. From this perspective, slag reuse should be considered not only as a waste-management option, but also as a route toward more sustainable construction practices and advanced materials development. However, before copper slags are used as material resources, recoverable metals should be extracted as far as possible, and environmental safety issues, particularly the leaching of heavy metals, must be carefully evaluated and controlled to ensure sustainable utilization (Klaffenbach et al., 2023; Priya et al., 2024).

Copper slags may also provide environmental benefits in specific applications (URL-1, 2025). Modified copper slag has been suggested as a potential adsorbent for the removal of heavy metals and phosphates from wastewater. In addition, its physicochemical properties may be useful for soil remediation and the stabilization of contaminated sites. Finely processed slag may also be used as a functional filler in polymers and friction materials. These examples show that the potential applications of copper slag are not limited to extractive metallurgy and construction, but may also extend to environmental technologies and advanced material systems.

Despite these promising opportunities, several barriers still restrict wider utilization. The most critical issues include variability in slag composition, uncertainties regarding long-term leaching stability, the cost of technologies required for high-value recovery, and limited market confidence in products derived from slag. Broader industrial acceptance will require reliable technical standards, environmental safety criteria, quality certification procedures, and supportive regulatory frameworks. Without these measures, the transition from low-value disposal to high-value utilization will remain only partially realized.

Table 6. Sustainability-environmental impacts of some copper slag treatment processes

Process	Energy Demand	Chemical Consumption	Environmental Impact	Sustainability Assessment
Flotation	Low	Low (collectors, frother, Na ₂ S)	Minimal emissions, low waste generation	Highly sustainable for selective Cu recovery; insufficient alone for Co
Direct acid leaching	Low-Medium	High (strong acids, oxidants)	High Fe dissolution, solution purification challenges, and potential gel formation	Chemically intensive; lower sustainability due to downstream processing burden
Pressure leaching	High	Medium	Controlled Fe dissolution; complex operation	Highly efficient but capital-intensive and energy-intensive
Pyrite roasting + water leaching	Medium-High (thermal treatment ~500°C)	Medium (pyrite, acid/water)	SO ₂ generation during roasting; manageable with gas treatment	Effective for Co recovery; requires emission control but enables multi-metal recovery
Integrated flotation + roasting + water leaching	Medium	Medium	Residue reusable (~60% Fe), reduced waste	Most sustainable option; supports circular economy and near-zero-waste strategy
Acid roasting + water leaching	Medium	High (H ₂ SO ₄)	High Fe dissolution increases purification load	High recovery but less sustainable due to iron contamination
Acid roasting + thermal decomposition + water leaching	Medium-High	Medium-High	Minimal Fe dissolution → cleaner solution	More sustainable due to the elimination of the iron removal step
Carbothermic reduction	Very high (≥850–1400°C)	Low	High CO ₂ emissions, slag modification required	Low sustainability due to high energy and carbon footprint

8. Conclusions

This review evaluates the characteristics of copper slags generated during smelting, converting, refining, and ancient metallurgical activities, together with the main processes developed for recovering valuable metals from these materials. The studies discussed show that slag composition, mineralogical assemblage, cooling history, and formation conditions strongly influence both process selection and metal recovery efficiency. The literature also reflects a clear development in slag-treatment strategies, progressing from conventional pyrometallurgical methods toward more selective, integrated, and environmentally compatible flowsheets. By bringing together studies on copper slags from both industrial operations and

historical deposits in Türkiye, this review further emphasizes the importance of these materials as secondary metal resources.

Overall, copper slags should not be regarded merely as residues requiring disposal. When properly characterized and processed, they can contribute to sustainable metallurgy by enabling metal recovery, reducing the demand for primary resources, and supporting circular-economy practices. Their potential also extends beyond extractive metallurgy, since suitably treated slags may be used in construction materials, environmental applications, and functional material production. The most rational approach is therefore an integrated strategy in which valuable metals are first recovered where technically and economically feasible, and the remaining slag matrix is then safely utilized in appropriate material applications. Such an approach would reduce environmental risks, conserve natural resources, and support the broader objectives of sustainable development and near-zero-waste slag valorization.

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