Pressure Leaching of Copper Slag Flotation Tailings in Oxygenated Sulfuric Acid Media

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1. INTRODUCTION

Metals were discovered and first used approximately 10,000 years ago. Copper was the first metal used as a substitute for stone by humans and is still an important metal in industry today. Smelting is the pyrometallurgical process used to produce copper metal with the use of mining concentrates or copper scrap as the primary source of feed. In 2019, world copper production reached nearly 20.4 million tons. Afterward, it increased slightly to 21.0 million tons at the end of 2021 due to mines returning to full production, as well as the ramp-up of new mines starting in 2021. Copper slag is a solid byproduct obtained during the matte smelting, converting, and refining of copper. It has been estimated that for every ton of copper produced, approximately 2.2–2.5 tons of slag is generated as a result of the relatively low grades of copper concentrates now available. There are several copper smelting plants throughout the world, and this has resulted in the production of approximately 40 million tons per year of slag, which is regarded as waste. This slag is generally disposed of near smelter sites. Although the properties of copper slag in flash smelting, reverberatory furnace smelting, and other processes are generally similar, these slags can have different characteristics depending on how they are cooled from the smelter. When copper slag is crystalline, the major phases are usually fayalite (Fe₅SiO₄), along with other silicates. However, copper-containing phases in slag can differ, and they may be in the form of oxides, sulfides, or a mixture of both. One of the other main components of slag is the silica phase, which consists of both fayalite and glassy silicate phases.

Received: May 10, 2022
Accepted: September 14, 2022
Published: September 26, 2022
emission of toxic gas, and possible recovery of leachants. Hydrometallurgical processes which include leaching (acid leaching, alkaline leaching, oxidative leaching, water leaching, pressure leaching, and bioleaching), ion exchange, chelating, adsorption, precipitation, and solvent extraction are successfully applied to recover precious metals from various wastes.

Furthermore, Lin and Chiu showed that hydrometallurgy offers a possibility and an opportunity to convert used dry batteries into pure metals or metal salts with little energy needed. In particular, cobalt is a metal that is absolutely critical in battery storage for electric vehicles. It is relevant that cobalt-bearing tailings are of particular importance because cobalt has been deemed a "critical metal" by the United States, Canada, and the European Union (EU) based on its relatively high economic importance and supply risk. Lithium-based batteries, such as LCO (LiCoO$_2$), LMO (LiMn$_2$O$_4$), LTO (Li$_2$TiO$_3$), NCA (LiNiCoAlO$_2$), NMC (LiNiMnCoO$_2$), and LPF (LiFePO$_4$) batteries, which use various combinations of anode and cathode materials, are currently the most widely used batteries in electric vehicles. NCA and NMC batteries in particular have very high market shares in electric vehicles. For example, the average 100 kWh lithium-ion battery pack (NCA) used to power a Tesla Model X has approximately 20 kg of cobalt. For this reason, cobalt has become an essential metal in the rechargeable battery manufacturing and electric car industries.

Several researchers have investigated the extraction of metals from slags using various extractants, such as ferric chloride, ferric sulfate, ammonium chloride, chlorine solution, sulfuric acid, hydrochloric acid, ammonium hydroxide, nitric acid, and aqua regia as leaching agents. Sulfating or chloride roasting can be applied to convert sulfide phases to soluble sulfate compounds prior to water or dilute acid leaching. Ammonium chloride was investigated as a chloride agent, whereas sulfating agents included ferric sulfate, ammonium sulfate, sodium sulfate, and sulfuric acid. To improve extraction efficiency, additional treatments in leaching systems, such as adding oxidants (H$_2$O$_2$, K$_2$Cr$_2$O$_7$, and NaClO$_3$), or applying oxidative pressure, have also been investigated. Moreover, Potysz et al. and Tian et al. presented detailed reviews on the recovery, leaching, and environmental evaluation of precious metals from copper slags, as well as the formation mechanism of slags and their chemical, physical, and phase composition.

Figure 1. Simplified flowchart for the copper smelting process in the Eti Bakır Company (FSF: flash smelting furnace, CF: converter furnace).
extraction efficiencies of copper, cobalt, and zinc, the leaching behavior of iron was examined under autoclave conditions.

2. EXPERIMENTAL SECTION

2.1. Materials. The experimental work was carried out on a representative sample of SFT obtained by the mining company Eti Bakır (Türkiye). The Eti Bakır Company basically consists of six main facilities (Figure 1): a copper smelter plant, a flotation plant, a sulfuric acid production plant, an electrolysis plant, an oxygen plant, and a crystallized ammonium sulfate plant. In the copper smelter plant, 99.9% pure cathode copper is produced using flash furnace technology. A simplified flowchart of the plant is given below. In the plant, flash and converter furnace slags are mixed in certain proportions and then subjected to a flotation process. The concentrate containing copper is sent back to the flash furnace. The SFT contains considerable amounts of copper, cobalt, and zinc.

The SFT sample and leach residue were characterized by X-ray diffraction (XRD). The XRD patterns were recorded on a Rigaku X-ray diffractometer using Cu Kα radiation with a scanning rate of 2° min⁻¹ from 3 to 80°. The generator voltage and current were 40 kV and 30 mA, respectively. Rietveld refinement analysis using XPert HighScore Plus software (PANanalytical) was performed to obtain the percentages of different phases in the samples. X-ray photoelectron spectroscopy (XPS) analyses were performed with a Thermo Scientific K-Alpha using an Al Kα X-ray source (microfocused monochromator) high-performance XPS spectrometer. Survey scans for the detection of all elements were carried out at a pass energy of 30 eV and a step size of 0.1 eV, enabling high-resolution spectra to be obtained. Grain size analysis was performed using a Partica LA-950V2 laser diffraction particle size distribution analyzer (Horiba) in wet mode. According to the particle size distribution curve (Figure 2), d_{50} and the mean particle size of the SFT sample were determined to be 58 and 35 μm, respectively. Elemental analysis of the filtrate or solid sample was performed by inductively coupled plasma optical emission spectrometry (ICP–OES) (Varian 710-ES). All chemical reagents (Merck) used in the pressure leaching experiments were of analytical grade. The samples used in the leach tests contained averages of 0.50% Cu, 0.15% Co, 3.93% Zn, 1.53% Al, 0.57% Ca, 0.14% S, and 39.50% Fe. The full chemical analysis results of the SFT sample are given in Table 1.

The elemental composition and chemical oxidation states of surface and near-surface species can be detected by XPS analysis. Therefore, XPS analysis was conducted to assess the chemical states of both the SFT sample and leaching residue. Many clear peaks summarized in Table 2 were observed for the SFT sample. No sulfur (S) peak was detected by XPS because of the high flotation recovery of sulfide minerals in the copper slag prior to leaching (Figure 1). For this reason, copper, cobalt, and zinc in the flotation tailings were mostly in the oxide-silicate or metallic forms. According to mineralogical examination, the SFT sample contained mainly fayalite (Fe₅SiO₄, 81.5%), magnetite (Fe₃O₄, 11.1%), zinc iron oxide (franklinite, (Zn₀.₉₈₆Fe₀.₀₁₃)Fe₃O₄, 4.0%), cristobalite (SiO₂, 1.5%), and clay-mica (KA₆(Si₆Al)₂-2(OH)₂, 1.8%) (Figure 3).

2.2. Method. The pressure leaching experiments were conducted in a 1 L titanium autoclave (Parr, Inc.). A schematic diagram of the autoclave system with a heating mantle, PID temperature controller, variable speed stirrer, sampling dip tube, and internally mounted serpentine-type cooling coil is given in Figure 4.

The experiments were carried out in batch mode using 100, 150, 200, and 250 g of SFT (d_{50} = 58 μm) and various concentrations of sulfuric acid, at oxygen pressure (Pₒ₂) of 0.7 MPa. The reaction vessel was first preheated for approximately 60–70 min. Then, oxygen and acid were added at the preset temperature, and the oxygen partial pressure was adjusted to the desired level and maintained constant for the duration of the experiment. The stirring rate was kept constant at 500 rpm during the test. In the experiments, 10–15 mL of slurry was sampled by a sampling dip tube. The slurry was cooled immediately, centrifuged, and filtered with a 0.45 μm PTFE syringe filter. After 2 h of residence time, the oxygen flow was shut down, and the autoclave was water-cooled to less than 60 °C. After solid–liquid separation by vacuum filtration, the solid was washed with deionized water several times. The leaching residues were dried for at least one day at 80 °C. Elemental analysis of the filtrate or solid residue was performed by ICP.

The percentage extraction efficiency of cobalt, copper, zinc, and iron during leaching was calculated according to the following formula

\[
R = \frac{C_M \times V \times 100}{C_O \times M}
\]

where R (%) is the extraction efficiency of metal (Co, Cu, Zn, or Fe); C_M (g/L) is the elemental concentration determined by ICP–OES in the leachate samples; V (L) is the total volume of the acid leaching solution; C_O (%) is the metal content of Co, Cu, Zn, or Fe in the slag sample; and M (g) is the mass of slag used.

Moreover, six additional tests were conducted under optimal leaching conditions for repeatability, and the percent extraction of metals was reported as the average ± standard deviation.

3. RESULTS AND DISCUSSION

3.1. Effect of H₂SO₄ Concentration. A series of high-pressure leaching experiments were carried out by varying the addition amount of sulfuric acid from 100 to 500 kg/t SFT at 220 °C with a leaching time of 2 h, an S/L ratio of 1:5 (i.e., 1 kg

![Figure 2. Particle size distribution plot of the slag sample. The y-axis q(%) indicates the amount of each size by volume.](image-url)
The dissolution of metal increased significantly with increasing sulfuric acid concentration. The extraction efficiency of Cu, Co, and Zn improved with increasing sulfuric acid concentration up to 250 kg/t. Figure 5 shows that the extraction of cobalt, copper, and zinc increased from 78.6 to 98.2%, 69.2 to 94.7%, and 74.7 to 93.3%, respectively, when the initial acid concentration increased from 100 to 250 kg/t (corresponding to 20 and 50 g/L). The effect of adding more acid on the leaching efficiency of base metals was limited. However, when the acid concentration was higher than 250 kg/t, iron dissolution significantly increased.

Table 1. Chemical Analysis Results for the SFT Sample

| element | unit | SFT sample content | element | unit | SFT sample content | element | unit | SFT sample content |
|---------|------|-------------------|---------|------|-------------------|---------|------|-------------------|
| Ag      | ppm  | 2                 | K       | %    | 0.70              | Sc      | ppm  | <10               |
| Al      | %    | 1.53              | La      | ppm  | <50               | Sr      | ppm  | 120               |
| Ba      | ppm  | 2340              | Mg      | %    | 0.35              | Th      | ppm  | <50               |
| Bi      | ppm  | 40                | Mn      | ppm  | 230               | Ti      | %    | 0.07              |
| Ca      | %    | 0.57              | Mo      | ppm  | 480               | Ti      | ppm  | 50                |
| Cd      | ppm  | 50                | Na      | %    | 0.23              | U       | ppm  | <50               |
| Co      | ppm  | 1480              | Ni      | ppm  | 10                | V       | ppm  | 60                |
| Cr      | ppm  | 480               | P       | ppm  | 90                | W       | ppm  | <50               |
| Cu      | ppm  | 5000              | Pb      | ppm  | 3230              | Zn      | %    | 3.93              |
| Fe      | %    | <50               | S       | ppm  | 0.14              | SiO₂    | %    | 29.27             |
| Ga      | ppm  | <50               | Sb      | ppm  | 240               |         |      |                   |

Table 2. X-ray Photoelectron Spectroscopy (XPS) Analysis Result of the SFT Sample

| peak name | binding energy (eV) | FWHM (eV) | area (P) | atomic (%) |
|-----------|---------------------|-----------|----------|------------|
| O 1s      | 531.96              | 3.21      | 738 994.9| 55.13      |
| Zn 2p     | 1022.25             | 2.77      | 195 546.2| 1.6        |
| Fe 2p     | 712.16              | 5.74      | 398 700.9| 2.34       |
| Si 2p     | 102.96              | 2.94      | 87 565.9 | 16.81      |
| Mg 1s     | 1304.14             | 2.87      | 40 407.6 | 2.02       |
| C 1s      | 285.12              | 2.79      | 67 348.4 | 14.42      |
| Cu 2p     | 935.01              | 3.97      | 154 657.3| 0.67       |
| Pb 4f     | 139.20              | 2.94      | 51 013.4 | 0.19       |
| Cl 2p     | 199.44              | 1.82      | 6634.6   | 0.45       |
| K 2p      | 294.39              | 1.65      | 10 193.0 | 0.5        |
| Co 2p     | 784.36              | 10.12     | 90 426.8 | 0.41       |
| Al 2p     | 75.03               | 4.28      | 9764.5   | 4.61       |
| Ca 2p     | 351.77              | 3.10      | 14 037.0 | 0.42       |
| Na 1s     | 1072.20             | 1.59      | 5290.3   | 0.43       |

Figure 3. X-ray diffraction pattern (a) and distribution of phases (b) of the SFT sample.

Figure 4. Experimental setup for pressure leaching.
(from 0.1 to 5.5%) with increasing initial acid concentration because of the redissolution of hematite formed in the leaching residue, which increases as the amount of acid added increases. There is a positive correlation between extraction efficiency and acid concentration, meaning that stronger acidity enhances metal extraction.\textsuperscript{32,33,35,37,38,53,59} Consequently, further tests were carried out with the addition amount of sulfuric acid fixed at 250 kg/t to achieve the highly selective leaching of Co, Cu, and Zn to inhibit the Fe dissolution and entry into the leaching solution. Moreover, experimental studies of metal extraction with strong acids also showed an important limitation due to the formation of silica gel (eq 2), which makes metal extraction and pulp filtration much more difficult.\textsuperscript{32,34,53,56,72} 

\[2\text{MeO} \times \text{SiO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{MeSO}_4 + \text{H}_4\text{SiO}_4 (\text{gel})\]  

\((\text{Me} = \text{Fe}, \text{Co}, \text{Zn}, \text{Cu})\)  

\((2)\)
3.2. Effect of Leaching Temperature on Metal Extraction. The leaching temperature also plays a significant role in metal extraction. Figure 6 shows the effect of leaching temperature on metal extraction with an acid addition amount of 250 kg/t, leaching time of 120 min, and S/L ratio of 1:5. Figure 6 shows that the extraction efficiency of cobalt, copper, and zinc was significantly affected by changes in temperature from 180 to 240 °C and that the maximum metal extraction was obtained at 220 °C. Further increasing the temperature had a slight influence. The dissolution temperature was found to be the most effective factor controlling the dissolution kinetics during oxidative pressure acid leaching. Increasing the temperature had an increasing effect on cobalt, copper, and zinc leaching recovery. At 220 °C, the extraction efficiencies of cobalt, copper, and zinc reached 96.4, 93.3, and 92.2% in the first 60 min, respectively. Similar findings were reported by Liao et al.\textsuperscript{73} They stated that when the temperature increased from 140 to 200 °C, under a $H_2SO_4$ concentration of 0.4 mol/L, S/L ratio of 1:6, and 0.6 MPa, the leaching efficiency of Cu increased from 58.3 to 95.1% for the leaching of copper smelting slag. As shown in Figure 6d, the total iron extraction was 1.3% at 180 °C, 1.1% at 200 °C, 0.6% at 220 °C, and 0.5% at 240 °C after 2 h. Changing the leaching temperature under oxidative conditions and a certain S/L ratio had no significant effect on iron dissolution. In all cases, iron in the fayalite, magnetite, and franklinite phases is easily dissolved into solution under acidic conditions. The oxidation of Fe$^{2+}$ with oxygen gas is an integral part of the precipitation process. The hydrolysis of ferric iron is favored at high temperatures and low pHs ($P_{O_2}$ $>$ 0.5 MPa, $t$ $>$ 185 °C). Under this condition, while iron precipitation takes place via simultaneous oxidation of Fe$^{2+}$ and hydrolysis of Fe$^{3+}$, other ions remain in solution. Thus, hydrolysis is a very efficient way to selectively remove iron from solution. The reactions for the oxidation and hydrolysis of iron (hematite precipitation) in sulfate media are given by eqs 3–5.

Ferrous sulfate oxidation to ferric sulfate

$$2FeSO_4(aq) + 1/2O_2(g) + H_2SO_4(aq) \rightarrow Fe_3(SO_4)_3(aq) + H_2O$$

(3)

Ferric sulfate hydrolysis to hematite

$$Fe_3(SO_4)_3(aq) + 3H_2O \rightarrow Fe_2O_3(s) + 3H_2SO_4(aq)$$

(4)

Overall: 2FeSO_4(aq) + 1/2O_2(g) + 2H_2O

$$\rightarrow Fe_2O_3(s) + 2H_2SO_4(aq)$$

(5)

3.3. Effect of Oxygen Partial Pressure. Oxygen is the main oxidant in the high-pressure leaching process of slags and plays a decisive role in the leaching processes. Oxygen considerably affects not only the dissolution of some metals or...
metal minerals but also the oxidation and hydrolysis of iron in slag. The oxidation reaction of ferrous sulfate with oxygen gas occurs in two physicochemical steps: (a) the mass transfer of oxygen from gas into the liquid phase and (b) the homogeneous oxidation of ferrous sulfate with oxygen (see eq 3). The solubility of oxygen in water decreases gradually as the temperature rises (from 0 to 100 °C). However, the solubility of oxygen in water increases with increasing temperature above the boiling point of water. In addition, an increase in oxygen partial pressure causes a significant increase in oxygen solubility. The effect of oxygen partial pressure on the degree of leaching of the SFT sample was studied at a leaching temperature of 240 °C. However, the solubility of oxygen in water increases with increasing temperature above the boiling point of water. In addition, an increase in oxygen partial pressure causes a significant increase in oxygen solubility. The effect of oxygen partial pressure on the degree of leaching of the SFT sample was studied at a leaching temperature of 240 °C, an acid concentration of 250 kg/t, an S/L ratio of 1:5, a particle size of 58 μm, and time of 120 min. Figure 7 shows the variations in the extraction efficiencies of cobalt, copper, and zinc as a function of oxygen partial pressure in the range of 0–2.1 MPa. Figure 7 shows that with increasing oxygen partial pressure, the dissolution of copper, cobalt, and zinc increased. At a 0.7 MPa oxygen partial pressure, the extraction efficiencies of cobalt, copper, zinc, and iron were 97.4, 93.9, 92.7, and 0.5%, respectively, whereas extraction efficiencies of 24.5, 5.3, 26.3, and 13.1% were achieved in the experiment without oxygen supply. It can be concluded from the results presented in Figure 7 that the optimal partial pressure of oxygen is 0.7 MPa and a further increase did not significantly change the degree of leaching of any of the metals. In addition, oxygenated conditions appear to be a factor promoting metal extraction with the simultaneous accomplishment of a low iron extraction efficiency. Increased oxygen pressure greatly improves the dissolved oxygen content in solution and increases the gas—liquid contact area, thereby accelerating the oxidation rate of Fe²⁺ to Fe³⁺, realizing rapid iron precipitation of the leaching solution and enhancing base metal extraction. Moreover, an increase in oxygen pressure accelerates the oxidation reactions of sulfide forms such as CuS, Cu₂S, Cu₅S₆, Cu₅Fe₅S₂₉, and CuFeS₂ that can exist in copper slag or SFT. Altundogan et al.⁵⁶ used potassium chromate (K₂Cr₂O₇) as an oxidant in sulfuric acid leaching of converter copper slag. They concluded that oxidant addition improves copper leaching, whereas it has adverse effects on the extraction of Co, Zn, and Fe. Urosevic et al.⁷¹ studied the effect of ferric sulfate or hydrogen peroxide on the leaching of copper slag and SFT using sulfuric acid. They reported that the highest copper extraction efficiency (63.4% when using 3 M H₂O₂ and 1 M H₂SO₄) was attained with hydrogen peroxide at room temperature. Banza et al.⁵⁵ investigated hydrogen peroxide as an oxidant in sulfuric acid media. According to the results reported in this work, H₂O₂ addition to the leaching system considerably decreased iron dissolution from 90% to less than 5%, while it increased copper recovery from 60 to 85% at 80 °C and did not affect cobalt or zinc recovery. The effect of hydrogen peroxide on the extraction of metals in sulfuric acid solutions using copper smelter flotation tailings was also studied by Yiğit et al.⁵⁸ They reported that a high leaching efficiency was achieved for copper (100%), zinc (86.3%), and iron (94.6%), but the extraction of cobalt was consistently limited to ≤10.7% even with a fine size (d₅₀ = 27 μm). High-pressure oxidative acid leaching of copper converter slag⁵⁵ converter slag, and pyrrhotite tailings,⁶⁶ nickel smelter slags,⁷⁴ and historical copper slag⁷⁵ yielded high leaching efficiencies in the range of 91–99% for valuable metals such as Ni, Cu, Co, and Zn. Recently, a study on the kinetics of copper extraction from copper smelting slag by pressure oxidative leaching in sulfuric acid solution was presented by Shi et al.⁷⁶ They reported that different leaching stages have different controlling steps according to the shrinking

![Figure 8](https://doi.org/10.1021/acsomega.2c02903)
core model: leaching is controlled by chemical reactions in the early stage, then mixed control occurs, and finally leaching is controlled by diffusion of the solid product layer. They found that the apparent activation energies of the chemical reaction-controlled and solid product layer diffusion-controlled processes were 47.3 and 11.35 kJ/mol, respectively.

In the present work, a high extraction efficiency (>92%) and selective dissolution of base metals for Co, Cu, and Zn were achieved within 45−60 min at 220 °C and a 50 g/L initial H₂SO₄ concentration. The general reactions for the leaching of Cu, Co, Ni, and Zn in slag can be written as follows:

Metal/metal oxide/sulfide/silicate (Me = Cu, Co, Zn, Ni, Fe) leaching by acid

\[
\begin{align*}
\text{Me}^{2+} + 2\text{H}^+ + \text{H}_2\text{O} & \rightarrow \text{Me}^{3+} + \text{H}_2\text{O} \\
\text{MeO}^{2-} + 2\text{H}^+ & \rightarrow \text{Me}^{2+} + \text{H}_2\text{O} \\
\text{MeS}^{2-} + 2\text{O}_2 & \rightarrow \text{MeO}^{2-} + \text{H}_2\text{O} \\
\text{Fe}_2\text{SiO}_4^{2-} + 4\text{H}^+ & \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{SiO}_4^{2-} \\
\text{Fe}_3\text{O}_4^{2-} + 8\text{H}^+ & \rightarrow 2\text{Fe}^{3+} + 2\text{Fe}^{2+} + 4\text{H}_2\text{O} \\
\text{ZnFe}_2\text{O}_4^{2-} + 8\text{H}^+ & \rightarrow \text{Zn}^{2+} + 2\text{Fe}^{3+} + 4\text{H}_2\text{O}
\end{align*}
\]

Fayalite, magnetite, and franklinite are dissolved by sulfuric acid, releasing ferrous and ferric iron into solution (eqs 9−11).

3.4. Effect of Solid/Liquid (S/L) Ratio on Metal Extraction. The S/L ratio used in metal extraction is one of the most important parameters for designing process equipment. Its optimum value depends on other parameters as well. Usually, higher recovery efficiencies can be achieved when the pulp density is lower due to the greater contact of the leachate with the surface of solid particles. The effect of S/L ratio on the dissolution of SFT was investigated under different S/L ratios (1:5, 1.5:5, 2:5, and 2.5:5). To obtain the desired ratio, the liquid volume was kept constant, and the amount of slag was changed. Figure 8a–c presents the extraction results for cobalt, copper, and zinc with respect to leaching time while Figure 8d shows metal extraction versus S/L ratio. Figure 8 shows that the extraction of Co, Cu, and Zn increased with a decrease in the amount of solids. The maximum extractions for Co, Cu, and Zn (>90%) were obtained at an S/L ratio of 1:5. The extraction efficiencies of Co, Cu, and Zn decreased sharply when the S/L ratio increased from 1.5:5 to 2:5 or 2.5:5. As the S/L ratio increases, the slurry density gradually increases, decelerating mass transfer, and therefore negatively affects slag dissolution. The cobalt, copper, and zinc leaching efficiencies decreased from 96.9, 94.2, and 92.6% to 33.5, 16.9, and 27.9%, respectively, as the S/L ratio increased from 1:5 to 2:5 at an acid concentration of 250 kg/t over 2 h. Moreover, the iron concentration in solution increased from 0.5 to 12.5 g/L with an increase in S/L ratio from 1:5 to 2.5:5 by weight of solids, indicating incomplete oxyhydrolysis. When the amount of sulfuric acid was kept constant at 250 kg/t and the S/L ratio increased, the acid concentration in the solution changed. Increasing free hydrogen ions in solution with the increase in H₂SO₄ promoted more silica gel formation at high S/L ratios (S/L = 2:5 and 2.5:5) (eq 2). The generation of silica gel significantly inhibited metal extraction. At the end of the experiments with relatively high S/L ratios (2:5 and 2.5:5), all of the leached material was in a gelatinous form and had very little fluidity. The considerable...
decrease in the extraction of Co, Cu, and Zn at an S/L ratio of 2.5:5 might be due to the combined effect of higher slurry viscosity, less dissolved oxygen, and the formation of a larger quantity of gelatinous material, thus coating the particles. Similar behavior was also noted in the oxidative pressure leaching of a copper slag.25 Further confirmation was provided by XRD analysis of the leaching residue obtained with an S/L ratio of 2.5:5; the diffraction pattern is provided in Figure 9e. This pattern shows that the residue contained ZnSO₄·H₂O, FeSO₄·H₂O, fayalite, magneteite, and hematite.

### 3.5. Characterization of Leaching Residues.

Extraction efficiencies of 96.3 ± 1.8% for cobalt, 93.1 ± 1.1% for copper, 92.3 ± 1.7% for zinc, and 0.5 ± 0.1% for iron were achieved under the optimum leaching conditions (H₂SO₄ = 250 kg/t, S/L = 1:5, P₀₂ = 0.7 MPa, τ = 60 min, stirring rate of 500 rpm). In contrast to the results reported in previous studies, the optimized conditions caused high selective leaching of cobalt, copper, and zinc compared to iron, strongly indicating the thorough removal of iron from the leaching liquor.

The XRD patterns of the selected leaching residues are given in Figure 9, and the phase names and their formulas are summarized in Table 3. The leaching residue at a low acid concentration (100 kg/t, corresponding to 30 g/L) mainly included hematite (α-Fe₂O₃), but it also contained some undissolved fayalite (iron silicate, Fe₆(Si₃O₁₀)(OH)₂) and maghemite (γ-Fe₂O₃). The leaching residue obtained under the optimal leaching conditions contained very low amounts of base metal and 39.17% iron, and the main phase was α-Fe₂O₃ with a small amount of γ-Fe₂O₃ (magneteite) (Figure 9b). At a high acid concentration (500 kg/t, corresponding to 100 g/L) and an S/L ratio of 1:5, high metal extraction was obtained, but iron dissolution was relatively high (5.5%). Under these leaching conditions, the leaching residue mainly contained hematite and small amounts of coesite (SiO₂) and anglesite (PbSO₄) (Figure 9c). Fayalite was not completely dissolved in the experiments performed in an oxygen-free environment, and the XRD analysis revealed that the leaching residue contained mainly fayalite, magneteite, zinc iron oxide (Zn₀.₄₅Fe₂₋₀.₅Zn₂₋₀.₅O₇⁻), and a small amount of hematite and sillimanite (Al₂SiO₅) (Figure 9d).

The SFT sample and the leaching residue obtained under the optimal leaching conditions were also analyzed using XPS to investigate the chemical changes involved in the oxidative pressure leaching process. The survey XPS spectra of the samples are represented in Figure 10a. To confirm the formation of Fe₂O₃ during the leaching of the SFT sample, the high-resolution photoelectron spectrum of Fe 2p was collected and is shown in Figure 10b. The Fe 2p spectrum was fitted, and the results after subtraction of the background are shown. Figure 10b shows the spectra of Fe 2p (SFT sample), where the binding energy (BE) of 710.9 eV is attributed to Fe²⁺ (fayalite), while the peak at 713.3 eV corresponds to Fe³⁺ due to the presence of magnetite and franklinite in the SFT sample. The Fe 2p₃/₂ peak of Fe 2p binding energies of Fe²⁺ ions in fayalite were reported to be 709—722.6, 710.7—724, 771.1—724.6, 80, and 709.7—723 eV. Satellite peaks are generally used to derive information regarding oxidation states. A weak satellite peak in the SFT sample was recorded. However, significant satellite peaks appeared at 719.0 and 732.9 eV in the leaching residue due to the formation of hematite. For the leaching residue (Figure 10b), the main Fe 2p₃/₂ peak and the Fe 2p₁/₂ peak had BEs of 710.9 and 724.6 eV, respectively. These results indicate that iron was completely in the Fe³⁺ state. This finding was also confirmed by the XRD results (see Figure 10b), which indicated that α-Fe₂O₃ and a small amount of γ-Fe₂O₃ (magneteite) contained only Fe³⁺ cations. It is also worth noting that the BE separation between the satellite peak and Fe 2p₁/₂ in the SFT sample (mainly fayalite) was 5.2 eV, while the BE separation of hematite was 8.1 eV. In other words, the satellite peak of Fe 2p₁/₂ was located approximately 8.1 eV higher than the main Fe 2p₃/₂ peak, agreeing well with the values reported for hematite.

The BE of the Si 2p peaks for the SFT sample was located at 102.3 eV, which corresponds to silicate (Fe₂SiO₄), while the BE

### Table 3. Phases Detected in the XRD Patterns

| Leaching Residue | Name         | Formula     | PDF Number |
|------------------|--------------|-------------|------------|
| (a)              | hematite (H) | α-Fe₂O₃     | 01-089-8103|
|                  | hercynite (Hs)| (Fe₃₅Al₃5s) | 01-082-0585|
|                  | maghemite (Mh)| γ-Fe₂O₃     | 01-089-3850|
|                  | iron silicate (IS)| Fe₆(Si₃O₁₀)(OH)₂ | 01-089-0842|
| (b)              | hematite (H) | α-Fe₂O₃     | 01-089-8103|
|                  | maghemite (Mh)| γ-Fe₂O₃     | 01-089-3850|
|                  | quartz (Q)| SiO₂        | 01-083-0542|
|                  | coesite (C)| SiO₂        | 01-076-1805|
|                  | anglesite (A)| PbSO₄     | 01-072-1389|
| (c)              | fayalite (F)| Fe₆SiO₄     | 01-071-1667|
|                  | magneteite (M)| FeO₄       | 01-075-1609|
|                  | hemate (H)| α-Fe₂O₃     | 01-089-8103|
|                  | cristobalite (C)| SiO₂  | 01-076-0936|
|                  | franklinite (zinc iron oxide) (Z)| Zn₀.₄₅Fe₂₋₀.₅Zn₂₋₀.₅O₇⁻ | 01-087-1230|
|                  | sillimanite (S)| Al₂SiO₅ | 01-088-0893|
| (d)              | fayalite (F)| Fe₆SiO₄     | 01-071-1667|
|                  | magneteite (M)| FeO₄       | 01-075-1609|
|                  | hemate (H)| α-Fe₂O₃     | 01-089-8103|
|                  | gunningite (Gu)| ZnSO₄·H₂O | 00-012-0781|
|                  | szolomnikite (Sz)| FeSO₄·H₂O | 00-001-0612|
|                  | fayalite (F)| Fe₆SiO₄     | 01-071-1667|
|                  | magneteite (M)| FeO₄       | 01-075-1609|
|                  | cristobalite (C)| SiO₂  | 01-076-0936|
|                  | franklinite (zinc iron oxide) (Z)| (Zn₀.₄₅Fe₂₋₀.₅) | 01-087-1230|
|                  | ilelite (clay-mica) (I)| KAl₆(Si₃Al)₂(OH)₂ | 00-043-0685|
of 103.5 eV indicates quartz (SiO$_2$), which is consistent with the corresponding XRD diagram (see Figure 3). Figure 10c also shows that the BE of Si 2p shifted to a higher value (103.6 eV) after pressure leaching, indicating that amorphous SiO$_2$ was generated in the process. Figure 10d presents the changes in the atomic percentages of Co, Cu, and Zn before and after the leaching process. The atomic percentages for Co 2p, Cu 2p, and Zn 2p decreased from 0.41, 0.67, and 1.6% to 0.04, 0.06, and 0.14%, respectively, indicating a high leaching efficiency.

4. CONCLUSIONS

The effects of the main parameters, such as sulfuric acid concentration, leaching temperature, oxygen partial pressure, leaching time, and solid/liquid (S/L) ratio, on the oxidative pressure acid leaching of copper slag flotation tailings (SFT) were determined. Pressure oxidative acid leaching, which has some advantages, such as selective dissolution, high leaching efficiency, and environmental considerations, was successfully applied to the SFT sample. It was possible to recover more than 90% of base metals with a single-step leaching process. In particular, cobalt is a metal that is critical in battery storage for electric vehicles as well as other storage applications. Since cobalt has been deemed a “critical metal”, it is important to effectively evaluate cobalt-bearing tailings.

The presence of oxygen in this leaching system is crucial since it enhances the dissolution of copper, cobalt, zinc, and the oxidation of sulfides as well as the transformation of iron in fayalite, magnetite, or franklinite to hematite. The extraction efficiencies of Co, Cu, Zn, and Fe were only 24.5, 5.3, 26.3, and 13.1%, respectively, without oxygen supply. Additionally, high acid concentrations and high S/L ratios lead to silica gel formation, which causes filtration problems and inhibits metal dissolution. The considerable decrease in the extraction efficiencies of Co, Cu, and Zn at S/L ratios of 2:5 and 2.5:5 might be due to the combined effect of a higher slurry viscosity, less dissolved oxygen, and the formation of a larger quantity of gelatinous material, thus coating the particles.

High extraction efficiencies of 96.3 ± 1.8% for cobalt, 93.1 ± 1.1% for copper, and 92.3 ± 1.7% for zinc were achieved under the optimum leaching conditions ($H_2SO_4 = 250$ kg/t, $S/L = 1:5$, $P_{O_2} = 0.7$ MPa, $r = 60$ min, stirring rate of 500 rpm, $d_{80} = 58 \mu m$). The extraction efficiency of iron was only 0.49 ± 0.12%. Compared to the results reported in previous studies, the optimized conditions cause high selective leaching of cobalt, copper, and zinc compared to iron, strongly indicating the thorough removal of iron from the leaching liquor. These metals in the leaching solution are easily recovered and separated by traditional processes such as ion exchange and solvent extraction. The final residue obtained under the optimum leaching conditions consisted mainly of ~56 wt % hematite ($\alpha$-Fe$_2$O$_3$) and amorphous SiO$_2$, indicating that the leaching...
residue can be safely stored or further used in the steel and iron or cement industries.

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**Notes**

The author declares no competing financial interest.

**ACKNOWLEDGMENTS**

The author expresses his deep gratitude to R&D Center Director Prof. Dr. Mehmet Canbazoğlu from Eti Bakır Company for providing the raw material. The author also acknowledges Res. Assist. A. Çağrı Kılınç and Assoc. Prof. Dr. Erkan Güler for performing and evaluating the XRD analyses and Dr. Sibel Oğuzlar for performing the XPS analyses.

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