Leaching of Cu, Zn, and Pb from Sulfidic Tailings Under the Use of Sulfuric Acid and Chloride Solutions

Tamara A. Schueler1 · Paula F. de Aguiar2 · Ysrael M. Vera3 · Daniel Goldmann1

Received: 20 May 2021 / Accepted: 5 October 2021 / Published online: 25 October 2021
© The Author(s) 2021

Abstract
The imbalance between raw materials of high economic importance and their supply has increased the search for new approaches to obtain valuable elements from mining tailings. In this study, the extraction of copper, zinc, and lead from sulfidic tailing in sulfate–chloride media was investigated. A 33 Box–Behnken design was applied to evaluate three variables over a 4-h testing period: sulfuric acid concentration (0.01–1.0 mol/L \( \text{H}_2\text{SO}_4 \)), sodium chloride (10–60 g/L NaCl), and temperature (20–70 °C). The design showed two optimum working regions: a combination of a high NaCl level, low \( \text{H}_2\text{SO}_4 \) level, and medium temperature level for lead leaching, while for copper and zinc, a combination of a medium–high \( \text{H}_2\text{SO}_4 \) level and a high temperature level. The concentration of NaCl had only a slight impact on their leaching. Based on these results, two-stage leaching was performed. The first stage was carried out under an experimental condition that favored the leaching of lead (60 g/L NaCl, 0.01 mol/L \( \text{H}_2\text{SO}_4 \), 45 °C, 1 h, 10:1 liquid-to-solid ratio), whereas the second stage maximized the leaching of copper and zinc (60 g/L NaCl, 0.5 mol/L \( \text{H}_2\text{SO}_4 \), 70 °C, 24 h, 10:1 liquid-to-solid ratio). The global leaching rate was 66.8 ± 3.0% copper, 84.1 ± 5.2% zinc, and 93.9 ± 3.2% lead. The iron and arsenic content were also leached by about 20 and 50% at the end of the second stage. The study demonstrated that the use of sulfate–chloride media in a two-stage leaching considerably improved the extraction of the desired metals and was, therefore, suitable for their recovery.

Graphical Abstract

Keywords Metals leaching · Two-stage leaching · Sulfidic mine tailings · Experimental design · Optimization

Introduction
The increasing economic importance of different industrial sectors, such as modern technology, has led to a growing demand for the production and extraction of metals.
However, there is an imbalance between some metal supplies and world demand [1] due to the reduction of primary resources and high-grade ores [2, 3]. For this reason, the interest in low-grade ores and mine tailings as metal sources has become significant over the years [4]. Mining activities generate large amounts of solid wastes that are usually stored long term under dam facilities [5]. These tailings can still contain valuable metals, such as copper, zinc, nickel, and gold, as well as hazardous elements, such as lead and arsenic [6]. Besides all this, there is an environmental risk associated with the liberation of toxic elements to the soil and groundwater, with the generation of acidic mine drainage [7], and also the disposal of waste on-site, such as dam failures [8].

Hydrometallurgy methods have been successfully used in the dissolution of metals from concentrated ores or low grades and tailings. Acid-chloride or hybrid sulfate–chloride systems have been widely used in hydrometallurgy processes for non-ferrous metals [9]. Chloride-based systems offer advantages for leaching of valuable metals due to their aggressive nature [10]. The addition of chloride ions allows a porous sulfur layer to be formed on the mineral surface, facilitating reagent diffusion and, consequently, higher solubility of the metal [11–14]. Moreover, the presence of chloride ions in sulfate systems changes the solution speciation, as the metals can form metal-chloride complexes, which may contribute to the leaching rate [15, 16]. Watling [16, 17] wrote comprehensive reviews of copper leaching from the chalcopyrite refractory mineral in sulfate- and chloride-based media. In summary, the addition of chloride ions enhances the leaching of copper by changing the speciation of copper to form a Cu complex, as cupric and cuprous ions are stabilized as chloride complexes, and also the Cu(I)/Cu(II) redox couple contributes to sulfide oxidation reactions. Chloride-complex formation is also an important factor for the leaching of lead-bearing minerals that forms soluble PbCl+ rather than PbSO4 [15, 18]. The higher solubility of lead chloride ($K_{sp} = 1.2 \times 10^{-5}$) in water compared to lead sulfate ($K_{sp} = 1.8 \times 10^{-8}$) and the formation of soluble lead-chloride complexes into solution, according to the following reactions (1)–(4) [19, 20], favor lead solubilization in an aqueous solution.

\[
Pb^{2+} + Cl^- \rightarrow PbCl^+ \quad K_1 = 12.59 \tag{1} \\
PbCl^+ + Cl^- \rightarrow PbCl_2 \quad K_2 = 14.45 \tag{2} \\
PbCl_2 + Cl^- \rightarrow PbCl_3^- \quad K_3 = 3.89 \times 10^{-1} \tag{3} \\
PbCl_3^- + Cl^- \rightarrow PbCl_2^2^- \quad K_4 = 8.92 \times 10^{-2} \tag{4}
\]

Different leaching strategies for copper, zinc, and lead have been described in the literature. Lu et al. [14] obtained up to 97% copper extraction in 9-h tests from chalcopyrite concentrate in solutions containing 0.8 mol/L H2SO4 and 1 mol/L NaCl at high temperatures (60–95 °C). The authors reported that chloride concentrations > 0.5 mol/L did not enhance the leaching rate of chalcopyrite and stated the importance of sufficient chloride ions present in solution rather than an excess. Examination of the residues showed that the sulfur reaction product obtained in the presence of 1 mol/L NaCl was crystalline and porous, allowing reactants to diffuse through the surface product layer to the unreacted mineral surface. Hernández et al. [12] investigated the leaching efficiency of copper from chalcopyrite in three different acid systems (H2SO4, HCl, HNO3) in seawater or pure water. The presence of Cl− (0.16 mol/L, NaCl) and Cu2+ (0.08 mol/L, CuCl2) enhanced the copper extraction for both systems (0.32 mol/L acid concentration), reaching the maximum extraction of 37.7% in the HCl–seawater–Cu2+ system after a 7-day test at 45 °C and a 1:10 solid–liquid ratio. The authors attributed the increase in ionic strength to the decrease in Cu extraction by the addition of Cl− in seawater-based media. A study with low-grade copper ore (0.36% Cu) [10] showed that there was no difference in the copper rate regarding the acid used (0.5 mol/L H2SO4 or HCl) in a seawater medium, and the high metal extraction (70–80%) was achieved in 48 h regardless of the water type (seawater or tap water). Zinc and lead were recovered from a zinc plant residue [21]. About 90% Zn was leached in a H2SO4 solution at 80 °C, while the recovery of Pb was possible only in the brine leaching step. Ye et al. [22] extracted zinc and lead from lead–zinc mine tailings by the combined sequential bioleaching and brine leaching. About 98% of Zn was extracted by bioleaching, and 99% of Pb was extracted in a brine leaching solution containing 150 g/L NaCl at 50 °C.

Studies covering the use of chloride-based media are of importance for regions where freshwater is scarce [10], but have a supply of brackish water (0.5–17 g/L salinity) or seawater (30–40 g/L salinity) [16, 23]. The use of seawater in the mining industry for mineral processing and hydrometallurgy operations has already become a reality in some countries [24]. In this context, the use of hybrid sulfate–chloride systems has commercial implications since they are considered to be cheaper than pure chloride systems [25]. The high corrosive action of chloride ions is a significant drawback in leaching processes as it requires corrosion-resistant materials, which are expensive [16, 26]. In addition, chlorine leaching requires additional care in order to prevent the health risks of chlorine gas production due to the handling of concentrated hydrochloric acid [27].

In view of the above, the aim of the present work was to understand the leaching behavior of zinc, copper, and lead metals from a fresh Cu–Zn tailing and to optimize the
Materials and Methods

Sulfidic Mining Tailings and Characterization

The solid material used in this work was a fresh sulfidic mining tailing (SUL_NC_02) from an active Cu–Zn mine located in Southern Portugal (Neves Corvo, Portugal). The sample was dried at 40 °C, homogenized, split, and stored in plastic bags under vacuum and then refrigerated (4 °C) for further analysis. The chemical composition of the elements of the SUL_NC_02 tailing was analyzed with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, ICP5100 Agilent technologies, USA). For ICP-OES, a combination of acid and melt digestion were applied. The sample was dissolved with HCl/HNO3, and the residue was molten with Li2B4O7 and leached with HCl melt digestion. To analyze sulfur, the sample was mixed with MgO/Na2CO3, ignited for 2 h at 850 °C, and dissolved in diluted HNO3. The mineralogical composition of the sample was determined by X-ray diffraction using a XPert Pro diffractometer (XRD, PANalytical, the Netherlands). The particle size distribution was measured with laser diffraction in suspension using a Sympatec Helos/KR with a Quixel disperser (Sympatec GmbH, Germany).

Experimental Methods

The leaching experiments were performed in glass beakers placed on combined heating-plate magnetic-stirrer devices, at 250 rpm and a 10:1 liquid-to-solid ratio. The temperature of the leaching solutions was controlled by a digital contact thermometer connected to the heating plate. Once the desired temperature was reached, the solid samples were added and the leaching time began. The pH and oxidation–reduction potential (ORP, Ag/AgCl reference electrode) of the solutions were measured throughout the experimental time. The pH was adjusted to ≤ 2.0 with H2SO4 (95.0–98.0%) at the beginning of the experiments, but only in conditions where the pH was higher than 2.0. This pH adjustment makes the system comparable with bioleaching processes, where this procedure is commonly reported [28, 29]. Solid–liquid separation was carried out using vacuum filtration. The solids were washed with deionized water and dried (40 °C) to be then weighed and stored in plastic bags under vacuum and refrigeration (4 °C) for further analysis.

The leachates were analyzed by ICP-OES (ICP5100 Agilent technologies, USA).

The leaching efficiencies for each metal were determined according to the mathematical treatment described by [30]. It considered the amount of metals analyzed in the leachate volume, the amount of metals in the starting solid sample, the evaporated volume, and the amount of solids and the volume withdrawn at each sampling time. All experiments were performed at least in duplicate (n ≥ 2), and the error bars were calculated as the standard deviation. The graphs were plotted using OriginPro® 2020 software (version 9.7.0.188).

### 3\textsuperscript{3} Box–Behnken Design

The 3\textsuperscript{3} Box–Behnken design was applied to investigate the optimum conditions of Cu, Zn, and Pb leaching from SUL_NC_02 tailings. This experimental design consists of an incomplete factorial design with three levels (low (−1), medium (0), and high (+1)) and k factors, which allows the first- and second-order coefficients of the mathematical model to be efficiently estimated. The number of experiments (N) is defined as $N = 2^k (k − 1) + C_0$, where $k$ is the number of factors and $C_0$ is the number of replicates at the central point [31]. The design performed in this study is composed of three factors (concentration of NaCl (A) and $H_2SO_4$ (B) and temperature (C)), three levels (−1, 0, and +1), and three central points, resulting in a total of 15 experimental runs performed randomly. The choice of variables and their ranges was based on preliminary experiments and literature review [10–12, 21, 22, 25, 32–35]. Preliminary tests revealed that leaching with 0–200 g/L of NaCl at room temperature reached the maximum extraction of 30–40% Pb in solutions containing 35–200 g/L of NaCl. The lowest Pb leaching rates of about 1% and 6% were detected when leaching with 0 and 10 g/L of NaCl, respectively; while for copper and zinc, the results were <1% Cu and ≈ 2.5% Zn regardless of the salt concentration range. The pH of these tests was around 5.5–6.0 after 4 h of leaching. In acidic media ($pH \leq 2.0$) and at higher temperatures (40–70 °C), the leaching rates of the three metals improved. Since similar results were obtained with 100 and 200 g/L of NaCl solutions in the preliminary studies, for the variable $A_{(NaCl \text{ concentration})}$, the upper limit of 60 g/L of NaCl was selected to allow the use of 10 and 35 g/L of NaCl (ranges comparable with brackish and seawater salt content), and also to avoid major corrosion problems. For the variable $B_{(H_2SO_4 \text{ concentration})}$, an acidic media ($pH \leq 2.0$) already showed promising results in the previous tests. The upper limit value of $B_{(H_2SO_4 \text{ concentration})}$ was selected based on both preliminary assays and literature, and also considered the process costs. The same strategy was applied to the variable $C_{\text{Temperature}}$. Table 1 shows the independent variables as well as their decodified values distributed in three levels.
Each experiment was analyzed by withdrawing samples at regular time intervals during 4 h of leaching. This study strategy reduces the number of experiments, while still studying time as a design variable. The State-Ease Design-Expert® software (version 10.0.8) was used to estimate the model coefficients through regression analysis and to build the response surfaces for each response measured (yields of copper, zinc, and lead).

Two-Stage Leaching Tests

The first stage of leaching was carried out in the lixiviant containing 60 g/L NaCl and 0.01 mol/L H₂SO₄ for 1 h at 45 °C. After that, the samples were filtered and the solids underwent the second stage of leaching. For that, the acid concentration (0.5 mol/L H₂SO₄), the temperature (70 °C), and the time (24 h) were increased to favor the leaching of Cu and Zn metals. Samples were taken at regular intervals up to 24 h. Due to the high Fe content in the tailing sample as well as the presence of the hazardous element As, their leaching rates were also determined in this step.

Results and Discussion

Characterization of Cu–Zn Tailings

Particle Size Distribution

The particle size distribution of the SUL_NC_02 tailing is shown in Fig. 1. The sample contains very fine grain size ($d_{90}=115.86 \mu m$). The leaching experiments were performed using the tailing sample without further comminution.

Chemical Analysis

The chemical composition of the sulfidic mine tailings is presented in Table 2. Results showed that the sample is mainly composed of the elements (mg/kg) sulfur (S), silicon

Table 1 Experimental parameters for the $3^3$ Box–Behnken design

| Independent variables | Low | Medium | High |
|-----------------------|-----|--------|------|
| A: NaCl (g/L)         | 10  | 35     | 60   |
| B: H₂SO₄ (mol/L)      | 0.01| 0.5    | 1.0  |
| C: Temperature (°C)   | 20  | 45     | 70   |

Table 2 Chemical composition of the SUL_NC_02 sample

| Elements | Content (mg/kg) | Elements | Content (mg/kg) |
|----------|-----------------|----------|-----------------|
| Fe       | 286,174         | Na       | 2187            |
| S        | 249,000         | Ti       | 2021            |
| Si       | 121,300         | Mn       | 643             |
| Al       | 30,410          | Ni       | 298             |
| Zn       | 10,321          | Sb       | 251             |
| Mg       | 9459            | Co       | 211             |
| Ca       | 5309            | P        | 150             |
| As       | 4809            | Ba       | 147             |
| K        | 4317            | Cr       | 100             |
| Cu       | 4007            | Sr       | 27              |
| Pb       | 3650            | Ag       | 20              |

Fig. 1 Particle size distribution of the Cu–Zn tailings used in the experiments ($d_{10}=2.16 \mu m$, $d_{50}=21.39 \mu m$, $d_{90}=115.86 \mu m$)
(Si), and iron (Fe), followed by aluminum (Al), manganese (Mg), and calcium (Ca). With respect to the target elements, Cu, Zn, and Pb were about 0.40, 1.03, and 0.36 wt%, respectively, of the total amount of the contents. A mineralogical analysis of sample SUL_NC_02 performed by Escobar et al. [36] demonstrated that Cu is present predominantly in the sulfide mineral chalcopyrite (0.46 wt%; CuFeS2) and other minor Cu-bearing minerals, such as tetrahedrite (0.10 wt%; (Cu,Fe)12Sb4S13); also, Zn is present in sphalerite (1.4 wt%; (Zn,Fe)S), and Pb is present in galena (0.36 wt%; PbS). XRD analysis (Fig. 2) showed that the sample is mainly composed of quartz and pyrite, followed by chlorite, illite, and dolomite. Due to the low accuracy of XRD in measuring small and very minor crystalline structures, the quantities of the main Cu, Zn, Pb phases were not detectible. Therefore, these mineral phases are not shown in Fig. 2.

Leaching Tests

Leaching Behavior of Cu, Zn, and Pb Using Design of Experiment

Table 3 summarizes the experimental setup performed and the results obtained for the desired metals Cu, Zn, and Pb in a 4-h experiment according to the 3³ Box–Behnken design. As shown, approximately 30% of Cu and Zn were leached within 4 h in experiment numbers 7, 8, and 12. These experimental conditions consisted of the three levels of sodium chloride concentration (10, 35, or 60 g/L), the medium and high levels of the acid concentration (0.5 or 1.0 mol/L H₂SO₄), and the highest temperature (70 °C). Particularly, for Cu, the high temperature showed great impact on its leaching. The four largest yielding extractions for Cu were found in the four experiments performed at 70 °C (experiment numbers 7, 8, 11, and 12); however, the lowest acid concentration in experiment 11 (0.01 mol/L H₂SO₄) led to a lower Cu extraction (≈ 15%) compared to the abovementioned experiments, indicating that not only temperature but also the acid concentration has an impact on the extraction, as expected. Other conditions with lower temperatures did not have much influence on the leaching of Cu within the range studied. The concentration ranges of NaCl had a slight impact on Cu and Zn extraction from the SUL_NC_02 sample compared to temperature and H₂SO₄ concentration.
Nevertheless, chloride ion is proposed to be an active agent in the dissolution of metals, increasing the leaching rate in sulfate-based media [16]. Santos et al. [30] studied the leaching of Cu and Zn from the concentrate ore of the same Cu–Zn mine (Neves Corvo mine, Portugal). The authors demonstrated that the leaching of Cu and Zn increased at a high temperature (80 °C), and a H2SO4 concentration between 0.25 and 5 mol/L did not affect the leaching yield when applying Fe2(SO4)3 as an oxidizing agent. The positive effect of high temperatures in Cu dissolution from low-grade and concentrate ores were confirmed by other authors [10, 34]. Fu and Lu [37] showed how the temperature plays an important role in the leaching of heavy metals from tailings. Furthermore, the effect of high temperatures on the leaching reactions can be explained by the Arrhenius Eq. (5). The increase in temperature increases the reaction speed due to the increase in the kinetic constant of the reaction [38, 39].

\[
k = A e^{-E_a/RT},
\]

(5)

where \( k \) is the rate constant, \( A \) is the pre-exponential factor, \( E_a \) is the activation energy (kJ/mol), \( R \) is the universal gas constant (8.314 J/mol K), and \( T \) is the absolute temperature (Kelvin).

Similar leaching behavior for Zn was demonstrated in this study. Experiments at the highest temperature (70 °C) promoted the highest leaching rate (≈ 30–35%), whereas at the lowest temperature, the extraction decreased to ≈ 10% at 4 h. Additionally, the acid concentration at medium and high levels (0.5–1.0 mol/L H2SO4) contributed to the maximum leaching of Zn obtained by the design. However, Zn extraction was easier to be reached than Cu at a medium temperature (45 °C) with a medium–high acid concentration. Approximately 20% Zn was leached under these conditions (experiment numbers 3, 4, and the central points), while about 10% Cu was obtained at the same trials. This observation can be associated with the mineralogical crystalline structure of the sulfate minerals. The zinc sulfide (ZnS, sphalerite) and the copper-bearing minerals (CuFeS2, chalcopyrite) are isostructural; however, the chalcopyrite matrix is more complex than sphalerite, requiring more aggressive leaching conditions to release Cu [40, 41]. Moreover, the chemical reaction of sphalerite with sulfuric acid is more thermodynamically favorable (Reaction (6); \( \Delta G°_70 °C = -18.04 \) kJ) than the chalcopyrite reaction (Reaction (7); \( \Delta G°_70 °C = 12.31 \) kJ). (Gibbs energy values were obtained from HSC Chemistry; version 9.9.2.3). In the same way, \( \Delta G° \) decreases as the temperature increases, demonstrating that increasing temperature promotes the dissolution of both minerals. Although the Gibbs free energy for chalcopyrite reacting with sulfuric acid is positive at standard conditions (\( \Delta G° \)), the \( \Delta G \) values of Reaction (7) are negative when considering the initial concentrations of the reactants and products of the experiments. For instance, at 70 °C, the partial pressure of H2S equals \( 1.0 \times 10^{-5} \) atm, and for H2SO4 concentrations of 0.01, 0.5, and 1.0 mol/L, the Gibbs free energies of the reaction are −11.88 kJ, −23.03 kJ, and −25.01 kJ, respectively. Thus, the reaction is thermodynamically favorable.

\[
\begin{align*}
\text{ZnS} + \text{H}_2\text{SO}_4 & \rightarrow \text{ZnSO}_4 + \text{H}_2\text{S}(g) \quad \Delta G°^{20 °C} = -13.13 \text{kJ} \\
\Delta G°^{45 °C} &= -15.62 \text{kJ} \\
\Delta G°^{70 °C} &= -18.04 \text{kJ}
\end{align*}
\]

(6)

On the other hand, the largest leaching yield of Pb (53.7 ± 1.6%, experiment number 2) was reached at the highest concentration of NaCl (60 g/L) and at the lowest acid concentration (0.01 mol/L H2SO4), as expected. In comparison, experiments containing the lowest chloride (KSp = 1.8 × 10−8) in brine solutions [Reactions (9) and (10) and (1)–(4)] [42] by the complexation equilibrium between the Pb ion and chloride ion concentrations [20].

\[
\begin{align*}
\text{Pb} + \text{H}_2\text{SO}_4 & \rightarrow \text{PbSO}_4(aq) + \text{H}_2\text{S}(g) \quad \Delta G°^{20 °C} = -57.18 \text{kJ} \\
\Delta G°^{45 °C} &= -59.80 \text{kJ} \\
\Delta G°^{70 °C} &= -62.32 \text{kJ}
\end{align*}
\]

(8)

\[
\begin{align*}
\text{PbSO}_4(aq) + 2\text{Cl}^- & \rightarrow \text{PbCl}_2(aq) + \text{SO}_4^{2-} \\
\text{PbCl}_2(aq) + 2\text{Cl}^- & \rightarrow \text{PbCl}_2^{2-}
\end{align*}
\]

(9) (10)

Thus, under experimental conditions where the chloride source is high and the concentration of H2SO4 is low, a high leaching rate of Pb can be obtained. Other examples of this solubility characteristic can be detected in experiment numbers 4, 6, and 8, in which the second highest Pb extraction was achieved (about 30%). The leaching solution of these assays contained the highest chloride concentration but a higher acid concentration (0.5 or 1.0 mol/L H2SO4). In comparison, experiments containing the lowest chloride source (10 g/L) were not favorable for Pb leaching even in conditions with low acid concentration (experiment numbers 1, 3, 5, and 7). The temperature did not seem to have much impact on the leaching of Pb, in accordance with the
findings of Farahmand et al. [21]; however, it contributed to the initiation of leaching of Cu and Zn, which was not disregarded in the two-stage leaching (‘Optimization Test Using Two-Stage Leaching’).

Based on the Box–Behnken results, the response surfaces were built up through the State-Ease Design-Expert® software. In view of the fact that the $3^3$ Box–Behnken design is a non-orthogonal model [43], the obtained models were evaluated by regression analysis and the lack of fit through the Analysis of Variance (ANOVA). A complete second-degree polynomial was chosen to model the data. The coded equations of the quadratic model for each metal are presented as Eqs. (10), (11), and (12); however, since the third-degree interactions were equal to zero, their values were not included in the equations. In the following, the results for Cu, Zn, and Pb at 4-h leaching time are described.

**Behavior of Cu and Zn**

Due to their similar leaching behavior, Cu and Zn responses are shown together. Equation (11) expresses the model for Cu leaching over the range of experimental conditions, while Eq. (12) is for Zn leaching.

\[
\begin{align*}
\text{Cu} &= 8.94 + 0.05A + 2.12B + 9.89C + 0.45AB - 0.23AC \\
&
+ 3.50BC + 2.17A^2 - 1.55B^2 + 6.87C^2 \tag{11}
\end{align*}
\]

\[
\begin{align*}
\text{Zn} &= 20.54 + 1.07A + 4.63B + 9.32C - 0.12AB + 0.87AC \\
&+ 2.52BC - 0.74A^2 - 2.51B^2 + 1.29C^2 \tag{12}
\end{align*}
\]

where $A$, $B$, and $C$ are the codified variables that, respectively, represent NaCl concentration, $\text{H}_2\text{SO}_4$ concentration, and temperature.

The lack of fit of the Cu yield response was considered significant ($p$ value < 0.05) for this model to a confidence level of 95% ($F_{\text{calculated}} = 92.14 > F_{\text{critical}} = 19.16$). However, the $R^2$ value (0.94) and the adj $R^2$ value (0.84) indicate that more than 80% of the leached Cu behavior can be explained by the estimated model. Moreover, these results are above 0.7, which indicates that the model is adequate to describe the behavior of the response [44]. On the other hand, the results obtained by the ANOVA for Zn leaching showed that the lack of fit was not significant ($p$ value > 0.05) to a confidence level of 95% ($F_{\text{calculated}} = 9.45 < F_{\text{critical}} = 19.16$). The regression analysis revealed that the values of both $R^2$ and adj $R^2$ are equal to 0.99.

The figures below (Fig. 3) show the contour plots (Fig. 3a, b) and response surfaces (Fig. 3c, d) for Cu and Zn leaching from the independent variables $B_{\text{H}_2\text{SO}_4\text{concentration}}$ and $C_{\text{Temperature}}$ ranging from 0.01 to 1.0 mol/L and from 20 to 70 °C, respectively, as the $x_1$ and $x_2$ axis. The variable $A_{\text{NaCl\,concentration}}$ was fixed at 60 g/L, which was one of the best conditions obtained by the design. It was observed that, as the levels of the variables increase, the extraction of metals also increases. Then, a high temperature (70 °C) and an acid concentration above 0.5 mol/L were essential for leaching Cu and Zn from SUL_NC_02 tailings, which corroborate the analysis of Table 3.

In order to compare the effects of all parameters at a particular point in the design space, the perturbation plots are presented in Fig. 4. The factor levels were selected by identifying the best working regions for Cu and Zn leaching. The curvature of the factors expresses the sensitivity of the response for a given factor. As can be seen in the figure (Fig. 4a, b), all three factors are sensitive to the responses of Cu and Zn (%); the responses are highly dependent on the factors $B_{\text{H}_2\text{SO}_4\text{concentration}}$ and $C_{\text{Temperature}}$ and have a lower sensitivity to the factor $A_{\text{NaCl\,concentration}}$. The steep curvatures of factor $C_{\text{Temperature}}$ demonstrate a higher sensitivity of the responses to this factor. The same observations were supported by the data presented in Table 3.

**Behavior of Pb**

Reaction (13) displays the coded model for the response of Pb leaching. The ANOVA analysis showed that the lack of fit was significant ($p$ value < 0.05) to a confidence level of 95% ($F_{\text{calculated}} = 64.11 > F_{\text{critical}} = 19.16$). Additionally, the regression analysis showed that the values for $R^2$ (0.97) and adj $R^2$ (0.92) are above 0.7.

\[
\begin{align*}
\text{Pb} &= 11.22 + 16.08A - 5.35B + 0.020C - 6.68AB \\
&+ 0.16AC + 2.00BC + 6.11A^2 + 4.17B^2 - 1.39C^2 \tag{13}
\end{align*}
\]

The contour plot and response surface can be seen in Fig. 5 for the Pb leaching yield, with $A_{\text{NaCl\,concentration}}$ and $B_{\text{H}_2\text{SO}_4\text{concentration}}$ as the $x_1$ and $x_2$ axis, respectively, and the variable $C_{\text{Temperature}}$ fixed at 45 °C. These test parameters were selected due to the best Pb yield obtained by the design; also showed by Table 3. Contrary to what was observed for the Cu and Zn leaching yield, the leaching of Pb was strongly favored by increasing the NaCl concentration. As discussed above, a high Cl$^-$ ion concentration provides higher solubility of Pb, leading to a higher soluble Pb content in solution. Also, a slightly acidic environment was an important factor to increase the leaching efficiency of lead from the SUL_NC_02 sample.

The perturbation plot (Fig. 6) for Pb extraction confirms the data discussed above. The Pb leaching yield presents a high sensitivity to the factors $A_{\text{NaCl\,concentration}}$ and $B_{\text{H}_2\text{SO}_4\text{concentration}}$. The relatively flat curvature of the factor $C_{\text{Temperature}}$ indicates a low sensitivity to this factor. The factor levels were chosen for having the best range for Pb extraction.
Leaching Behavior of the Metals over 4 h of Testing

Figure 7 presents the leaching rate (%) of Cu, Zn, and Pb throughout the 4-h experiment. For comparison purposes, the best conditions obtained by the design for each element are shown. The highest leaching yield for Pb (roughly 70%) was reached at 1 h in the lixiviant containing 60 g/L of NaCl and 0.01 mol/L of H₂SO₄ at 45 °C (experiment number 2). As can be seen in the figure, the amount of soluble Pb decreased over time, and this effect can be associated with the pH control (≈ 2.0, H₂SO₄ concentrate) during the experimental time, resulting in a drop of Pb²⁺ solubility as a function of SO₄²⁻ addition to the system [21]. Previous tests without pH control showed slower Pb leaching rates compared to the tests with pH control. Approximately 70% of Pb was leached at 4 h and pH 4.0, while controlling the pH to around 2.0 in the beginning of the experiment, ≈ 70% of Pb was leached at 1 h. Furthermore, controlling the pH increased the redox potential from 257 to 367 mV at 1 h. Conversely, experiment number 8, which contained the same amount of NaCl (60 g/L) as experiment number 2 but had a higher acid concentration (0.5 mol/L H₂SO₄) and temperature (70 °C), demonstrated an increased leaching rate of Cu and Zn over the 4-h testing time (approximately 30 and 35%...
Due to the higher acid concentration used in the test, the pH value was < 1.0. The redox potential increased over time from 340 to 406 mV. Lundström et al. [33] described that an increase in the leaching rate is kinetically linked to a decrease in the redox potential. On the other hand, concurrent increases in the redox potential and metal extraction have already been demonstrated by Hernández et al. [32]. However, due to the complex mineralogical composition of the tailings sample (see Table 2), several redox pairs are involved in the resultant redox potential. Therefore, it is not possible to determine which reactions are driving the redox potential behavior. Nevertheless, in both cases (experiments 2—with and without pH adjustment—and 8), a higher redox potential and lower pH were connected to the increase in the metal leaching rates. This indicates that the leaching efficiency of the desired metals is more effective under higher redox potentials and lower pH values.

In addition to the drop in Pb concentration after 1 h of the leaching test, the figure also shows that, by increasing the reaction time, more Cu and Zn could be extracted from the SUL_NC_02 sample. Based on this information, two-stage leaching was performed, and their results are discussed in the following section ("Optimization Test Using Two-Stage Leaching").
Optimization Test Using Two-Stage Leaching

The results presented in the previous sections (‘Leaching Behavior of Cu, Zn, and Pb Using Design of Experiment’ and ‘Leaching Behavior of the Metals over 4 h of Testing’) showed two different optimum working regions for leaching the metals from the sulfidic tailing sample, as also observed in the response surfaces (Figs. 3 and 5; Pb: about 70%, 1 h, experiment number 2; Cu and Zn: about 30%, 4 h, experiment numbers 7, 8, and 12). Therefore, in order to improve the leaching rate of Cu, Zn, and Pb, these experimental conditions were chosen for further investigation. For that, two-stage leaching was conducted (Fig. 8). The first stage was carried out for 1 h in the lixiviant that favored the leaching of Pb in the 3³ Box–Behnken design (experiment number 2: 60 g/L of NaCl and 0.01 mol/L of H₂SO₄ at 45 °C). After that, the solids were filtrated and underwent the second stage for the leaching of Cu and Zn. In order to increase their extraction rates, this stage was performed for 24 h. The lixiviant containing 60 g/L of NaCl and 0.5 mol/L of H₂SO₄ (experiment number 8, 3³ Box–Behnken design) was chosen for presenting the same salt concentration as experiment number 2.

During the first stage of leaching (Fig. 8a), 70.6 ± 4.4% of Pb was leached from the SUL_NC_02 tailing, whereas for Cu and Zn, it was 6.1 ± 1.0% and 8.4 ± 0.1%, respectively. The second stage (Fig. 8b) resulted in a significant improvement in the Cu and Zn rates, reaching the global rate of 66.8 ± 3.0% and 84.1 ± 5.2%, respectively, in 24 h. In addition, Pb extraction rose by a little more than 20%, resulting in a final rate of 93.9 ± 3.2%. The increased recovery of Cu and Zn can be attributed to the acid-tailing contact time along with the high temperature. As for higher acid concentrations and lower temperatures, the results were not enhanced (Table 3, ‘Leaching Behavior of Cu, Zn, and Pb Using Design of Experiment’).

Zhong and Li [45] demonstrated that temperature strongly affected the leaching of Cu from chalcopyrite over a 144-h test time in a 0.1 mol/L NaCl and pH 1.0 (H₂SO₄) solution. 17%, 34%, and 67% of Cu were extracted at 45, 55, and 65 °C, respectively, and nearly 100% Cu were leached at 75 °C. Furthermore, the metal extraction increased almost linearly as time progressed. The leaching of Cu, In, Zn, and Pb from a hydrometallurgical residue [42] was significantly affected by the temperature; however, for Pb, it contributed to only 4.5% of its recovery. Sequential stage leaching has been also described in the literature for metal recovery from residues. Zinc–lead-rich residue [21] was first leached with H₂SO₄ at 80 °C followed by water leaching at 70 °C to bring zinc to the solution (global leaching of 92% Zn). For the leaching of Pb (89.4%), the acid-leaching residue was leached in a brine solution containing 300 g/L NaCl and pH 1.0. Applying bioleaching as a pretreatment for chloride leaching, 98% of Cu and 63% Au were extracted from the bioleached residue, while 80% Cu and 30% Au were reached in the untreated sample at pH 1 (H₂SO₄), 250 g/L NaCl, and O₂ as the oxidant for 72 h. 99%, 80%, and 90% of Ni, Co, and Zn, respectively, were leached in the biotreated feed with Cu²⁺ as the oxidant [46]. For comparison purposes, Table 4 presents a compilation of metal leaching studies using sulfuric acid and sodium chloride as the lixiviants.

By analyzing Table 4, it is possible to observe metal leaching results similar or even slightly higher than those obtained in this study (see Table 4, row 1). However, most of them applied higher concentrations of H₂SO₄ or NaCl and
**Fig. 8** Leaching rate of Cu, Zn, Pb, Fe, and As during the two-stage leaching test. **a** First stage at 1 h (60 g/L NaCl, 0.01 mol/L H₂SO₄, and 45 °C) and **b** second stage over 24 h (global leaching rate [first stage + second stage]; 60 g/L NaCl, 0.5 mol/L H₂SO₄, and 70 °C). The error bars were calculated as the standard deviation.

**Table 4** Experimental conditions and the final results for sulfate–chloride media studies

| Samplea | 1st stage | 2nd stage | Final resultsb | References |
|---------|-----------|-----------|----------------|------------|
| Sulfidic tailing (d₉₀ = 115.9 µm) (CuFeS₂, ZnS, PbS) | 1 h | 24 h | Cu: 66.8 ± 3.0% | This study |
| Zinc plant residue (ZPR) (− 74 µm) (ZnSO₄, PbSO₄) | 30 min—roasting | 10 min | Zn: 86% | [35] |
| Zinc plant residue (PhSO₄, ZnSO₄, Zn₉Si₂O₇, ZnO, ZnFe₃–xO₄) | 1 h—acid leaching pH 2.5 (H₂SO₄) 80 °C | 30 min | Zn: 92.8% | [21] |
| Zinc plant residue (PhSO₄, ZnSO₄, Zn₉Si₂O₇, ZnO, ZnFe₃–xO₄) | 1 h—water leaching pH 1.0 (H₂SO₄) 70 °C | 37 °C | Pb: 89.4% | [21] |
| Chalcopyrite ore (CuFeS₂) | 144 h | No | Cu: ≈ 100% | [45] |
| Hydrometallurgical residue (120 µm) (CuS, ZnS, Zn₉Si₂O₇, PbSO₄) | 1 h | No | Cu: 93.6% | [42] |
| Raw complex sulfide ores (74 µm) (ZnS, PbS) | 20 days | Bioleaching | Zn: 95% | [46] |
| Flotation tailing (d₉₀: 150 µm—as-received) (CuFeS₂, ZnS) | 15 days | Bioleaching | Cu: 98% | [47] |
| Flotation tailing (d₉₀: 26 µm—grounded) (CuFeS₂, ZnS) | 11 days | Bioleaching | Zn: 90% | [47] |

aThe main Cu, Zn, and Pb phases are presented.
bFinal results mean global leaching results (first stage + second stage).
temperatures, and/or longer time processes and the addition of oxidizing agents, such as O2 or Cu2+, to improve their leaching rate. These settings might be important industrial drawbacks that must be considered, for instance, with regard to operational costs.

Figure 8 also shows the leaching rate (%) for Fe and As over the two leaching stages. Particularly notable was that the Fe content was kept around 20% over the second stage and that the hazardous element As reached about 50% at the end of the leaching test. Iron is typically removed from the pregnant solutions prior to the recovery of the base metals [48]. The high concentration of Fe in the pregnant leach solution can hinder the recovery of the base metals from the leachates. For instance, the pH should be very well controlled to avoid a high degree of co-precipitation of other metals [49]. Therefore, due to the high Fe content compared to the target metal concentrations (see Table 2), further studies to improve the leaching of metals along with a lower Fe dissolution should be investigated.

XRD analysis of the sample after two-stage leaching is shown in Fig. 9. Comparing the XRD pattern of the leached residue with the starting material (Fig. 2), the final residue is still mainly composed of pyrite and quartz. Dissolution of chlorite and dolomite was observed. These are important findings to assess valorization possibilities to the final (cleaned) residues, as they can be used, for instance, as construction materials [50]. Furthermore, additional studies to reduce operational costs, mainly related to energy supply, should be carried out. Nevertheless, the adoption of a filtration step followed by the second leaching step in sulfate–chloride media allowed the high metal recovery in this study, thereby proving it to be a good approach for the extraction of economic-importance metals as well as hazardous elements from the sulfidic tailing.

Conclusions

The results obtained in this study showed that the use of a 33 Box–Behnken design allowed for the observation of two different conditions to leach the desired metals from the tailing sample. The lead extraction was strongly influenced by the sodium chloride concentration, while copper and zinc yields were strongly affected by the increase in temperature. The leaching rates of copper and zinc significantly increased as time progressed in the two-stage leaching test, leading to a high global extraction of the three metals. Likewise, in the two-stage leaching step, the leaching treatment proved to be effective in the reduction of the heavy metal content compared to the untreated sample, and the amount of Fe leached did not rise over the two stages. Analysis of the solid residues by XRD analysis showed no significant difference in the main mineral phases between the starting sample and the final residue, allowing for an alternative final destination of the (cleaned) residue.

Acknowledgements The authors thank the company SOMINCOR-Lundin Mining for providing the tailings sample. The authors also thank Petra Sommer, Heike Große for the ICP-OES analysis, Sarah Tuchtfeld for the particle size measurement, and Thomas Schirmer for the XRD analysis. This work is part of the MSCA-ETN SULTAN project, and it has received funding from the European Union’s EU Framework Programme for Research and Innovation Horizon 2020 under Grant Agreement No. 812580. Project website: https://etn-sultan.eu/.

Funding Open Access funding enabled and organized by Projekt DEAL.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.
References

1. European commission (2020) Critical raw materials resilience: charting a path towards greater security and sustainability.
2. Calvo G, Mudd G, Valero A, Valero A (2016) Decreasing ore grades in global metallic mining: a theoretical issue or a global reality? Resources. https://doi.org/10.3390/resources5040036
3. Northey S, Mohr S, Mudd GM, Weng Z, Giurco D (2014) Modeling future copper ore grade decline based on a detailed assessment of copper resources and mining. Resour Conserv Recy. https://doi.org/10.1016/j.resconrec.2013.10.005
4. Aznar-Sánchez J, García-Gómez J, Velasco-Muñoz J, Carretero-Gómez A (2018) Mining waste and its sustainable management: advances in worldwide research. Minerals. https://doi.org/10.3390/min8070284
5. Fatagán C, Grail BM, Johnson DB (2017) New approaches for extracting and recovering metals from mine tailings. Miner Eng. https://doi.org/10.1016/j.mineng.2016.10.008
6. Altinkaya P, Liipo J, Kolehmainen E, Haapalainen M, Leikola M, Lundström M (2019) Leaching of trace amounts of metals from flotation tailings in cupric chloride solutions. Min Metall Explor. https://doi.org/10.1007/s42461-018-0015-9
7. Dold B (2014) Evolution of acid mine drainage formation in sulphidic mine tailings. Minerals. https://doi.org/10.3390/min4038621
8. Hatie V, Pedreira RMA, Rezende CE, França CA, Souza GC, Marin DC, Hashpaker PC (2017) The environmental impacts of one of the largest tailing dam failures worldwide. Sci Rep. https://doi.org/10.1038/s41598-017-1143-x
9. Senanayake G, Muir DM (2003) Chloride processing of metal sulphides: review of fundamentals and applications. TMS, Warrendale
10. Torres CM, Taboada ME, Graber TA, Herreros OO, Ghorbani Y, Watling HR (2015) The effect of seawater based media on copper dissolution from low-grade copper ore. Miner Eng. https://doi.org/10.1016/j.mineng.2014.11.008
11. Carneiro M, Lêo VA (2007) The role of sodium chloride on surface properties of chalcopyrite leached with ferric sulphate. Hydrometallurgy. https://doi.org/10.1016/j.hydromet.2007.01.005
12. Hernández PC, Taboada ME, Herreros OO, Torres CM, Ghorbani Y (2015) Chalcopyrite dissolution using seawater-based acidic media in the presence of oxidants. Hydrometallurgy. https://doi.org/10.1016/j.hydromet.2015.09.007
13. Lawson F, Cheng C-Y, Lee SYY (1992) Leaching of copper sulphides and copper mattes in oxygenated chloride/sulphate leachants. Miner Process Extr Metall Rev. https://doi.org/10.1080/08827509208952686
14. Lu ZY, Jeffrey MI, Lawson F (2000) The effect of chloride ions on the dissolution of chalcopyrite in acidic solutions. Hydrometallurgy. https://doi.org/10.1016/S0303-368X(00)00075-X
15. Byrne RH, Yao W, Luo Y, Millero FJ (2010) Complexation of Pb(I) by chloride ions in aqueous solutions. Aquat Geochem. https://doi.org/10.1007/s10498-010-9101-4
16. Watling HR (2013) Chalcopyrite hydrometallurgy at atmospheric pressure: 1. Review of acidic sulfate, sulfate–chloride and sulfate–nitrate process options. Hydrometallurgy. https://doi.org/10.1016/j.hydromet.2013.09.013
17. Watling HR (2014) Chalcopyrite hydrometallurgy at atmospheric pressure: 2. Review of acidic chloride process options. Hydrometallurgy. https://doi.org/10.1016/j.hydromet.2014.03.013
18. Dutrizac JE (1992) The leaching of sulphide minerals in chloride media. Hydrometallurgy. https://doi.org/10.1016/0304-386X(92)90004-J
19. Behnajady B, Moghaddam J, Behnajady MA, Rashchi F (2012) Determination of the optimum conditions for the leaching of lead from zinc plant residues in NaCl–H2SO4–Cat(OH)2 media by the Taguchi method. Ind Eng Chem Res. https://doi.org/10.1021/ie202571x
20. Ye M, Li G, Yan P, Zheng L, Sun S, Huang S, Haifei L, Chen Y, Yang L, Huang J (2017) Production of lead concentrate from bioleached residue tailings by brine leaching followed by sulfide precipitation. Sep Purif Technol. https://doi.org/10.1016/j.seppur.2017.04.020
21. Farahmand F, Moradkhani D, Safarzadeh MS, Rashchi F (2009) Brine leaching of lead-bearing zinc plant residues: Process optimization using orthogonal array design methodology. Hydrometallurgy. https://doi.org/10.1016/j.hydromet.2008.07.012
22. Ye M, Yan P, Sun S, Han D, Xiao X, Zheng L, Huang S, Chen Y, Zhuang S (2017) Bioleaching combined brine leaching of heavy metals from lead-zinc mine tailings: transformations during the leaching process. Chemosphere. https://doi.org/10.1016/j.chemosphere.2016.10.095
23. Nthunya LN, Mafadi S, Mamba BM, Arne RV, Sabelo DM (2018) Spectroscopic determination of water salinity in brackish surface water in Nandoni dam, at Vhembe district, Limpopo Province, South Africa. Water. https://doi.org/10.3390/w10080990
24. Cisternas LA, Gálvez ED (2018) The use of seawater in mining. Miner Process Extr Metall Rev. https://doi.org/10.1080/08827509.2017.1389729
25. Veloso TC, Peixoto JJ, Pereira MS, Leão VA (2016) Kinetics of chalcopyrite leaching in either ferric sulphate or cupric sulphate media in the presence of NaCl. Int J Miner Process. https://doi.org/10.1016/j.minpro.2016.01.014
26. Bobadilla-Fazzini RA, Pérez A, Gautier V, Jordan H, Parada P (2017) Primary copper sulphides bioleaching vs chloride leaching: advantages and drawbacks. Hydrometallurgy. https://doi.org/10.1016/j.hydromet.2016.08.008
27. Castillo J, Sepúlveda R, Araya G, Guzmán D, Toro N, Pérez K, Rodríguez M, Navarra M (2019) Leaching of white metal in a NaCl–H2SO4 system under environmental conditions. Minerals. https://doi.org/10.3390/min9050319
28. Zhang R, Hedrich S, Römer F, Goldmann D, Schippers A (2020) Bioleaching of cobalt from Cu/Co-rich sulfidic mine tailings from the polymetallic Rammelsberg mine, Germany. Hydrometallurgy. https://doi.org/10.1016/j.hydromet.2020.105443
29. Schippers A, Tanne C, Stummmeyer J, Gaupner T (2019) Sphalerite bioleaching comparison in shake flasks and percolators. Miner Eng. https://doi.org/10.1016/j.mineng.2018.12.007
30. Santos SM, Machado RM, Correia MJN, Reis MTA, Ismael MRC, Carvalho JMR (2010) Ferric sulphate/chloride leaching of zinc and minor elements from a sphalerite concentrate. Miner Eng. https://doi.org/10.1016/j.mineng.2010.02.005
31. Ferreira SLC, Bruns RE, Ferreira HS, Matos GD, David JM, Brandão GC, da Silva EGP, Portugal LA, dos Reis PS, Souza AS, dos Santos WNL (2007) Box-Behnken design: an alternative for the optimization of analytical methods. Anal Chim Acta. https://doi.org/10.1016/j.aca.2007.07.011
32. Hernández PC, Taboada ME, Herreros OO, Graber TA, Ghorbani Y (2018) Leaching of chalcopyrite in acidified nitrate using seawater-based media. Minerals. https://doi.org/10.3390/min8030608
33. Lundström M, Liipo J, Aromaa J (2012) Dissolution of copper and iron from sulfide concentrates in cupric chloride solution. Int J Miner Process. https://doi.org/10.1016/j.minpro.2011.11.005
34. Ruiz MC, Montes KS, Padilla R (2011) Chalcopyrite leaching in sulfate–chloride media at ambient pressure. Hydrometallurgy. https://doi.org/10.1016/j.hydromet.2011.05.007
35. Turan MD, Altundoğan HS, Tümen F (2004) Recovery of zinc and lead from zinc plant residue. Hydrometallurgy. https://doi.org/10.1016/j.hydromet.2004.07.008
36. Escobar AG, Relvas JMRS, Pinto AMM, Oliveira M (2021) Physical–chemical characterization of the Neves Corvo extractive mine residues: A perspective towards future mining and reprocessing of sulfidic tailings. J Sustain Metall. https://doi.org/10.1007/s40831-021-00428-1
37. Fu S, Lu J (2019) Temperature-driven variation in the removal of heavy metals from contaminated tailings leaching in northern Norway. Environ Monit Assess. https://doi.org/10.1007/s10661-019-7244-3
38. Ebrahimzade H, Khayati GR, Schaffie M (2018) Leaching kinetics of valuable metals from waste Li-ion batteries using neural network approach. J Mater Cycles Waste Manage. https://doi.org/10.1007/s10163-018-0766-x
39. Yuliusman RF, Silvia AN (2018) Acid leaching and kinetics study of cobalt recovery from spent lithium-ion batteries with nitric acid. E3S Web Conf. https://doi.org/10.1051/e3sconf/20186703025
40. Li Y, Kawashima N, Li J, Chandra AP, Gerson AR (2013) A review of the structure, and fundamental mechanisms and kinetics of the leaching of chalcopyrite. Adv Colloid Interface Sci. https://doi.org/10.1016/j.cis.2013.03.004
41. de Oliveira C, de Lima GF, de Abreu HA, Duarte HA (2012) Reconstruction of the chalcopyrite surfaces—a DFT study. J Phys Chem C. https://doi.org/10.1021/jp300713z
42. Guo Z, Pan F, Xiao X, Zhang L, Jiang K (2010) Optimization of brine leaching of metals from hydrometallurgical residue. T Nonferr Metal Soc. https://doi.org/10.1016/S1003-6326(09)60408-8
43. Box GEP, Behnken DW (1960) Some new three level designs for the study of quantitative variables. Technometrics. https://doi.org/10.1080/00401706.1960.10489912
44. Ratner B (2009) The correlation coefficient: Its values range between +1/−1, or do they? J Target Meas Anal Mark. https://doi.org/10.1057/jt.2009.5
45. Zhong S, Li Y (2019) An improved understanding of chalcopyrite leaching kinetics and mechanisms in the presence of NaCl. J Mater Res Technol. https://doi.org/10.1016/j.jmrt.2019.06.020
46. Liao MX, Deng TL (2004) Zinc and lead extraction from complex raw sulfides by sequential bioleaching and acidic brine leach. Miner Eng. https://doi.org/10.1016/j.mineng.2003.09.007
47. Altinkaya P, Mäkinen J, Kinnunen P, Kolehmainen E, Haapaleinen M, Lundström M (2018) Effect of biological pretreatment on metal extraction from flotation tailings for chloride leaching. Miner Eng. https://doi.org/10.1016/j.mineng.2018.09.012
48. Keber S, Brückner L, Elwert T, Kuhn T (2020) Concept for a hydrometallurgical processing of a copper-cobalt-nickel alloy made from manganese nodules. Chem Ing Tech. https://doi.org/10.1002/cite.201900125
49. Wang H, Friedrich B (2015) Development of a highly efficient hydrometallurgical recycling process for automotive Li-ion batteries. J Sustain Metall. https://doi.org/10.1007/s40831-015-0016-6
50. Gou M, Zhou L, Then NWY (2019) Utilization of tailings in cement and concrete: a review. Sc Eng Compos Mater. https://doi.org/10.1515/secm-2019-0029

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Authors and Affiliations

Tamara A. Schueler1 · Paula F. de Aguiar2 · Ysrael M. Vera3 · Daniel Goldmann1

1 Department of Mineral and Waste Processing, Institute of Mineral and Waste Processing, Waste Disposal and Geomechanics, Clausthal University of Technology, Walther-Nernst-Str. 9, 38678 Clausthal-Zellerfeld, Germany
2 Institute of Chemistry, Federal University of Rio de Janeiro, Athos da Silveira Ramos 149, Rio de Janeiro 21941-909, Brazil
3 Coordination of Metallurgical and Environmental Process, Center for Mineral Technology, Av. Pedro Calmon 900, Rio de Janeiro 21941-908, Brazil