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

Tamara A. Schueler[1] · Paula F. de Aguiar[2] · Ysrael M. Vera[3] · Daniel Goldmann[1]

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 3^3 Box–Behnken design was applied to evaluate three variables over a 4-h testing period: sulfuric acid concentration (0.01–1.0 mol/L H_2SO_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 H_2SO_4 level, and medium temperature level for lead leaching, while for copper and zinc, a combination of a medium–high H_2SO_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 H_2SO_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 H_2SO_4, 70 °C, 24 h, 10:1 liquid-to-solid ratio). The global leaching rate was $66.8 \pm 3.0\%$ copper, $84.1 \pm 5.2\%$ zinc, and $93.9 \pm 3.2\%$ 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
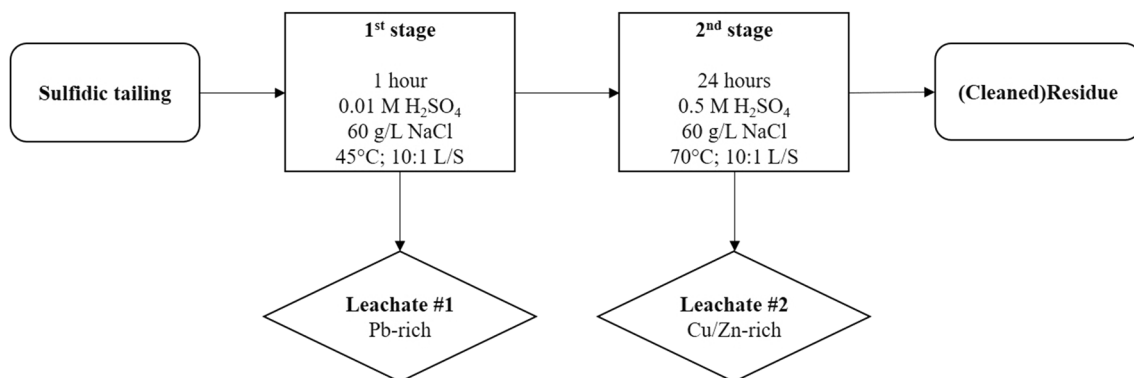
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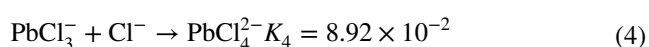
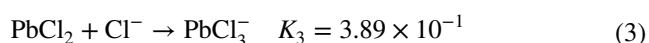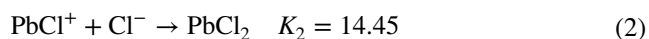✉ Daniel Goldmann
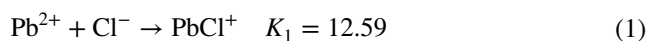 daniel.goldmann@tu-clausthal.de

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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 acid 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 $PbSO_4$ [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.

$$Pb^{2+} + Cl^- \rightarrow PbCl^+ \quad K_1 = 12.59 \tag{1}$$

$$PbCl^+ + Cl^- \rightarrow PbCl_2 \quad K_2 = 14.45 \tag{2}$$

$$PbCl_2 + Cl^- \rightarrow PbCl_3^- \quad K_3 = 3.89 \times 10^{-1} \tag{3}$$

$$PbCl_3^- + Cl^- \rightarrow PbCl_4^{2-} \quad K_4 = 8.92 \times 10^{-2} \tag{4}$$

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 H_2SO_4 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 (H_2SO_4, HCl, HNO_3) in seawater or pure water. The presence of Cl^- (0.16 mol/L, NaCl) and Cu^{2+} (0.08 mol/L, $CuCl_2$) enhanced the copper extraction for both systems (0.32 mol/L acid concentration), reaching the maximum extraction of 37.7% in the HCl–seawater–Cu^{2+} 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 H_2SO_4 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 H_2SO_4 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

extraction route. For this purpose, the effect of three parameters, sulfuric acid concentration, sodium chloride concentration, and temperature, on the yield of the desired metals was studied using a 3^3 Box–Behnken design over regular time intervals. The adoption of two-stage leaching was further investigated according to the results obtained by the design.

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 $Li_2B_4O_7$ and leached with HCl melt digestion. To analyze sulfur, the sample was mixed with MgO/Na_2CO_3, ignited for 2 h at 850 °C, and dissolved in diluted HNO_3. The mineralogical composition of the sample was determined by X-ray diffraction using a X'Pert 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 H_2SO_4 (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 ($n \geq 2$), and the error bars were calculated as the standard deviation. The graphs were plotted using OriginPro® 2020 software (version 9.7.0.188).

3^3 Box–Behnken Design

The 3^3 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 $N = 2k\,(k-1) + C_0$, 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 ≤ 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 $A_{\text{(NaCl concentration)}}$, 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 $B_{\text{(H}_2\text{SO}_4\text{ concentration)}}$, an acidic media (pH ≤ 2.0) already showed promising results in the previous tests. The upper limit value of $B_{\text{(H}_2\text{SO}_4\text{ concentration)}}$ 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.

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

Independent variables	Low −1	Medium 0	High +1
A: NaCl (g/L)	10	35	60
B: H_2SO_4 (mol/L)	0.01	0.5	1.0
C: Temperature (°C)	20	45	70

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 H_2SO_4 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 H_2SO_4), 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 ($d_{90} = 115.86$ μm). 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 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
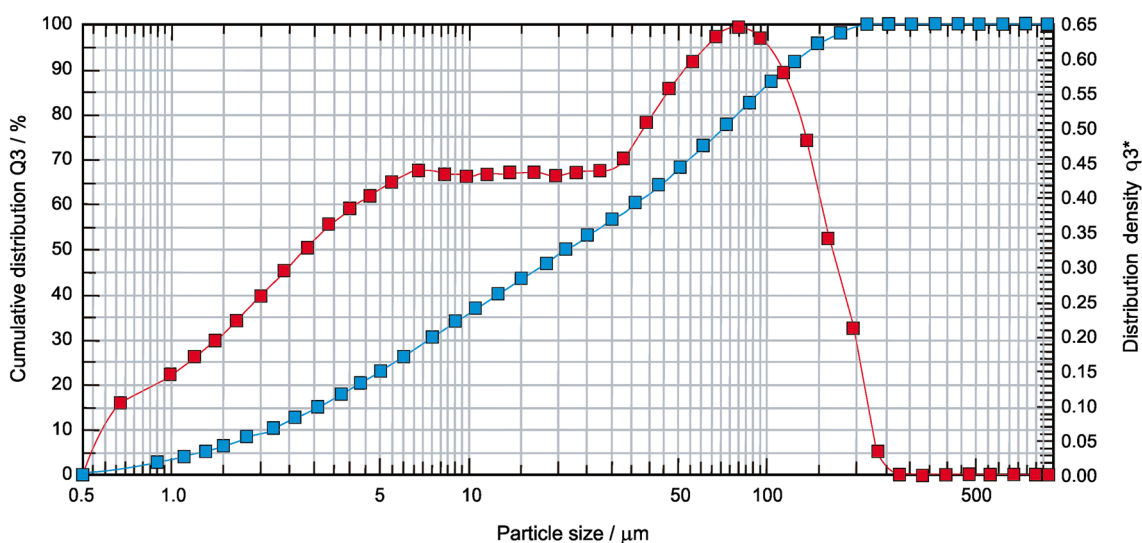
Fig. 1 Particle size distribution of the Cu–Zn tailings used in the experiments ($d_{10} = 2.16$ μm, $d_{50} = 21.39$ μm, $d_{90} = 115.86$ μm)

(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%; $CuFeS_2$) and other minor Cu-bearing minerals, such as tetrahedrite (0.10 wt%; $(Cu,Fe)_{12}Sb_4S_{13}$); 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
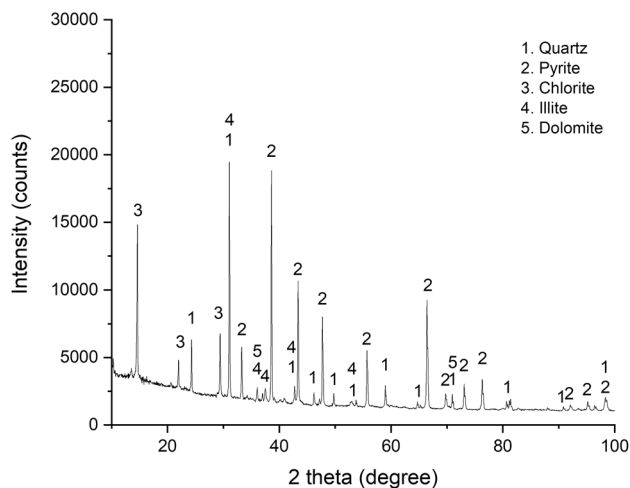

Fig. 2 XRD pattern of the SUL_NC_02 tailing (quartz: SiO_2; pyrite: FeS_2; chlorite: $A_{5-6}T_4Z_{18}$, where A = Al, Fe^{2+}, Fe^{3+}, Li, Mg, Mn, or Ni, while T = Al, Fe^{3+}, Si, or a combination of them, and Z = O and/or OH; illite: $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)])$; dolomite: $CaMg(CO_3)_2$

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

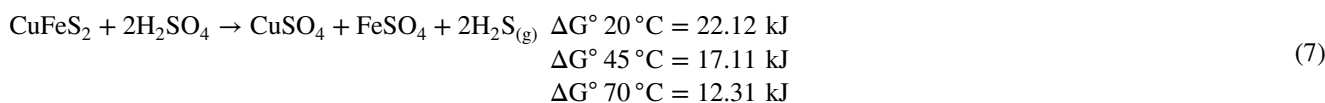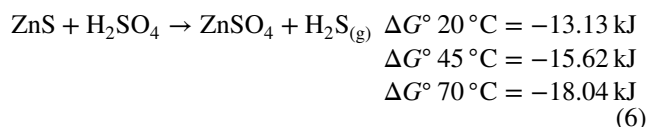### Leaching Behavior of Cu, Zn, and Pb Using Design of Experiment

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 3^3 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 H_2SO_4), 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 H_2SO_4) led to a lower Cu extraction (≈ 15%) compared to the above-mentioned 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 H_2SO_4 concentration.

Table 3 Experiments performed in the 3^3 Box–Behnken design and the results obtained at 4-h leaching of the three target metals

Experiment	NaCl (g/L)	H_2SO_4 (mol/L)	Temperature (°C)	Response		
				Cu (%)	Zn (%)	Pb (%)
1	10	0.01	45	9.9 ± 0.2	12.1 ± 0.6	2.6 ± 0.1
2	60	0.01	45	9.1 ± 1.0	13.6 ± 1.0	53.7 ± 1.6
3	10	1.0	45	9.1 ± 0.8	21.2 ± 0.5	2.6 ± 0.4
4	60	1.0	45	10.1 ± 0.5	22.2 ± 0.7	27.0 ± 0.5
5	10	0.5	20	6.0 ± 0.03	10.8 ± 0.1	2.7 ± 0.1
6	60	0.5	20	6.6 ± 0.05	12.0 ± 0.4	28.9 ± 0.4
7	10	0.5	70	29.8 ± 1.7	28.4 ± 2.2	2.7 ± 0.1
8	60	0.5	70	29.5 ± 0.03	33.2 ± 0.1	29.5 ± 4.3
9	35	0.01	20	5.4 ± 0.3	8.1 ± 0.8	20.2 ± 0.2
10	35	1.0	20	6.9 ± 0.7	12.7 ± 0.5	8.1 ± 0.5
11	35	0.01	70	14.6 ± 3.2	20.9 ± 2.2	15.9 ± 2.5
12	35	1.0	70	30.1 ± 0.2	35.6 ± 0.6	11.9 ± 3.1
13	35	0.5	45	9.5 ± 0.4	20.9 ± 0.6	10.5 ± 2.1
14	35	0.5	45	8.8 ± 0.2	20.2 ± 0.6	11.6 ± 1.6
15	35	0.5	45	8.6 ± 0.2	20.5 ± 0.1	11.6 ± 2.4

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 H_2SO_4 concentration between 0.25 and 5 mol/L did not affect the leaching yield when applying $Fe_2(SO_4)_3$ 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

$$k = Ae^{-E_a/RT}, \tag{5}$$

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 ($\approx$ 30–35%), whereas at the lowest temperature, the extraction decreased to $\approx$ 10% at 4 h. Additionally, the acid concentration at medium and high levels (0.5–1.0 mol/L H_2SO_4) contributed to the maximum leaching of Zn obtained by the design. However, Zn extraction was easier to be leached 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 sulfide minerals. The zinc sulfide (ZnS, sphalerite) and the copper-bearing minerals ($CuFeS_2$, 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 ΔG 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 H_2S equals 1.0×10^{-5} atm, and for H_2SO_4 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.
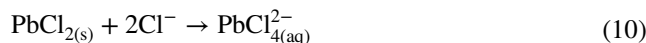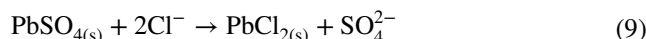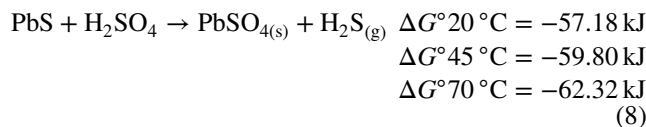
$$ZnS + H_2SO_4 \rightarrow ZnSO_4 + H_2S_{(g)} \quad \begin{array}{l} \Delta G° \, 20\,°C = -13.13\,kJ \\ \Delta G° \, 45\,°C = -15.62\,kJ \\ \Delta G° \, 70\,°C = -18.04\,kJ \end{array} \tag{6}$$

$$CuFeS_2 + 2H_2SO_4 \rightarrow CuSO_4 + FeSO_4 + 2H_2S_{(g)} \quad \begin{array}{l} \Delta G° \, 20\,°C = 22.12\,kJ \\ \Delta G° \, 45\,°C = 17.11\,kJ \\ \Delta G° \, 70\,°C = 12.31\,kJ \end{array} \tag{7}$$

On the other hand, the largest leaching yield of Pb ($53.7 \pm 1.6\%$, experiment number 2) was reached at the highest concentration of NaCl (60 g/L) and at the lowest acid concentration (0.01 mol/L H_2SO_4), as expected. In the presence of sulfuric acid, insoluble lead sulfate ($K_{sp} = 1.8 \times 10^{-8}$) is spontaneously formed (Reaction (8), $\Delta G°$ is negative). It can then be dissolved into soluble lead chloride ($K_{sp} = 1.2 \times 10^{-5}$) in brine solutions [Reactions (9) and (10) and (1)–(4)] [42] by the complexation equilibrium between the Pb ion and chloride ion concentrations [20].

$$PbS + H_2SO_4 \rightarrow PbSO_{4(s)} + H_2S_{(g)} \quad \begin{array}{l} \Delta G°\, 20\,°C = -57.18\,kJ \\ \Delta G°\, 45\,°C = -59.80\,kJ \\ \Delta G°\, 70\,°C = -62.32\,kJ \end{array} \tag{8}$$

$$PbSO_{4(s)} + 2Cl^- \rightarrow PbCl_{2(s)} + SO_4^{2-} \tag{9}$$

$$PbCl_{2(s)} + 2Cl^- \rightarrow PbCl_{4(aq)}^{2-} \tag{10}$$

Thus, under experimental conditions where the chloride source is high and the concentration of H_2SO_4 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 H_2SO_4). 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.

$$Cu = 8.94 + 0.05A + 2.12B + 9.89C + 0.45AB - 0.23AC + 3.50BC + 2.17A^2 - 1.55B^2 + 6.87C^2 \tag{11}$$

$$Zn = 20.54 + 1.07A + 4.63B + 9.32C - 0.12AB + 0.87AC + 2.52BC - 0.74A^2 - 2.51B^2 + 1.29C^2, \tag{12}$$

where A, B, and C are the codified variables that, respectively, represent NaCl concentration, H_2SO_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% ($F_{calculated} = 92.14 > F_{critical} = 19.16$). 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% ($F_{calculated} = 9.45 < F_{critical} = 19.16$). 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 $B_{(H_2SO_4 \text{ concentration})}$ and $C_{(Temperature)}$, 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

$A_{(NaCl \text{ concentration})}$ 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 $B_{(H_2SO_4 \text{ concentration})}$ and $C_{(Temperature)}$ and have a lower sensitivity to the factor $A_{(NaCl \text{ concentration})}$. The steep curvatures of factor $C_{(Temperature)}$ demonstrate a higher sensibility 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% ($F_{calculated} = 64.11 > F_{critical} = 19.16$). Additionally, the regression analysis showed that the values for R^2 (0.97) and adj R^2 (0.92) are above 0.7.

$$Pb = 11.22 + 16.08A - 5.35B + 0.020C - 6.68AB + 0.16AC + 2.00BC + 6.11A^2 + 4.17B^2 - 1.39C^2 \tag{13}$$

The contour plot and response surface can be seen in Fig. 5 for the Pb leaching yield, with $A_{(NaCl)}$ and $B_{(H_2SO_4)}$ as the x_1 and x_2 axis, respectively, and the variable $C_{(Temperature)}$ 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 sensibility to the factors $A_{(NaCl)}$ and $B_{(H_2SO_4)}$. The relatively flat curvature of the factor $C_{(Temperature)}$ indicates a low sensitivity to this factor. The factor levels were chosen for having the best range for Pb extraction.
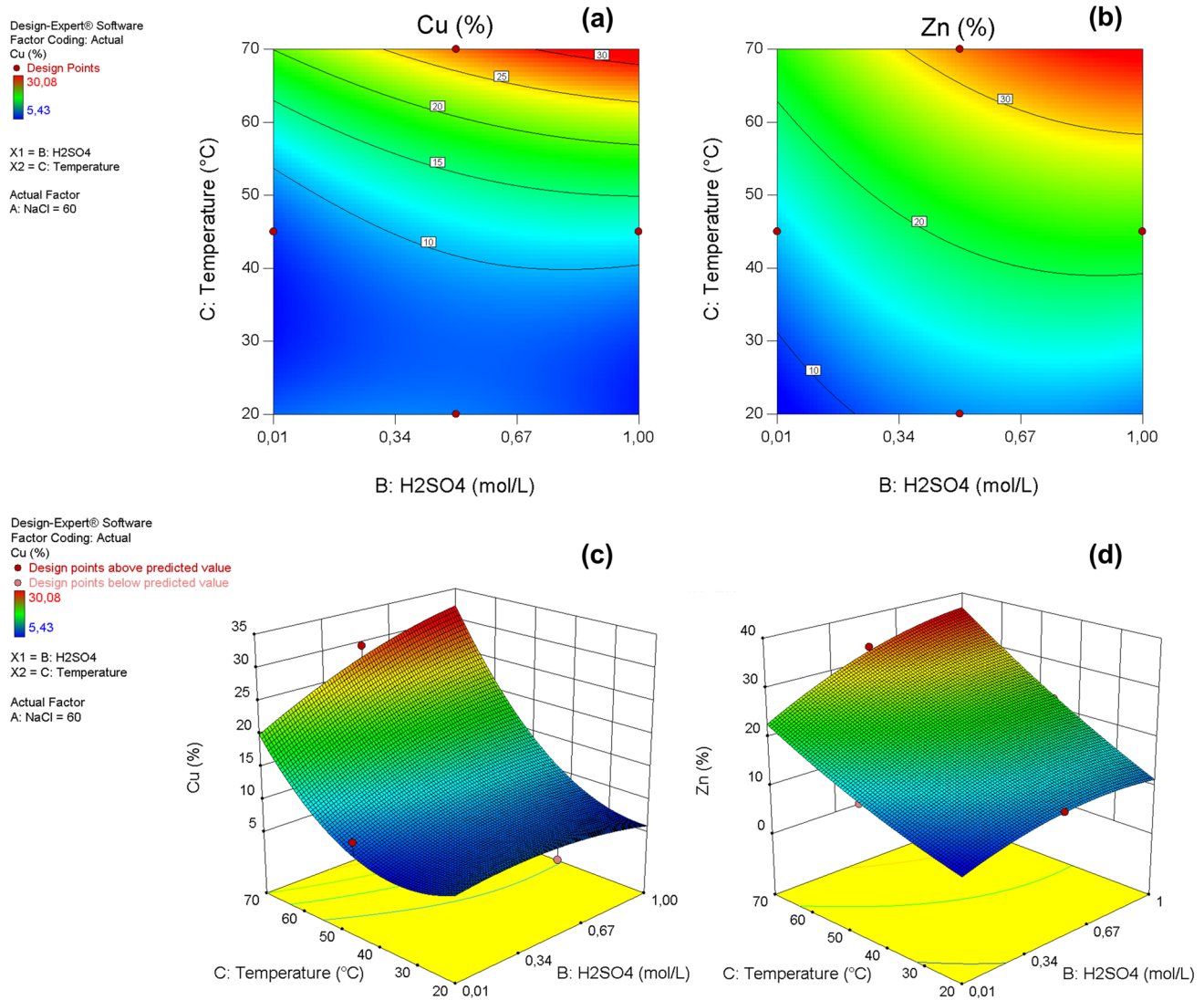
Fig. 3 Contour plots (**a** and **b**) and surface responses (**c** and **d**) of independent variables $B_{(H_2SO_4\ concentration)}$ and $C_{(Temperature)}$ on the leaching of Cu and Zn from SUL_NC_02 tailings. The fixed factor is $A_{(NaCl\ concentration)}$ at 60 g/L

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 H_2SO_4 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 ($\approx$ 2.0, H_2SO_4 concentrate) during the experimental time, resulting in a drop of Pb^{2+} solubility as

a function of SO_4^{2-} 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, $\approx$ 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 H_2SO_4) and temperature (70 °C), demonstrated an increased leaching rate of Cu and Zn over the 4-h testing time (approximately 30 and 35%
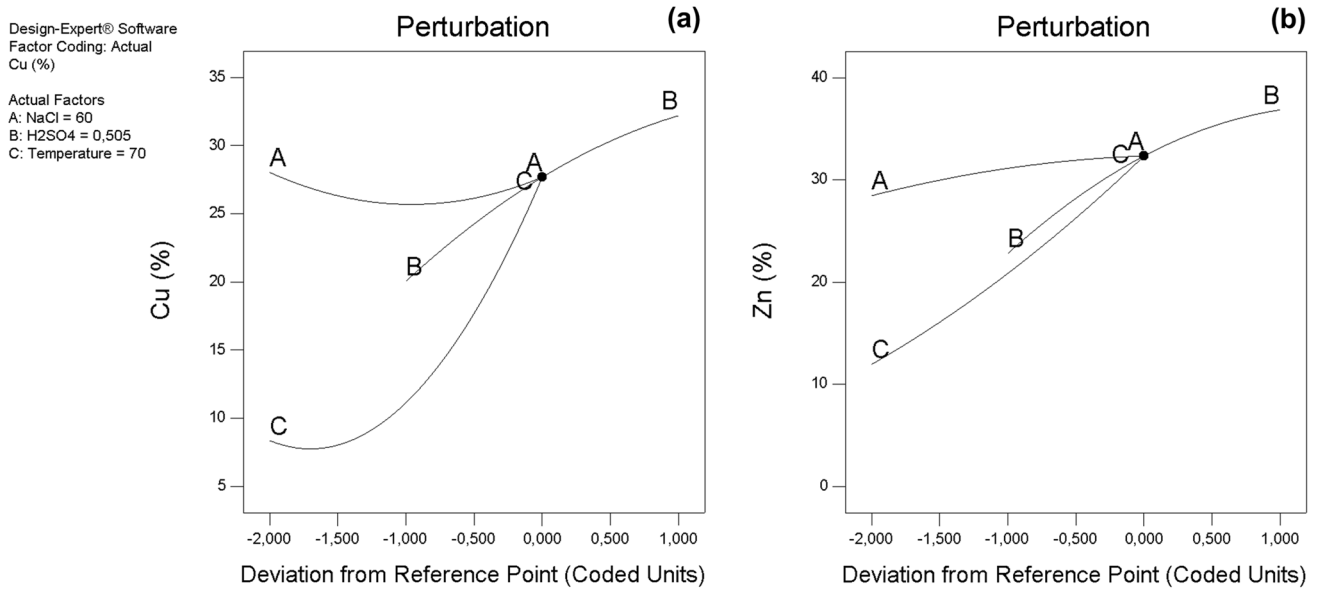
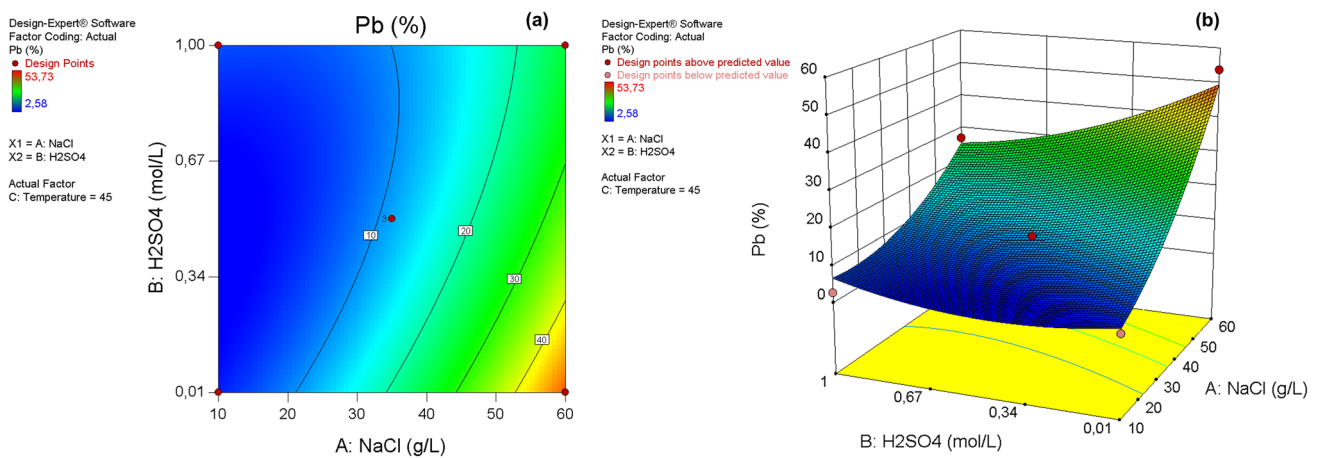**Fig. 4** Perturbation plots for the responses of Cu (**a**) and Zn (**b**) (%)

Fig. 5 Contour plot and surface response of independent variables $A_{(NaCl\ concentration)}$ and $B_{(H_2SO_4\ concentration)}$ and on the leaching of Pb from SUL_NC_02 tailings. The fixed factor is $C_{(Temperature)}$ at 45 °C

at 4 h). 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').
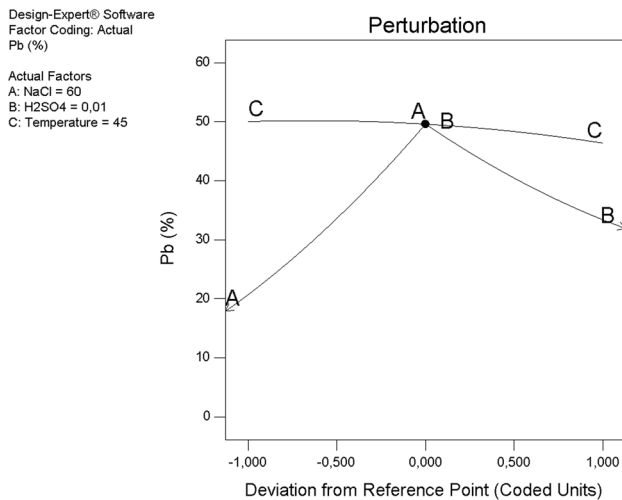
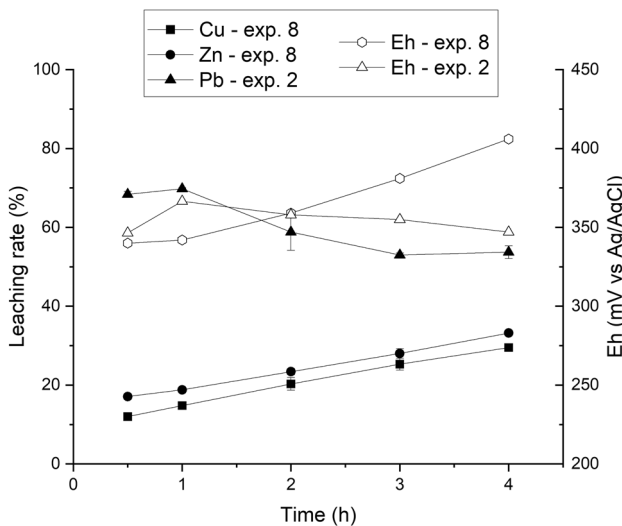**Fig. 6** Perturbation plot for the response of Pb (%)

Fig. 7 Leaching rate of Cu, Zn, and Pb, and the redox potentials values obtained throughout the 4-h experiment in experiment number 2 (60 g/L NaCl, 0.01 mol/L H$_2$SO$_4$, and 45 °C) and number 8 (60 g/L NaCl, 0.5 mol/L H$_2$SO$_4$, and 70 °C). The error bars were calculated as the standard deviation

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 3^3 Box–Behnken design (experiment number 2: 60 g/L of NaCl and 0.01 mol/L of H$_2$SO$_4$ 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 H$_2$SO$_4$ (experiment number 8, 3^3 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 (H$_2$SO$_4$) 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 H$_2$SO$_4$ 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 (H$_2$SO$_4$), 250 g/L NaCl, and O$_2$ as the oxidant for 72 h. 99%, 80%, and 90% of Ni, Co, and Zn, respectively, were leached in the biotreated feed with Cu^{2+} 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 H$_2$SO$_4$ 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 H_2SO_4, 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 H_2SO_4, and 70 °C). The error bars were calculated as the standard deviation
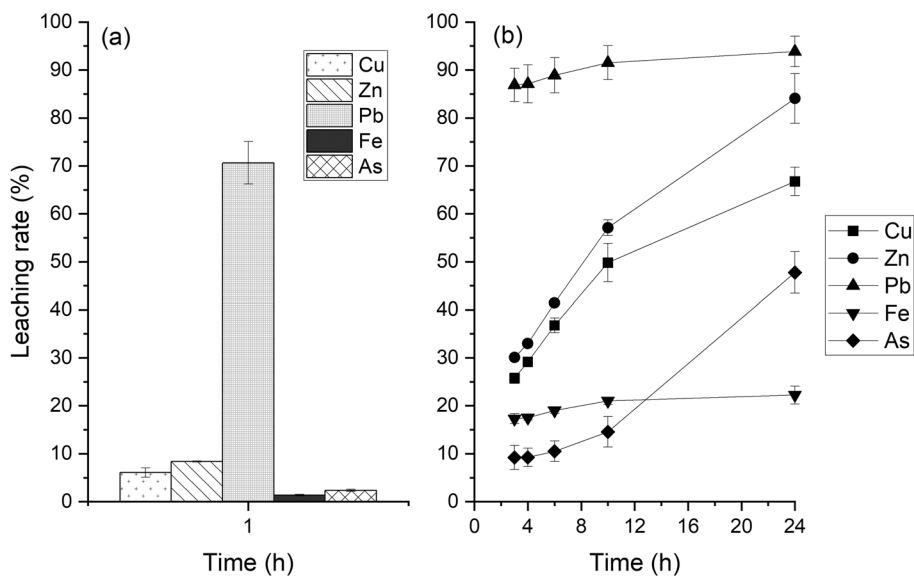

Table 4 Experimental conditions and the final results for sulfate–chloride media studies

Sample[a]	1st stage	2nd stage	Final results[b]	References
Sulfidic tailing (d_{90} = 115.9 μm) ($CuFeS_2$, ZnS, PbS)	1 h 0.01 mol/L H_2SO_4 60 g/L NaCl 45 °C	24 h 0.5 mol/L H_2SO_4 60 g/L NaCl 70 °C	Cu: 66.8 ± 3.0% Zn: 84.1 ± 5.2% Pb: 93.9 ± 3.2% As: 47.8 ± 4.3%	This study
Zinc plant residue (ZPR) (−74 μm) ($ZnSO_4$, $PbSO_4$)	30 min—roasting 1:1 ZPR/H_2SO_4 200 °C 60 min—leaching H_2O 25 °C	10 min 200 g/L NaCl 25 °C	Zn: 86% Pb: 89%	[35]
Zinc plant residue ($PbSO_4$, $ZnSO_4$, $Zn_4Si_2O_7$, ZnO, Zn_xFe_3–xO_4)	1 h—acid leaching pH 2.5 (H_2SO_4) 80 °C 1 h—water leaching 70 °C	30 min pH 1.0 (HCl) 300 g/L NaCl 37 °C	Zn: 92.8% Pb: 89.4%	[21]
Chalcopyrite ore ($CuFeS_2$)	144 h pH 1.0 (H_2SO_4) 0.1 mol/L NaCl 75 °C	No	Cu: ≈ 100%	[45]
Hydrometallurgical residue (120 μm) (CuS, ZnS, $Zn_4Si_2O_7$, $PbSO_4$)	1 h 1.0 mol/L H_2SO_4 250 g/L NaCl 85 °C	No	Cu: 93.6% Zn: 93.2% Pb: 91.6% In: 94.1%	[42]
Raw complex sulfide ores (74 μm) (ZnS, PbS)	20 days Bioleaching	1.5 h 0.5 mol/L HCl 140 g/L NaCl 60 °C	Zn: 95% Pb: 94%	[46]
Flotation tailing (d_{80}: 150 μm—as-received) ($CuFeS_2$, ZnS)	15 days Bioleaching	72 h pH 1.0 (H_2SO_4) 250 g/L NaCl 95 °C, O_2	Cu: 98% Au: 63%	[47]
Flotation tailing (d_{80}: 26 μm—grounded) ($CuFeS_2$, ZnS)	11 days Bioleaching	24 h pH 1.8 (H_2SO_4) 250 g/L NaCl 95 °C, Cu^{2+}	Zn: 90% Ni: 99% Co: 80%	

[a]The main Cu, Zn, and Pb phases are presented

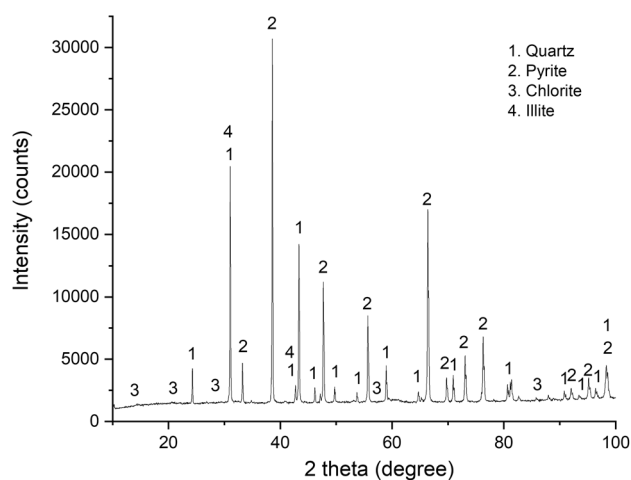[b]Final results mean global leaching results (first stage + second stage)

Fig. 9 XRD pattern of the leached residue after two-stage leaching (quartz: SiO_2; pyrite: FeS_2; chlorite: $A_{5-6}T_4Z_{18}$, where $A = Al$, Fe^{2+}, Fe^{3+}, Li, Mg, Mn, or Ni, while $T = Al$, Fe^{3+}, Si, or a combination of them, and $Z = O$ and/or OH; illite: $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)])$

temperatures, and/or longer time processes and the addition of oxidizing agents, such as O_2 or Cu^{2+}, 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 3^3 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.

Declarations

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

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