



# Article Removal of Base Metals from Mine Tailings in Chloride- and Seawater-Based Media Followed by Solvent Extraction

Tamara Azevedo Schueler <sup>1,\*</sup>, Paula Fernandes de Aguiar <sup>2</sup>, Bengi Yagmurlu <sup>1</sup>, and Daniel Goldmann <sup>1,\*</sup>

- <sup>1</sup> Institute of Mineral and Waste Processing, Recycling and Circular Economy Systems, Clausthal University of Technology, Walther-Nernst-Str. 9, 38678 Clausthal-Zellerfeld, Germany; bengi.yagmurlu@tu-clausthal.de
- <sup>2</sup> Institute of Chemistry, Federal University of Rio de Janeiro, Athos da Silveira Ramos 149, Rio de Janeiro 21941-909, Brazil; paulafda@iq.ufrj.br
- \* Correspondence: tamara.azevedo.schueler@tu-clausthal.de (T.A.S.); daniel.goldmann@tu-clausthal.de (D.G.)

Abstract: The high volume of mine tailings generated during mining activities poses significant worldwide storage risks. However, these tailings often contain valuable metals that can be recovered. Therefore, reprocessing mine tailings has emerged as a crucial strategy to assess secondary metals resources and mitigate storage risks. Furthermore, the mining industry's extensive use of freshwater necessitates exploring alternative water sources. In this study, the leaching of base metals from mine tailings in chloride-based media was investigated. Approximately 52% Cu, 73% Zn, and 100% Pb were leached from the sample in the presence of HCl and NaCl. The substitution of freshwater with seawater yielded comparable results, demonstrating the potential of seawater as an alternative freshwater source that does not compromise leaching effectiveness. Additionally, 77% of Pb precipitated as PbSO<sub>4</sub> from the pregnant leach solution. Through solvent extraction, approximately 100% Cu was recovered using LIX 984 as an extractant, and 71% Zn with D2EHPA. The use of Fe<sup>0</sup> significantly reduced the co-extraction of Fe in the Zn recovery step. Overall, this study provides a potential route for reprocessing mine tailings, ensuring maximum leaching and efficient recovery of metals from sulfide mine tailings.

Keywords: mine tailings; leaching; seawater; solvent extraction; metals recovery; optimization

# 1. Introduction

Mine tailings represent the primary waste stream produced in mining operations [1,2]. It is estimated that between 5 and 7 billion tons of tailings are generated annually [3]. Tailings can be described as mixtures of waste materials and process fluids produced during the extraction of minerals and metals from an ore, with their mineralogical composition dependent on the original ore body [1]. Sulfide tailings, resulting from the extraction of base or precious metals such as Cu, Co, Zn, and Au, typically contain, among others, pyrite (FeS<sub>2</sub>) as the most common mineral, alongside gangue fractions as quartz (SiO<sub>2</sub>).

Tailings are stored in impoundments, known as tailings storage facilities, often referred to as "tailings dams" or "tailings ponds", designed to contain the waste material and prevent its contamination of the surrounding environment [2]. The production of acid mine drainage (AMD) significantly impacts the environment, as it results from the oxidation of sulfide minerals, particularly pyrite [4]. The resulting high concentration of acid and dissolved metals forms a hazardous mixture that can contaminate groundwater, streams, and rivers, leading to significant environmental damage. Additionally, the rupture of tailings dams poses a critical environmental and humanitarian issue, causing the destruction of ecosystems and resulting in incalculable impacts on local populations, including the displacement of residents and the loss of numerous lives [5,6].

Mining activities also consume a significant volume of water. For example, in Chile, mining operations accounted for approximately 3% of the total freshwater consumption in the country [3]. Of this consumption, 14% was attributed to hydrometallurgical processes



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). in 2019. The use of seawater in mining operations offers an alternative solution to alleviate water scarcity issues, particularly in regions where freshwater resources are limited [3,7]. However, the corrosive nature of seawater presents a significant challenge for its use. Furthermore, the desalination process required to make seawater usable can be both energy-intensive and expensive [3]. To address these challenges associated with chloride systems, various strategies have been developed, including the use of reactors constructed from materials with anti-corrosive properties [8,9]. Nevertheless, the positive impact of using non-desalinized seawater in copper ore processing to mitigate AMD has been demonstrated [10].

The reprocessing of mining tailings on a large scale is still in its early stages, and it is therefore difficult to estimate its cost [3,11]. However, its role as a secondary source of metals is a crucial approach to reduce waste and mitigate storage-related risks. While the concentration of valuable metals in tailings is generally lower than that in concentrates or ores, there is still significant potential for recovery since the mining and particle size reduction processes have already been completed during ore processing [2,12].

Hydrometallurgical processes have been successfully implemented over the years due to their versatility, offering various processing options (e.g., leaching, oxidation, and complexing agents) for a wide range of valuable metals [13]. Chloride-based leaching systems are known for their aggressive nature, providing several advantages, including increased metal solubility, faster leaching kinetics compared to sulfate-based systems, low pyrite reactivity, and the production of elemental sulfur instead of sulfate, which can be stored for further processing [14,15]. Moreover, the formation of chloro-complexes in aqueous solutions makes chloride-based media ideal for leaching base metals like Cu, Zn, and Pb [16,17]. Numerous studies have explored chloride-based systems in leaching processes [9,16,18–24], including bioleaching with chloride-tolerant bacteria [25,26]. However, more research employing mine tailings in chloride-based media is needed. While the use of seawater in mining processing has been implemented on a large scale [7], the application of seawater-based media in chemical leaching processes, particularly in the context of mine tailings, remains largely unexplored to the best of our knowledge. In light of these considerations, this study primarily aims to assess the extraction of base metals, namely Cu, Zn, and Pb, from sulfide mine tailings in the presence of saltwater (NaCl and artificial seawater). Furthermore, the recovery of the metals from the leached solution was investigated by solvent extraction.

## 2. Materials and Methods

## 2.1. Mine Tailings Sample

The tailings sample used in this study was sourced from the Neves-Corvo mine, located in the southeastern region of Portugal. This mine is a high-grade Cu–(Sn)–Zn underground deposit and is situated within the Portuguese sector of the Iberian Pyrite Belt (IPB). It is estimated that 17 Mt of tailings were stored at the Cerro do Lobo tailings management facility (TMF) between 2010 and 2019 [27,28]. About 25 kg of sample was received under water to prevent oxidation. Prior to its use, the sample was dried at 40 °C, homogenized, split, and stored in vacuum-sealed plastic bags for further use.

The chemical composition of the starting sample was analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, ICP5100 Agilent Technologies, Santa Clara, CA, USA). For ICP-OES analysis, a combination of acid and melt digestion methods was employed. The sample was first dissolved using HCl and HNO<sub>3</sub>, and the residue was then fused with Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and leached with HCl melt digestion. To analyze sulfur content, the sample was mixed with MgO and Na<sub>2</sub>CO<sub>3</sub>, ignited at 850 °C for 2 h, and subsequently dissolved in diluted HNO<sub>3</sub>. The mineralogical composition was determined through X-ray diffraction using an X'Pert Pro diffractometer (XRD, PANalytical, Almelo, the Netherlands). Particle size distribution was assessed by laser diffraction in suspension using a Sympatec Helos/KR with a Quixel disperser (Sympatec GmbH, Clausthal-Zellerfeld, Germany).

# 2.2. Chemicals

The following chemicals were utilized in this work: hydrochloric acid (fuming HCl  $\geq$  37%, P.A., Honeywell | Fluka, Brunn am Gebirge, Austria); sodium chloride (NaCl  $\geq$  99%, USP, Carl Roth, Karlsruhe, Germany); magnesium chloride hexahydrate (MgCl<sub>2</sub>\*6H<sub>2</sub>O  $\geq$  98%, Carl Roth, Germany); sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>  $\geq$  98.5%, Carl Roth, Germany); calcium chloride (CaCl<sub>2</sub>  $\geq$  99%, USP, Carl Roth, Germany); potassium chloride (KCl  $\geq$  99%, USP, Carl Roth, Germany); sodium bicarbonate (NaHCO<sub>3</sub>  $\geq$  99.7%, P.A., Honeywell | Riedel-de-Häen, Seelze, Germany); potassium bromide (KBr  $\geq$  99%, P.A., Carl Roth, Germany); boric acid (H<sub>3</sub>BO<sub>3</sub>  $\geq$  99.8%, PanReac AppliChem, Darmstadt, Germany); strontium chloride hexahydrate (SrCl<sub>2</sub>\*6H<sub>2</sub>O  $\geq$  99%, P.A., Carl Roth, Germany); sodium hydroxide (NaOH  $\geq$  98%, USP, PanReac AppliChem, Germany); LIX 984 (2-hydroxy-5 nonyl-acetonphenoneoxime and 2-hydroxy5-dodecylsalicylaldoxime, BASF, Ludwigshafen, Germany); D2EHPA (di-2-ethyl-hexyl phosphoric acid, Obermeier, Bayern, Germany); EXXSOL D100 (Biesterfeld, Hamburg, Germany).

#### 2.3. Leaching Experiments

The leaching experiments were carried out in glass reactors containing 10:1 liquid-tosolid ratio. The glasses were placed on a combined heating plate–magnetic stirrer device (MR Hei-Tec, Heidolph, Schwabach, Germany) at 250 rpm and set temperatures for each assay. The temperature of the solutions was measured and controlled using an external temperature sensor connected to the heating plate. The tailings sample was added to the lixiviant solution as soon as the desired temperature was reached. The leaching time started at the time the solid sample was added. The pH and oxidation–reduction potential (ORP, Ag/AgCl reference electrode) were measured over the experimental time. Samples were withdrawn at regular time intervals. The metals concentration in the filtrated aliquots of the pregnant leaching solution (PLS) were analyzed by ICP-OES (ICP5100 Agilent technologies, USA) in triplicate (n = 3). The leached solid residues were filtered, washed, and dried at 40 °C overnight. The assays were performed in duplicate or more ( $n \ge 2$ ), and the error bars were calculated as the standard deviation.

### 2.4. Design of Experiments

The optimum leaching efficiencies regions were investigated based on a  $3^3$  Box-Behnken design. This design of experiment (DoE) is a non-orthogonal model and an incomplete factorial design containing three levels (low, medium, and high, or -1, 0, and +1, respectively) and *N* numbers of experiments according to the Equation (1):

$$N = 2k \times (k - 1) + C_0, \tag{1}$$

where, k is the number of factors and  $C_0$  is the number of replicates at the central point [29,30].

Three factors were studied in this work: the concentration of (A) NaCl, (B) HCl, and (C) the temperature. In total, 15 experiments were randomly carried out in three levels and three central points (Table 1). The factors levels were selected based on preliminary studies, as described in [17], as well as a literature review [9,15,16,18–24]. Samples were taken at 0.5 h and 1–4 h of testing to observe the leaching behavior of the metals over the leaching period tested. The State-Ease Design-Expert<sup>®</sup> software (version 10.0.8) was used to estimate the model coefficients through regression analysis. It was also used to build the response surfaces for each response measured: the leaching efficiencies of Cu, Zn, and Pb.

**Table 1.** Experimental parameters of the 3<sup>3</sup> Box-Behnken design.

		Levels		
Factors	Unit	-1	0	+1
A: NaCl	g/L	10	35	60
B: HCl	mol/L	0.1	0.5	1.0
C: Temperature	°C	20	45	70

# 2.5. Leaching Time and Seawater Tests

The optimum leaching condition obtained by the DoE was further studied by increasing the leaching time up to 24 h. Samples were taken at defined time intervals. The use of artificial seawater in the leaching efficiency of Cu, Zn, and Pb metals from the tailings sample was also tested over 24 h. The seawater solution was prepared according to ASTM D1141–98 standards [31] (Table S1). The lixiviant solution was prepared by replacing the deionized water with artificial seawater.

# 2.6. Metals Recovery

The precipitation of Pb from the pregnant leach solution (PLS) was performed by adding Na<sub>2</sub>SO<sub>4</sub> based on the stoichiometric ratio of SO<sub>4</sub><sup>2–</sup>/Pb<sup>2+</sup>. The test was conducted in a glass beaker placed on a stirring plate at 500 rpm for 30 min at room temperature. At the end of the experiments, the solutions were filtered, and aliquots were withdrawn for ICP-OES analysis.

For Cu and Zn recoveries, the solvent extraction (SX) method was used. The extraction tests were carried out at pH levels ranging from 0.5 to 5.0, adjusted with HCl and NaOH solutions. LIX 984 and D2EHPA were used as Cu and Zn extractants, respectively. The extractants were diluted in a 1:10 (v/v) EXXSOL D100 solution. The volume phase ratio of aqueous (A) to organic (O) phases was fixed at 1:1. The experiments were performed in glass beakers at room temperature, with stirring at 500 rpm for 15 min. The concentration of Cu and Zn in the aqueous phases were determined by ICP-OES.

# 3. Results and Discussion

# 3.1. Tailings Sample Characterization

As shown in Table 2 [17,27,28], the sample is primarily composed of iron (Fe, 28.6 wt%), sulfur (S, 24.9 wt%), and silicon (Si, 23.1 wt%). The content of the target metals is 0.4 wt% Cu, 1.03 wt% Zn, and 0.36 wt% Pb. The minerals phases detected by the XRD analysis (Figure 1, [17]) indicated the presence of quartz, pyrite, chlorite, illite, and dolomite. The mineralogical analysis performed by Escobar et al. [27] demonstrated that Cu is predominantly present in chalcopyrite (CuFeS<sub>2</sub>), Zn in sphalerite [(Zn,Fe)S], and Pb in galena (PbS). The fresh sulfide mine tailings sample was received with a fine grain size of d<sub>90</sub> = 115.86  $\mu$ m, meaning that 90% of the total particles are below this size (Figure S1). The starting sample was studied without further comminution.

Table 2. Elemental composition of the mine tailings sample.

Element	wt%	Element	wt%
Fe	28.6	Na	0.2
S	24.9	Ti	0.2
Si	12.1	Mn	0.06
Al	3.0	Ni	0.03
Zn	1.0	Sb	0.03
Mg	0.9	Со	0.02
Ca	0.5	Р	0.01
As	0.5	Ba	0.01
K	0.4	Cr	0.01
Cu	0.4	Sr	0.003
Pb	0.4	Ag	0.002

Adapted from [17].



**Figure 1.** XRD pattern of the starting mine tailings sample (quartz: SiO<sub>2</sub>; pyrite: FeS<sub>2</sub>; chlorite:  $A_{5-6}T_4Z_{18}$ , where A = Al, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Li, Mg, Mn, or Ni, while T = Al, Fe<sup>3+</sup>, Si, or a combination of them, and Z = O and/or OH; illite: (K,H<sub>3</sub>O)(Al,Mg,Fe)<sub>2</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>[(OH)<sub>2</sub>,(H<sub>2</sub>O)]); dolomite: CaMg(CO<sub>3</sub>)<sub>2</sub> [17].

#### 3.2. Leaching of Base Metals from the Mine Tailings Sample

Leaching, which involves the dissolution of metals from ore into a liquid solvent, has traditionally been used for the extraction of precious metals from ores [32,33]. However, in recent years, great attention has been given to the leaching of metals from alternative sources, such as mine tailings. This shift in focus can be attributed to the depletion rates of high-grade ore reserves, along with the advancements in technology that have made feasible the extraction of valuable metals from low-grade sources [34,35]. Additionally, there is a growing environmental and sustainable awareness regarding the recycling and reprocessing of mine tailings to minimize waste generation [2]. In this study, the leaching behavior of base metals from a mine tailings sample was investigated with the assistance of a DoE. This statistical and mathematical tool enables researchers to plan and conduct experiments with a varying set of parameters across different levels (minimum, intermediate, and maximum) while performing a relatively small number of experiments [36]. The leaching efficiencies of Cu, Zn, and Pb were determined by exploring the effects of NaCl and HCl concentrations and temperature through the 3<sup>3</sup> Box-Behnken design. The experiments were conducted over a 4 h period to evaluate the response of these factors at the different levels. These results are presented in Tables S2-S4.

Temperature appears to play an important role in the leaching efficiencies of the metals from the sample, especially for Cu and Zn. Very low extraction rates of Cu ( $\leq$ 7%) and Zn (<12%) were observed for all conditions carried out at 20 °C, regardless the acid and salt concentrations. At a temperature of 45 °C, with 0.5–1.0 mol/L HCl and 10–60 g/L NaCl, Cu yields ranged from 7–11% and Zn ranged from 12–22% after 4 h (exp. 3, 4, and 13–15). On the other hand, at a temperature of 70  $^{\circ}$ C, the highest Cu and Zn leaching efficiencies were achieved. The extraction of these metals increased from 12–17% at 0.5 h to about 29–36% at 4 h in experiments with 0.5 or 1.0 mol/L HCl and 10–60 g/L NaCl as lixiviants (exp. 7, 8, and 12). Conversely, in the test performed at 70 °C with the lowest acid concentration (0.1 mol/L HCl), the extraction of Cu was only around 11%, and for Zn, it was 19% at 4 h (exp. 11). These findings strongly suggest that the extraction of Cu and Zn within the studied parameter range is closely associated with an acidic media, specifically HCl concentrations exceeding 0.5 mol/L, and higher temperatures of  $\geq$ 70 °C. High temperature is often described as an important factor for leaching the refractory Cu-bearing mineral chalcopyrite (CuFeS<sub>2</sub>). In the presence of NaCl, increasing the temperature from 45 to 75 °C resulted in an increase from 17 to almost 100% of Cu leached after 144 h [37]. The reaction

was found to be controlled by the surface reaction model. Significant improvements in Zn leaching were observed as the temperature increased from 40 to 80 °C over 4 h [38]. After 15 min, 2 and 13% of Zn was leached from a zinc concentrate, while at 4 h, the Zn recoveries increased to 14 and 82% for 40 °C and 80 °C, respectively. The increase in temperature (15–90 °C), HCl concentration (1–5 mol/L), liquid-to-solid ratio (2–10 mL/g), and chloride ion concentration (3–6 mol/L) also promoted higher metal extraction from pre-treated mine tailings [39]. Among other metals, approximately 70% of Pb and 40% of Zn were leached from the roasted sample. The authors pointed out that using high acid concentration and liquid-to-solid ratio would significantly increase leaching costs, and the use of lower levels would be more appropriate.

Moreover, chloride ions have been associated with enhancing the solubility of metals through the formation of both metal chloro-complexes and an S<sup>0</sup> porous layer on the mineral surface [40,41]. The S<sup>0</sup> porous layer facilitates reagent diffusion to the mineral surface and, consequently, increases metal extraction. Nevertheless, the results obtained in the present work indicated that the leaching efficiencies of Cu and Zn metals were not significantly affected by the concentration of NaCl within the studied range. Altinkaya et al. [42] investigated the impact of varying NaCl concentrations (150–250 g/L) and cupric ions as an oxidant (0–50 g/L) on the leaching efficiencies (>50%, 24–72 h) for all the studied metals, even in the absence of an external oxidant. The authors suggested that inherently occurring oxidizing ions in the sample were sufficient for dissolving metals from low-grade tailings. In the presence of the oxidant, an increase in NaCl concentration was found to enhance the leaching of all metals except for Cu, which exhibited a higher leaching efficiency at the lower chloride concentration. The positive effect of an adequate amount of chloride ions in the solution, rather than an excess, has been demonstrated [43].

The leaching efficiencies of Cu, Zn, and Pb as a function of time are shown in Figure 2 (also refer to Tables S2–S4). For better visualization, only the three best results (exp 7, 8, and 12) are shown in this figure. Additionally, the pH values and redox potentials found for these conditions are presented in Figure S2. As displayed in Figure 2, the extraction of each metal gradually increased as time progressed from 0.5 to 4 h. While the extraction of Cu, Zn, and Pb was approximately 12, 16, and 75% after 30 min, after 4 h, the leaching efficiencies reached an average of around 30, 33, and 84%, respectively. This increase in metals' leaching efficiencies can also be associated with accelerated reaction kinetics at higher temperatures, as explained by the Arrhenius equation ( $k = Ae^{-E_a/RT}$ , 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 in Kelvin). High temperatures increase the reaction speed due to the increase in the kinetic constant of the reaction [17]. This association may also explain the lower extraction of the metals obtained at lower temperatures, even at higher acid concentrations (exp. 3–6, 10, 13–15, Tables S2–S4).



**Figure 2.** Highest leaching efficiencies (LE %) of Cu (a), Zn (b), and Pb (c) obtained from the  $3^3$  Box-Behnken design throughout 4 h leaching test.

Interestingly, high leaching efficiency of Pb was achieved in almost all conditions tested (60–87% Pb at 4 h test, Table S4), except for the experiment that contained the lowest Cl<sup>-</sup> content (exp. 1). This result can be attributed to the formation of soluble lead–chloride complexes (Equations (2)–(5)) in aqueous solution in the presence of an excess of Cl<sup>-</sup>, which promotes the solubilization of lead chloride (K<sub>sp</sub> =  $1.2 \times 10^{-5}$ ) [44,45]. As displayed in Figure 2c, between 70–90% of Pb was leached from the sample under the best leaching conditions found for Cu and Zn.

$$Pb^{2+} + Cl^- \rightarrow PbCl^+ K_1 = 12.59$$
 (2)

$$PbCl^{+} + Cl^{-} \rightarrow PbCl_2 K_2 = 14.45$$
(3)

$$PbCl_2 + Cl^- \rightarrow PbCl_3^- K_3 = 3.89 \times 10^{-1}$$
 (4)

$$PbCl_{3}^{-} + Cl^{-} \rightarrow PbCl_{4}^{2-} K_{4} = 8.92 \times 10^{-2}$$
 (5)

The results from the  $3^3$  Box-Behnken design were evaluated through regression analysis and analyzed for the lack of fit using analysis of variance (ANOVA). To model the data, a complete second-degree polynomial was chosen. Equations (6)–(8) represent the quadratic model for each metal.

$$Cu = +10.07 - 0.31A + 2.16B + 9.43C + 0.20AB - 0.83AC + 4.48BC + 2.99A^2 - 2.01B^2 + 5.77C^2$$
(6)

$$Zn = +20.03 - 0.41A + 4.22B + 9.29C - 0.15AB + 0.025AC + 3.25BC + 0.67A^2 - 1.70B^2 + 0.57C^2$$
(7)

$$Pb = +79.30 + 4.71A + 12.76B + 4.88C - 13.35AB - 0.43AC + 0.025BC - 5.15A^{2} - 13.30B^{2} + 5.37C^{2}$$
(8)

where A, B, and C are the codified variables that, respectively, represent NaCl concentration, HCl concentration, and temperature. All three models presented significant lack of fit to a confidence level of 95% (*p*-value < 0.05). Nevertheless, the coefficients of determination ( $\mathbb{R}^2$ ) were 0.89 for Cu, 0.98 for Zn, and 0.83 for Pb, indicating that more than 80% of the metals' leaching behavior can be explained by the estimated model.

Figure 3 shows the contour plots for Cu, Zn, and Pb leaching, respectively. Figure 3a,c,e set the axis  $x_1$  and  $x_2$  of the graphs as the independent variables  $B_{([HCI])}$  and  $C_{(Temperature)}$ , varying from 0.1–1.0 mol/L and from 20–70 °C. The factor  $A_{([NaCI])}$  was fixed at –1. Conversely, Figure 3b,d,f present the axis  $x_1$  and  $x_2$  as  $B_{([HCI])}$  and  $A_{([NaCI])}$ , ranging from 0.1–1.0 mol/L and from 10–60 g/L. In this case, the factor  $C_{(Temperature)}$  was fixed at +1.

Figure 3a,c demonstrate a correlation between the increase in leaching efficiencies of Cu and Zn metals and the rise in temperature and HCl concentration, supporting the findings in Tables S2 and S3. Additionally, as observed in Figure 3b,d, NaCl did not appear to have a strong effect on the leaching of those metals, as long as a sufficient amount of acid was present (<0.5 mol/L HCl), which also corroborates the analysis of the Tables S2 and S3.

On the other hand, Pb leaching was strongly affected by the concentration of Cl<sup>-</sup> available in the solution. Figure 3e indicates that the Pb leaching efficiency was not significantly affected by  $C_{(Temperature)}(x_2)$ ; however, a minimum concentration of 0.5 mol/L of factor  $B_{([HCI])}(x_1)$  is necessary when factor  $A_{([NaCI])}$  is fixed at -1. For a high leaching efficiency of Pb, intermediate levels of factors  $A_{([NaCI])}(x_1)$  and  $B_{([HCI])}(x_2)$  should be present, as depicted in Figure 3f. As previously discussed, the solubility of Pb is favored in the presence of an excess of chloride ions, leading to the formation of lead–chloride complexes.



**Figure 3.** Contour plots of the leaching of Cu (a,b), Zn (c,d), and Pb (e,f) from the tailings sample obtained by the DoE. Fixed factor for (a,c,e) was NaCl at -1; fixed factor for (b,d,f) was temperature at +1.

Based on the results obtained by the DoE, the leaching efficiency of the metals was mainly affected by (i) temperature (Cu and Zn), (ii) concentration of the acid (Cu and Zn), and (iii) availability of chloride ions in solution (Pb). Among the three optimum conditions identified (see Figure 2), the condition consisting of 10 g/L NaCl, 0.5 mol/L HCl, and  $70 \degree C$  (exp. 7) was selected for further investigation. As the impact of NaCl concentration did not appear to have a strong effect on the leaching efficiencies of the metals, the solution containing its lowest concentration was chosen.

# 3.3. Effect of Time and Artificial Seawater

As demonstrated in Figure 2, the leachability of the three target metals also increased as time progressed, and the leaching was not finalized at 4 h. Therefore, a leaching test over

24 h was carried out with the best condition selected from the DoE (exp. 7; 10 g/L NaCl, 0.5 mol/L HCl, and 70 °C). Under this condition, two tests were performed (Figure 4): one in deionized water (a) and one in seawater (b) (without NaCl addition). At the end of the 24 h, 52.3% of Cu, 72.6% of Zn, and  $\approx$ 100% of Pb (<0.5 mg/L limit of detection (LOD) of the ICP-OES) was extracted from the tailings sample in deionized water (Figure 4a), whereas 56% Cu, 74.8% Zn, and  $\approx$ 100% of Pb (<0.5 mg/L LOD of the ICP-OES) was extracted in the seawater test (Figure 4b). An increase of 61% for Cu, 130% for Zn, and 15% for Pb was achieved by increasing the leaching duration from 4 h to 24 h. In addition, in both tests, Fe content remained around 20% after 24 h. These results show very similar leaching behavior of the metals regardless of the type of water used. The XRD analysis (Figure S3) also presented no significant differences in the mineral phases after leaching. This finding paves the way for the substitution of freshwater by seawater in leaching processes of tailings samples without detriment to the metals extraction. This is especially of interest in arid regions where freshwater is scarce.



**Figure 4.** Leaching efficiencies of Cu, Zn, Pb, and Fe in (**a**) deionized water and (**b**) artificial seawater over 24 h leaching test.

Other studies have already investigated the use of seawater in hydrometallurgical processes, particularly for chalcopyrite (CuFeS<sub>2</sub>). For instance, Hernandéz et al. [46] compared the dissolution of chalcopyrite ore in seawater-based media (in HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub>) for 168 h at 45 °C. The mixture of HCl and seawater provided higher Cu extraction (33.7%) than in distilled water (13.9%). Conversely, the addition of 0.16 mol/L of Cl<sup>-</sup> (from NaCl) did not improve the leaching efficiency of Cu in seawater-based media (25.3% compared to 32.1% of Cu in distilled water). The authors attributed this result to the increase in the ionic strength of the solution due to a higher Cl<sup>-</sup> concentration (HCl + seawater + NaCl) that might have led to a decrease in the mobility of the ions. Nonetheless, Torres et al. [14] studied the effect of tap water, seawater, and synthetic process water on the leaching of Cu from a low-grade copper ore. In H<sub>2</sub>SO<sub>4</sub>-based media, there was no difference in Cu extraction between tap water and seawater media within the 24 h test, whereas the use of process water enhanced the recovery of Cu from 24 to 48 h.

In our previous study carried out under hybrid sulfate–chloride system [17], the extraction of the three target metals was proposed in two-step leaching due to the lower Pb extraction when a higher sulfuric acid concentration is employed. Nevertheless, using an acid–chloride system enabled a high co-extraction of the metals in a single step. This not only significantly reduced the total leaching time but also eliminated the need for a solid–liquid separation step that was required between the multiple leaching stages previously

used. Moreover, the use of seawater was investigated, which yielded promising results without compromising extraction efficiency. This outcome offers a sustainable alternative by replacing a non-renewable resource (freshwater) with seawater in the leaching of mine tailings. To the best of our knowledge, there are no studies to date exploring the leaching of Cu, Zn, and Pb from sulfide mine tailings in seawater-based media; most leaching studies under this experimental condition are related to concentrates or low-grade ores.

#### 3.4. Metals Recovery

After leaching of the tailings sample under the optimal condition (0.5 mol/L HCl, 10 g/L NaCl, 70 °C, 24 h), an acidic PLS (pH  $\approx$  1.0) containing the target metals was obtained. Different strategies were applied for the maximum removal of the metals from the PLS (Figure 5).



**Figure 5.** Individual recovery of metals from the PLS: (**a**) precipitation efficiency of Pb in presence of  $SO_4^{2-}$ , (**b**) Cu recovery by SX with LIX 984, and (**c**) Zn recovery by SX with D2EHPA.

For the recovery of Pb, stoichiometric amounts of  $Na_2SO_4$  were added to the solution to precipitate Pb as PbSO<sub>4</sub> (K<sub>sp</sub> =  $1.8 \times 10^{-8}$ ), according to Equation (9):

$$PbCl_2 + SO_4^{2-} \rightarrow PbSO_{4(s)} + 2Cl_{(ag)}^{-}, \tag{9}$$

As shown in Figure 5a, about 70 to 80% of Pb was precipitated from the solution containing 3.3 to  $5.7 \text{ SO}_4^{2-}/\text{Pb}^{2+}$  stoichiometric ratio. The high  $\text{SO}_4^{2-}/\text{Pb}^{2+}$  ratio found in this study might be attributed to the consumption of  $\text{SO}_4^{2-}$  from other ions present in the PLS. Therefore, an excess of  $\text{SO}_4^{2-}$  was needed for the precipitation of PbSO<sub>4</sub> from the solution. Additionally, other parameters could be investigated, like temperature and pH; however, an increase in pH is linked to precipitation of the other metals (target or undesirable metals).

Cu and Zn were recovered from the PLS by SX. This metal recovery technique involves the reaction of metal ions present in an aqueous solution with an organic solvent, resulting in the formation of an organic–metal complex. This causes the metal ions to transition from the aqueous phase into the organic phase. The pH of the aqueous solution is one of the most important parameters that directly affect the efficiency of extraction in an SX process, since H<sup>+</sup> ions are taking part of the process (Equation (10)) [33]:

$$\mathbf{M}_{(\mathrm{aq})}^{2+} + 2\mathbf{H}\mathbf{R}_{(\mathrm{org})} \leftrightarrow \mathbf{M}\mathbf{R}_{2(\mathrm{org})} + 2\mathbf{H}_{(\mathrm{aq})'}^{+}$$
(10)

where HR is the extractant and M is the ion metal. According to Equation (11), the equilibrium of the reaction is influenced by the pH value, as 1 mol of R releases 1 mol of  $H^+$ .

Then, if the pH value is low, the equilibrium shifts towards the left, leading to a decrease in the extraction efficiency. Conversely, if the pH value is high, the equilibrium moves towards the right, causing the extraction efficiency to rise. However, an increase in pH also leads to the precipitation of metals from the solution. Therefore, the pH value has a great impact on the recovery of metals from SX and should be particularly considered to achieve optimal efficiency.

In this work, the recovery of the Cu and Zn metals in the chloride medium through SX was investigated under pH ranging from 0.5 to 5.0. The effect of pH in Cu recovery is illustrated in Figure 5b. The extractant LIX 984 was used as the Cu extractant, as it has been reported to present high Cu selectivity over other metals, such as Fe [47]. As shown, the recovery efficiency increased from 83 to  $\approx$ 100% of Cu (<0.5 mg/L LOD of the ICP-OES) by increasing the pH from 0.5 to 1.5. Higher pH values did not result in any changes in recovery; therefore, they are not shown on the graph. Hence, pH 1.5 was found to be the optimal Cu efficiency with the extractant LIX 984.

D2EHPA extractant was used for the recovery of Zn from the PLS. As presented in Figure 5c, 72% of Zn was recovered from the solution at pH 3.0; this agreed with [48,49], which determined the optimal pH range of 2.5–3.0 for Zn extraction in a chloride medium. pH values greater than 3.0 resulted in large precipitation of iron as iron (III) hydroxide, observed by the change in color to reddish-brownish and the formation of gelatinous precipitates, which hindered the filtration of the solution. Moreover, co-precipitation of other target metals, e.g., Zn and Pb, was also noticed (Figure 6). Consequently, higher pH values were not considered due to the high loss of target metals.



Figure 6. Precipitation of metals based on the pH of the PLS.

## 3.5. Proposed Multi-Stage Recovery Process

Based on the results presented in the previous sections, a combined multi-stage metals recovery (Figure 7) was performed under the best conditions identified in this study. Firstly, high leaching efficiency of the target metals was obtained after 24 h in 10 g/L NaCl, 0.5 mol/L HCl, and 70 °C from the tailings sample in the chloride-based media. The PLS generated underwent the metals recovery processes.



**Figure 7.** Combined leaching and metals recovery processes. Basis 1 ton of sulfidic tailings. Leaching of mine tailings with 10 g/L NaCl, 0.5 mol/L HCl, 70 °C, and 24 h; Pb recovery from the PLS with  $4.15 \text{ SO}_4^{2-}/\text{Pb}^{2+}$  stoichiometric ratio for 30 min and 500 rpm; Cu recovery by SX with LIX 984 and EXXSOL at pH 1.5 for 15 min and 500 rpm; direct Zn recovery by SX with D2EHPA and EXXSOL at pH 3.0 for 15 min and 500 rpm; and reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> by addition Fe<sup>0</sup> followed by Zn recovery with D2EHPA and EXXSOL at pH 3.0 for 15 min and 500 rpm; and reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> by addition Fe<sup>0</sup> followed by Zn recovery with D2EHPA and EXXSOL at pH 3.0 for 15 min and 500 rpm.

The precipitation of Pb as PbSO<sub>4</sub> from the PLS was carried out by the addition of  $4.15 \text{ SO}_4^{2^-}/\text{Pb}^{2+}$  stoichiometric ratio. After 30 min under vigorous agitation, 77% of Pb was precipitated from the PLS with low coprecipitation of Cu (2.1%), Zn (2.0%), and Fe (3.8%). Then, the pH of the Pb-depleted aqueous phase was adjusted to 1.5, and the filtered solution underwent Cu SX with LIX 984 for 15 min. As a result, almost complete Cu recovery was attained with the co-extraction of only 2.9% Pb, 2.0% Zn, and 1.5% Fe. This confirms the high selectivity of LIX 984 for Cu over Pb, Zn, and Fe.

It is known that D2EHPA readily extracts Fe(III) from aqueous solutions [50], and it can also be used for the removal of Pb under a suitable pH range [51]. For that reason, for the recovery of Zn in the third and final stage, two approaches were investigated. On the one hand, the pH of the Cu-free aqueous phase was increased to 3.0 with NaOH. The filtrated solution was then treated with D2EHPA for 15 min, and 70.8% of Zn was extracted from the aqueous phase, along with 11.7% Fe and 12.5% Pb. On the other hand, to minimize Fe co-extraction during Zn removal, Fe<sup>0</sup> was added to the solution to reduce Fe<sup>3+</sup> to Fe<sup>2+</sup>, as displayed in Equation (11):

$$2Fe_{(aq)}^{3+} + Fe_{(s)} \to 3Fe_{(aq)}^{2+},$$
(11)

After 1 h of agitation with  $\text{Fe}^0$ , the solution was filtrated, and the pH was adjusted to 3.0. Interestingly, after the rise of the pH, the filtration of the solution was fast, as no gel-like precipitate formation was observed due to the elimination of  $\text{Fe}^{3+}$ . As seen in Figure 7, 71.1% of Zn was extracted. The efficiency achieved in the second approach was comparable to that of the first approach, indicating that the addition of  $\text{Fe}^0$  did not negatively affect the Zn removal process. Moreover, the Fe co-extraction was reduced to only 4.7%.

The findings suggest a potential route for the leaching of the three base metals followed by their selective recovery from the leachate. Firstly, efficient leaching of the target metals from the tailings sample in chloride-based media was obtained. Additionally, the replacement of freshwater by seawater was proposed since no significant change was observed. The leach residue could be, for instance, incorporated as a feed material in the construction sector [52,53], while the PLS undergoes the metals recovery steps. Secondly, Pb could be easily precipitated as PbSO<sub>4</sub> from the PLS; however, in this work, a stoichiometric ratio cannot be directly proposed, as a higher  $SO_4^{2-}/Pb^{2+}$  ratio was needed. It might be possible to further purify the Pb concentrate with an additional solvent extraction or ion exchange steps. Thirdly, SX was successful in selectively removing both Cu and Zn from the aqueous solutions, and the Cu/Zn-rich organic phases can be further processed (i.e., scrubbing, stripping, and electrowinning) for the recovery of the metal, depending on the desired product [54]. The use of Fe<sup>0</sup> to minimize the co-extraction of Fe in the Zn recovery stage was demonstrated, with a reduction of 60% of Fe co-extraction. To optimize the extraction of the metals, multiple stages of SX are typically employed, which may increase Zn recovery from the PLS. Other parameters should also be investigated in detail, such as the aqueous–organic ratio, concentration of the extractant, time, and temperature [48], although these were out of the scope of this work.

## 4. Conclusions

High leaching efficiencies of the metals were achieved in chloride-based media in a single step under the optimum leaching region determined by the design of the experiments' results. The replacement of freshwater by artificial seawater was demonstrated without detriment to the leaching efficiencies. This result proved that seawater is a viable alternative water source for leaching processing, which is particularly important for arid areas that are affected by a scarcity of freshwater. Furthermore, the recovery of the metals from the pregnant leach solution was shown through precipitation and solvent extraction with high recovery efficiencies. The findings presented in this work demonstrate a potential route for achieving high extraction and recovery of base metals from sulfide mine tailings.

**Supplementary Materials:** The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/su152115515/s1, Table S1. Composition of artificial seawater (ATSM D1141–98 (2003)), Table S2. Experimental parameters and Cu leaching results of DoE, Table S3. Experimental parameters and Zn leaching results of DoE, Table S4. Experimental parameters and Pb leaching results of DoE, Figure S1. Particle size distribution of the Cu–Zn tailings used in the experiments ( $d_{10} = 2.16 \mu m$ ,  $d_{50} = 21.39 \mu m$ ,  $d_{90} = 115.86 \mu m$ ), Figure S2. pH and ORP measured during the DoE experiment, Figure S3. XRD pattern of the mine tailings sample leached with (a) deionized water and (b) artificial seawater (quartz: SiO<sub>2</sub>; pyrite: FeS<sub>2</sub>; chlorite: A<sub>5–6</sub>T<sub>4</sub>Z<sub>18</sub>, where A = Al, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Li, Mg, Mn, or Ni, while T = Al, Fe<sup>3+</sup>, Si, or a combination of them, and Z = O and/or OH; illite: (K,H<sub>3</sub>O)(Al,Mg,Fe)<sub>2</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>[(OH)<sub>2</sub>,(H<sub>2</sub>O)])).

**Author Contributions:** T.A.S. conceived and conducted the experiments. T.A.S., P.F.d.A. and B.Y. analyzed the experimental results. T.A.S. prepared the original draft. T.A.S., P.F.d.A., B.Y. and D.G. reviewed and edited the manuscript. D.G. managed supervision, project administration, and funding acquisition. All authors have read and agreed to the published version of the manuscript.

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# References

- 1. Kossoff, D.; Dubbin, W.E.; Alfredsson, M.; Edwards, S.J.; Macklin, M.G.; Hudson-Edwards, K.A. Mine tailings dams: Characteristics, failure, environmental impacts, and remediation. *Appl. Geochem.* **2014**, *51*, 229–245. [CrossRef]
- 2. Kinnunen, P.; Karhu, M.; Yli-Rantala, E.; Kivikytö-Reponen, P.; Mäkinen, J. A review of circular economy strategies for mine tailings. *Clean. Eng. Technol.* 2022, *8*, 100499. [CrossRef]
- 3. Marín, O.A.; Kraslawski, A.; Cisternas, L.A. Estimating processing cost for the recovery of valuable elements from mine tailings using dimensional analysis. *Miner. Eng.* **2022**, *184*, 107629. [CrossRef]
- 4. Simate, G.S.; Ndlovu, S. Acid mine drainage: Challenges and opportunities. J. Environ. Chem. Eng. 2014, 2, 1785–1803. [CrossRef]
- dos Santos Vergilio, C.; Lacerda, D.; Da Silva Souza, T.; de Oliveira, B.C.V.; Fioresi, V.S.; de Souza, V.V.; Da Rocha Rodrigues, G.; de Araujo Moreira Barbosa, M.K.; Sartori, E.; Rangel, T.P.; et al. Immediate and long-term impacts of one of the worst mining tailing dam failure worldwide (Bento Rodrigues, Minas Gerais, Brazil). *Sci. Total Environ.* 2021, 756, 143697. [CrossRef] [PubMed]
- Owen, J.R.; Kemp, D.; Lèbre, É.; Svobodova, K.; Pérez Murillo, G. Catastrophic tailings dam failures and disaster risk disclosure. Int. J. Disaster Risk Reduct. 2020, 42, 101361. [CrossRef]
- 7. Cisternas, L.A.; Gálvez, E.D. The use of seawater in mining. Miner. Process. Extr. Metall. Rev. 2018, 39, 18–33. [CrossRef]
- 8. Xanthopoulos, P.; Bevandić, S.; Spooren, J.; Binnemans, K.; Kukurugya, F. Recovery of copper, zinc and lead from photovoltaic panel residue. *RSC Adv.* **2022**, *12*, 2351–2360. [CrossRef]
- 9. Winand, R. Chloride hydrometallurgy. Hydrometallurgy 1991, 27, 285–316. [CrossRef]
- 10. Texeira, L.; Calisaya-Azpilcueta, D.; Cruz, C.; Botero, Y.L.; Cisternas, L.A. Impact of the use of seawater on acid mine drainage from mining wastes. *J. Clean. Prod.* 2023, *383*, 135516. [CrossRef]
- 11. Kinnunen, P.H.-M.; Kaksonen, A.H. Towards circular economy in mining: Opportunities and bottlenecks for tailings valorization. J. Clean. Prod. 2019, 228, 153–160. [CrossRef]
- 12. Falagán, C.; Grail, B.M.; Johnson, D.B. New approaches for extracting and recovering metals from mine tailings. *Miner. Eng.* 2017, 106, 71–78. [CrossRef]
- 13. Free, M. Hydrometallurgy: Fundamentals and Applications/Michael L. Free; TMS-Wiley: Hoboken, NJ, USA, 2013; ISBN 9781118230770.
- 14. Torres, C.M.; Taboada, M.E.; Graber, T.A.; Herreros, O.O.; Ghorbani, Y.; Watling, H.R. The effect of seawater based media on copper dissolution from low-grade copper ore. *Miner. Eng.* **2015**, *71*, 139–145. [CrossRef]
- 15. Watling, H.R. Chalcopyrite hydrometallurgy at atmospheric pressure: 2. Review of acidic chloride process options. *Hydrometallurgy* **2014**, *146*, 96–110. [CrossRef]
- 16. Dutrizac, J.E. The leaching of sulphide minerals in chloride media. *Hydrometallurgy* 1992, 29, 1–45. [CrossRef]
- 17. Schueler, T.A.; de Aguiar, P.F.; Vera, Y.M.; Goldmann, D. Leaching of Cu, Zn, and Pb from Sulfidic Tailings Under the Use of Sulfuric Acid and Chloride Solutions. *J. Sustain. Metall.* **2021**, *7*, 1523–1536. [CrossRef]
- Senanayake, G.; Muir, D.M. Chloride processing of metal sulphides: Review of fundamentals and applications. In Proceedings of the Hydrometallurgy 2003: 5th International Symposium Honoring Professor Ian M. Ritchie; Volume 1: Leaching and Solution Purification, Vancouver, BC, Canada, 24–27 August 2003; TMS (The Minerals, Metals & Materials Society). pp. 517–531.
- 19. Abo Atia, T.; Spooren, J. Microwave assisted chloride leaching of zinc plant residues. *J. Hazard. Mater.* **2020**, *398*, 122814. [CrossRef]
- 20. Miki, H.; Nicol, M. The kinetics of the copper-catalysed oxidation of iron(II) in chloride solutions. In Proceedings of the Hydrometallurgy 2008: Proceedings of the 6th International Symposium, Phoenix, AZ, USA, 17–21 August 2008; pp. 971–979.
- Hernández, P.; Dorador, A.; Martínez, M.; Toro, N.; Castillo, J.; Ghorbani, Y. Use of Seawater/Brine and Caliche's Salts as Clean and Environmentally Friendly Sources of Chloride and Nitrate Ions for Chalcopyrite Concentrate Leaching. *Minerals* 2020, 10, 477. [CrossRef]
- 22. Lawson, F.; Cheng, C.-Y.; Lee, L.S.Y. Leaching of Copper Sulphides and Copper Mattes in Oxygenated Chloride/Sulphate Leachants. *Miner. Process. Extr. Metall. Rev.* **1992**, *8*, 183–203. [CrossRef]
- 23. Miki, H.; Nicol, M. The dissolution of chalcopyrite in chloride solutions. IV. The kinetics of the auto-oxidation of copper(I). *Hydrometallurgy* **2011**, *105*, 246–250. [CrossRef]
- 24. Ruiz, M.C.; Montes, K.S.; Padilla, R. Chalcopyrite leaching in sulfate–chloride media at ambient pressure. *Hydrometallurgy* **2011**, 109, 37–42. [CrossRef]
- 25. Opara, C.B.; Kamariah, N.; Spooren, J.; Pollmann, K.; Kutschke, S. Interesting Halophilic Sulphur-Oxidising Bacteria with Bioleaching Potential: Implications for Pollutant Mobilisation from Mine Waste. *Microorganisms* **2023**, *11*, 222. [CrossRef]
- 26. Noguchi, H.; Okibe, N. The role of bioleaching microorganisms in saline water leaching of chalcopyrite concentrate. *Hydrometallurgy* **2020**, *195*, 105397. [CrossRef]
- Escobar, A.G.; Relvas, J.M.R.S.; Pinto, Á.M.M.; Oliveira, M. Physical–Chemical Characterization of the Neves Corvo Extractive Mine Residues: A Perspective Towards Future Mining and Reprocessing of Sulfidic Tailings. J. Sustain. Metall. 2021, 7, 1483–1505. [CrossRef]
- De Carvalho, A.L.C.B.; de Carvalho, V.A.; Blannin, R.; Escobar, A.G.; Frenzel, M.; Rudolph, M.; Silva, A.C.; Goldmann, D. A study on the desulfurization of sulfidic mine tailings for the production of a sulfur-poor residue. *Miner. Eng.* 2023, 202, 108285. [CrossRef]

- Ferreira, S.L.C.; Bruns, R.E.; Ferreira, H.S.; Matos, G.D.; David, J.M.; Brandão, G.C.; Da Silva, E.G.P.; Portugal, L.A.; dos Reis, P.S.; Souza, A.S.; et al. Box-Behnken design: An alternative for the optimization of analytical methods. *Anal. Chim. Acta* 2007, 597, 179–186. [CrossRef]
- 30. Box, G.E.P.; Behnken, D.W. Some New Three Level Designs for the Study of Quantitative Variables. *Technometrics* **1960**, *2*, 455–475. [CrossRef]
- D 1141-98 (Reapproved 2003); Standard Practice for the Preparation of Substitute Ocean Water. ASTM International: West Conshohocken, PA, USA, 2003.
- 32. Habashi, F. (Ed.) Handbook of Extractive Metallurgy; Wiley-VCH: Weinheim, Germany, 1997; ISBN 3527287922.
- 33. Habashi, F. Textbook of Hydrometallurgy, 2nd ed.; Métallurgie Extractive Québec: Québec, QC, Canada, 1999; ISBN 2-980-3247-7-9.
- 34. Johnson, D. The Evolution, Current Status, and Future Prospects of Using Biotechnologies in the Mineral Extraction and Metal Recovery Sectors. *Minerals* **2018**, *8*, 343. [CrossRef]
- 35. Calvo, G.; Mudd, G.; Valero, A.; Valero, A. Decreasing Ore Grades in Global Metallic Mining: A Theoretical Issue or a Global Reality? *Resources* **2016**, *5*, 36. [CrossRef]
- 36. Montgomery, D.C. Design and Analysis of Experiments, 9th ed.; John Wiley & Sons Inc: Hoboken, NJ, USA, 2017.
- 37. Zhong, S.; Li, Y. An improved understanding of chalcopyrite leaching kinetics and mechanisms in the presence of NaCl. *J. Mater. Res. Technol.* **2019**, *8*, 3487–3494. [CrossRef]
- Aydogan, S.; Aras, A.; Canbazoglu, M. Dissolution kinetics of sphalerite in acidic ferric chloride leaching. *Chem. Eng. J.* 2005, 114, 67–72. [CrossRef]
- Lei, C.; Yan, B.; Chen, T.; Wang, X.-L.; Xiao, X.-M. Silver leaching and recovery of valuable metals from magnetic tailings using chloride leaching. J. Clean. Prod. 2018, 181, 408–415. [CrossRef]
- 40. Carneiro, M.; Leão, V.A. The role of sodium chloride on surface properties of chalcopyrite leached with ferric sulphate. *Hydrometallurgy* **2007**, *87*, 73–82. [CrossRef]
- 41. Byrne, R.H.; Yao, W.; Luo, Y.; Millero, F.J. Complexation of Pb(II) by Chloride Ions in Aqueous Solutions. *Aquat. Geochem.* 2010, 16, 325–335. [CrossRef]
- 42. Altinkaya, P.; Liipo, J.; Kolehmainen, E.; Haapalainen, M.; Leikola, M.; Lundström, M. Leaching of Trace Amounts of Metals from Flotation Tailings in Cupric Chloride Solutions. *Min. Metall. Explor.* **2019**, *36*, 335–342. [CrossRef]
- 43. Lu, Z.Y.; Jeffrey, M.I.; Lawson, F. The effect of chloride ions on the dissolution of chalcopyrite in acidic solutions. *Hydrometallurgy* **2000**, *56*, 189–202. [CrossRef]
- 44. Farahmand, F.; Moradkhani, D.; Safarzadeh, M.S.; Rashchi, F. Brine leaching of lead-bearing zinc plant residues: Process optimization using orthogonal array design methodology. *Hydrometallurgy* **2009**, *95*, 316–324. [CrossRef]
- Behnajady, B.; Moghaddam, J.; Behnajady, M.A.; Rashchi, F. Determination of the Optimum Conditions for the Leaching of Lead from Zinc Plant Residues in NaCl–H 2 SO 4 –Ca(OH) 2 Media by the Taguchi Method. *Ind. Eng. Chem. Res.* 2012, *51*, 3887–3894. [CrossRef]
- Hernández, P.C.; Taboada, M.E.; Herreros, O.O.; Torres, C.M.; Ghorbani, Y. Chalcopyrite dissolution using seawater-based acidic media in the presence of oxidants. *Hydrometallurgy* 2015, 157, 325–332. [CrossRef]
- Copper. Available online: https://energy-resources.basf.com/global/en/mining\_solutions/solvent\_extraction/copper.html# accordion\_v2-0abbbc400b-item-0e2e7ad963 (accessed on 19 June 2023).
- 48. Jafari, H.; Abdollahi, H.; Gharabaghi, M.; Balesini, A.A. Solvent extraction of zinc from synthetic Zn-Cd-Mn chloride solution using D2EHPA: Optimization and thermodynamic studies. *Sep. Purif. Technol.* **2018**, *197*, 210–219. [CrossRef]
- 49. Soltani, F.; Darabi, H.; Aram, R.; Ghadiri, M. Leaching and solvent extraction purification of zinc from Mehdiabad complex oxide ore. *Sci. Rep.* **2021**, *11*, 1566. [CrossRef] [PubMed]
- 50. Biswas, R.K.; Begum, D.A. Solvent extraction of Fe3+ from chloride solution by D2EHPA in kerosene. *Hydrometallurgy* **1998**, *50*, 153–168. [CrossRef]
- Escobar, A.; Schimmel, K.A.; de Gyves, J.; de San Miguel, E.R. Hollow-fiber dispersion-free extraction and stripping of Pb(II) in the presence of Cd(II) using D2EHPA under recirculating operation mode. J. Chem. Technol. Biotechnol. 2004, 79, 961–973. [CrossRef]
- Martins, N.P.; Srivastava, S.; Simão, F.V.; Niu, H.; Perumal, P.; Snellings, R.; Illikainen, M.; Chambart, H.; Habert, G. Exploring the Potential for Utilization of Medium and Highly Sulfidic Mine Tailings in Construction Materials: A Review. *Sustainability* 2021, 13, 12150. [CrossRef]
- Veiga Simão, F.; Chambart, H.; Vandemeulebroeke, L.; Cappuyns, V. Incorporation of sulphidic mining waste material in ceramic roof tiles and blocks. J. Geochem. Explor. 2021, 225, 106741. [CrossRef]
- 54. Wilson, A.M.; Bailey, P.J.; Tasker, P.A.; Turkington, J.R.; Grant, R.A.; Love, J.B. Solvent extraction: The coordination chemistry behind extractive metallurgy. *Chem. Soc. Rev.* **2014**, *43*, 123–134. [CrossRef]

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