

Article



Prospective (Bio)leaching of Historical Copper Slags as an Alternative to Their Disposal

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Abstract: The aim of this study was to evaluate the feasibility of (bio)hydrometallurgical methods for metal extraction from historical copper slags. Two types of slags (amorphous slag-AS, and crystalline slag—CS) were subjected to 24 to 48 h of leaching with: (i) Sulfuric acid at 0.1, 0.5, and 1 M concentrations at 1%, 5%, and 10% pulp densities (PDs); and (ii) normality equivalent (2 N) acids (sulfuric, hydrochloric, nitric, citric, and oxalic) at pulp densities ranging from 1% to 2%. Bioleaching experiments were performed within 21 days with Acidithiobacillus thiooxidans accompanied by an abiotic control (sterile growth medium). The results demonstrated that the most efficient treatment for amorphous and crystalline slag was bioleaching at 1% PD over 21 days, which led to extraction of Cu at rates of 98.7% and 52.1% for AS and CS, respectively. Among the chemical agents, hydrochloric acid was the most efficient and enabled 30.5% of Cu to be extracted from CS (1% PD, 48 h) and 98.8% of Cu to be extracted from AS (1% PD, 24 h). Slag residues after leaching were characterized by strong alteration features demonstrated by the complete dissolution of fayalite in the case of CS and the transformation of AS to amorphous silica and secondary gypsum. Based on this study, we conclude that amorphous slag is a more suitable candidate for potential metal recovery because of its generally high susceptibility to leaching and due to the generation of residue significantly depleted in metals as the end product. The inventory of economically relevant metals showed that 1 ton of historical copper slag contains metals valued at \$47 and \$135 for crystalline and amorphous slag, respectively, suggesting that secondary processing of such materials can potentially be both economically and environmentally viable.

Keywords: Cu-slag; (bio)leaching; metal recovery; Acidithiobacillus thiooxidans

1. Introduction

Pyrometallurgical processes involve the generation of various by-products, such as slags, sludges, ashes, and other solid residues [1]. The slags produced are substantial in volume, for example, every ton of copper produced result in the generation of a double volume equivalent of slag material [2]. In addition, slags are notable for carrying toxic elements, necessitating the suitable handling of these wastes.

Former slag disposal methods did not consider environmental safety carefully enough, which led to contamination of soils located in the vicinity of slag heaps and smelters (see [3] for a review). Some studies have also pointed out that improper slag disposal may cause serious ecological problems. For example, the study of Kasemodel et al. (2019) reveals that during transportation of slags from the smelter to the disposal site, a dirt road was heavily contaminated by slag fragments [4]. The authors conclude that high metal content in the dirt road constitutes a serious risk for the nearby population because the material is easily aerated and transported on the wind, and can be easily absorbed through inhalation [4]. Another study of Forghani et al. (2018) aimed at human risk assessment in southeastern

Iran indicated a non-carcinogenic and carcinogenic risk to the population related with Cu smelting, which caused elevated concentrations of Cu and As in soils [5].

Despite the negative environmental effects of Cu slags, their binding properties result in these materials often being used for construction, with the cement industry being the most dominant consumer [6,7]. However, it is important to note that proper slag management is possible, provided that it does not entail any risk of metal discharge. If this condition is not met, then the application of slags as an engineering product is unsuitable [8,9].

On the other hand, the relatively high residual metal content in slags makes these wastes appealing as secondary metal resources [10], especially when viewed in the context of the depletion of natural resource reserves. Optimal metal extraction is a process resulting in a high metal yield, but the geochemical characteristic of the remaining residue is also crucial. As a result of slag treatment, the generation of metal-free or metal-depleted residue is strongly desired [10]. Therefore, the development of suitable extraction protocols is a hotly contested subject of waste management debates [11–15].

Furthermore, the consideration of metallurgical slags as secondary metal resources has received important interest not only for environmental reasons but also for economic ones [16]. The latter involves the finite quantities of natural reserves of raw ores [17] and society's increasing demand for metal-based commodities [18,19]. Metal extraction from solid wastes is performed by means of chemical, biological, or combined methods [20–23]. Extraction efficiency strongly depends on slag composition and operative parameters, mainly the grain size, pulp density, temperature, and treatment time. Optimal parameters have to be selected so that energy consumption and cost-intensive operations are satisfactorily minimized. Biological methods involve the use of bacteria and/or fungi in single- or multi-species suspensions [10]. A biological process is preferred due to its environmentally friendly specification, but it usually requires a longer time to reach a comparable efficiency to that achieved by a chemical process. In addition, the optimization of bioleaching conditions is more challenging as compared to chemical leaching, mainly due to a possible metal toxicity effect on the microorganisms and the associated concerns with microbial survivors and activity [24]. These shortcomings are often difficult to overcome, which has driven the development of hybrid processes combining chemical and biotic techniques [25]. A hybrid approach can be accomplished in a way that a microbial-derived solution is generated in a reactor and then diverted to a separate slag-containing reactor in order to execute the extraction process. Chemical leaching involving the use of chemical agent(s) simulating a microbial by-product is thus a model approach. A well-crafted feasibility study allows for the evaluation of slag vulnerability in respect to metal leaching with a simultaneous preliminary optimization of the operative parameters. In this vein, sulfuric acid (H_2SO_4) leaching is well known for its good metal extraction efficiency [20]; however, this traditional chemical reagent can also be replaced by a biologically produced one [11,13,14]. Likewise, organic acids produced in the presence of microbial consortia can contribute to the extraction process as well [15,26,27]. Therefore, the use of these acids is reasonable for a simplified model of the biotic process and for shaping its optimal conditions.

Literature data presents a number of (bio)leaching approaches undertaken for copper slags (see [10,20] for a review). It has been demonstrated that chemical leaching can be carried out with various extractants, such as: Ferric chloride [28], ferric sulfate [22,29,30], ammonium sulfate [31], ammonium chloride [32], chlorine solution [30,33], hydrochloric acid, ammonium hydroxide [34], and sulfuric acid [21,23,28–31,34–39]. Some studies reveal that an additional treatment step, such as slag roasting following leaching [28,29,31,37], aging of slag [23], oxidant addition [21,34,35,38], or high-temperature leaching [21–23,28,30,32,34,36], may be required in order to improve the leaching yield. However, it has to be noted that each additional step consumes energy, while an economically viable process requires the number of cost-intensive operations to be minimized. Furthermore, numerous approaches have also addressed the bioleaching of copper slags. It has been shown that a high yield of copper can be achieved under optimized conditions (for an extended review, see [10]). However, based on review data, it has been established that uniform laboratory bioleaching conditions that are efficient for any type of copper slag have not yet been defined [10]. Nevertheless, among

the (bio)leaching parameters strongly affecting the process efficiency, particle size and pulp density were found to be very important. Furthermore, a key slag feature to the efficiency of the (bio)leaching processes is the sample crystallinity. It is known that crystalline and amorphous slags reveal different chemical and phase compositions [20]. Thus, the susceptibility of these slags to the leaching process also varies. Some recent comparative studies addressing the behavior of amorphous and crystalline slags demonstrated that element release is strongly dependent on the phase component that the metal is associated with [14,40]. For this reason, the search for optimal (bio)leaching conditions should definitely take into account the crystallinity aspect because it will deliver important information on how the behavior of different materials varies under specific conditions. In regard to the aforementioned facts, there seems to be interest in undertaking laboratory work dedicated to the search for optimal (bio)leaching conditions, with a special focus given to slag crystallinity.

The aim of this study was to investigate the feasibility of biological and chemical treatments of metal-laden historical metallurgical slags disposed of in Poland. The main novelty of this study is that it compared chemical and biological treatments of two types of copper historical slags (crystalline and amorphous). The specific research objectives included the search for the optimal operating parameters among acid types (inorganic vs. organic normality equivalent acids), pulp density for metal extraction, as well as the optimal conditions for biotic treatment, with a particular focus placed on pulp density. In addition, the economic potential of each approach was estimated based on the amounts of recovered metals.

2. Materials and Methods

2.1. Materials

The metallurgical slags chosen for this study were: (i) Crystalline fayalite-bearing slag (CS) and (ii) amorphous slag (AS), both resulting from former copper production. An overview of the chemical and mineralogical composition of these wastes is presented in Table 1 and Figure 1, whereas a detailed characterization is given elsewhere [41–43]. Crystalline slag is mainly (nearly 83%) composed of SiO₂ and FeO, whereas amorphous slag's main components are SiO₂, FeO, and CaO (nearly 78%). Amorphous slag contains a higher content of Cu than CS, whereas the latter is more abundant in Zn (Table 1). Fayalite and glass are volumetrically major components of CS, whereas amorphous slag is mainly composed of glass. Both slag types contain various metal-bearing phases (mainly sulfides in the case of CS or metallic Cu in the case of AS) occurring in minor volumetric proportions (Table 1).

| $\begin{tabular}{ c c c c c c } \hline Major and minor elements (wt. \%) \\ \hline SiO_2 & 38.26 & 48 \\ TiO_2 & 0.58 & 0. \\ Al_2O_3 & 9.29 & 11 \\ FeO & 44.33 & 12 \\ MnO & 0.25 & 0. \\ MgO & 2.97 & 2. \\ CaO & 0.68 & 17 \\ Na_2O & 0.19 & 0. \\ K_2O & 1.27 & 4. \\ \hline Minor and trace elements (mg kg^{-1}) \\ \hline Cu & 3761 & 19, \end{tabular}$ | S | | | |
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| $\begin{tabular}{ccc} CaO & 0.68 & 17 \\ Na_2O & 0.19 & 0. \\ K_2O & 1.27 & 4. \\ \hline & & \\ \hline & & \\ \hline & & \\ \hline Cu & 3761 & 19, \\ \hline \end{tabular}$ | 10 | | | |
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| $\begin{tabular}{ c c c c c c } \hline K_2O & 1.27 & 4. \\ \hline M inor and trace elements (mg kg^{-1}) & \\ \hline Cu & 3761 & 19, \\ \hline \end{tabular}$ | 21 | | | |
| $\begin{tabular}{ c c c c } \hline Minor and trace elements (mg kg^{-1}) \\ \hline Cu & 3761 & 19, \end{tabular}$ | 59 | | | |
| Cu 3761 19, | | | | |
| | 724 | | | |
| Pb 55 5 | 3 | | | |
| Zn 3628 58 | 87 | | | |
| Phase composition | | | | |
| Favalite ($Fe^{2+}_2SiO_4$) ++ Glas | s ++ | | | |
| $Glass^{++}$ Chalcocite (Cu ₂ | | | | |
| Hercynite (FeAl ₂ O ₄) $^+$ Quartz | $(SiO_2)^+$ | | | |
| Bornite $(Cu_5 FeS_4)^+$ Cristobali | te (SiO ₂) + | | | |
| Pyrrhotite ($Fe_{(x-1)}S$) + Metallic Cu + | | | | |
| Chalcopyrite (CuFeS ₂) $^{(+)}$ | | | | |

Table 1. Chemical composition of studied slags (CS: crystalline slag, AS: amorphous slag).

++ major, + minor, (+) traces.



Figure 1. Scanning electron microscope images and XRD patterns of fresh samples of crystalline (**upper pictures**) and amorphous slag (**bottom pictures**). Abbreviations: Fa: fayalite, Hc: hercynite, Qtz: quartz, Crs: cristobalite, Cu: metallic copper, Bn: bornite, Cc: chalcocite.

2.2. Experimental Procedures

Metallurgical slags were subjected to extraction with an inorganic solution in order to demonstrate the samples' general behavior and the effect of the processing parameters. The first series of experiments was carried out with sulfuric acid (H_2SO_4) and the evaluated parameters were as follows: Acid concentration (0.1 M L^{-1} , 0.5 M L^{-1} , and 1 M L^{-1}), pulp density (1%, 5%, and 10%), and extraction

time (24 and 48 h). Sulfuric acid (H_2SO_4) was chosen, as this extracting agent is known for its good performance in the slag leaching process [20]. The slag section used for the screening experiments was 0.25 to 0.5 mm in order to increase the slag surface area and therefore improve the accessibility of the leaching solution to the metal bearing phases contained within. The agitation speed was set at 150 rpm and kept constant for all the experiments.

Once the most optimal parameters were selected based on the results from the first experimental series, other extracting configurations were tested. The extracting normality equivalent (2 N) solutions were 1 M L⁻¹ sulfuric acid (H₂SO₄), 2 M L⁻¹ hydrochloric acid (HCl), 2 M L⁻¹ nitric acid (HNO₃), 0.66 M L⁻¹ citric acid (C₆H₈O₇), and 1 M L⁻¹ oxalic acid (H₂C₂O₄); all the reagents were analytical grade. The pulp densities used consisted of 1%, 2%, and 3% concentrations. The leaching time was extended from 24 to 48 h. All the extractions were carried out at least in duplicate. The leachates were filtered using 0.45-µm PTFE (polytetrafluoroethylene) syringe filters, acidified using 2 vol. % Suprapur HNO₃ (Merck) and stored at 4 °C until analysis.

Bioleaching experiments (GMB) were performed with *Acidithiobacillus thiooxidans* (strain number DSM 9463; purchased from Deutsche Sammlung von Mikroorganismen und Zellkulturen) and were accompanied by control experiments done with a sterile growth medium (GM). The growth medium used was composed of 2 g ammonium sulfate ($(NH_4)_2SO_4$), 0.25 g magnesium sulfate ($MgSO_4.7H_2O$), 0.1 g dipotassium hydrogen phosphate (K_2HPO_4), 0.1 g potassium chloride (KCl), and 1% (wt./v) elemental sulfur (S) per 1 L of ultrapure water. The pH of the growth medium was adjusted to 3.5. No additional pH adjustments were done while the experiment was run, because leaving the pH in a free drift enables the tracking of microbial activity in the biotic incubation. When *Acidithiobacillus thiooxidans* acts, a gradual pH depletion is expected as the result of sulfur oxidation. The bacterial culture used for the bioleaching experiment was pre-grown in a growth medium for a period of two weeks. Then, 2% (v/v) of inoculum was introduced to each biotic incubation, whereas no bacteria were added to the abiotic control.

The duration of the experiments was 21 days, because a previous study on copper slags revealed this time frame to be optimal for metal extraction yields. The section size of 0.25 to 0.5 mm was selected because a previous study [14] revealed that a smaller (<2 mm) slag particle size allows a better extraction efficiency to be reached. Thus, an intermediate fraction was used in this study with a slightly higher pulp density range (i.e., 1%, 2%, and 5%). At the end of the extraction procedure, slag residue grains were gently rinsed with ultrapure water and dried at room temperature.

As the metals leached from slags may pose a toxicity stress to bacteria, the microbial survivor rate was evaluated via an activity test [14,44]. In total, 1 mL of leachate from each biotic (GMB) and abiotic (GM) flask was transferred to tubes containing a sterile growth medium supplemented with 1% elemental sulfur. The test was accompanied by a procedural blank with growth medium and sulfur (with no leachate addition). After leachate addition, all tubes were closed with cotton plugs, kept for 10 days, and observed with respect to sulfur oxidation. A lack of microbial activity occurred when sulfur remained floating on the medium surface, whereas positive bacterial activity occurred when sulfur settled down in the tube.

2.3. Analytical Measurements

2.3.1. Solution Chemistry

The leaching solution was analyzed for elemental composition using inductively coupled plasma atomic mass spectrometry (Agilent Technologies-Agilent 7700x, Agilent Technologies, Inc., Santa Clara, CA, USA), with Sc used as an internal standard. The standard deviation of the measurements was below 5%. Each 10-sample standard solution was analyzed in order to check the accuracy of the measurement. Samples were analyzed using different dilutions in order to ensure quality and check the repeatability of the obtained data. The pH of the leachates was measured using an Elmetron CP-411

pH-meter (Elmetron, Zabrze, Poland) equipped with an ERH-11S electrode (Elmetron, Zabrze, Poland). The pH values for each leachate are presented in Table 2.

| | | Final pH Values in the Leachates | | | | | |
|-----------------------------------|-----------------------------|----------------------------------|----------------|--|--|--|--|
| Solution Used as Extracting Agent | Operating Parameters | Crystalline Slag | Amorphous Slag | | | | |
| Sulfuric Acid (0.1–1 M) | | | | | | | |
| | 0.1 M, PD: 1%, T: 48 h | 1.22 | 1.45 | | | | |
| Sulfuric acid | 0.1 M, PD: 5%, T: 48 h | 1.31 | 1.60 | | | | |
| | 0.1 M, PD: 10%, T: 48 h | 1.36 | 1.68 | | | | |
| | 0.5 M, PD: 1%, T: 48 h | 0.51 | 0.56 | | | | |
| Sulfuric acid | 0.5 M, PD: 5%, T: 48 h | 0.52 | 0.62 | | | | |
| | 0.5 M, PD: 10%, T: 48 h | 0.60 | 0.70 | | | | |
| | 1 M, PD: 1%, T: 48 h | 0.38 | 0.31 | | | | |
| Sulfuric acid | 1 M, PD: 5%, T: 48 h | 0.40 | 0.35 | | | | |
| | 1 M, PD: 10%, T: 48 h | 0.39 | 0.36 | | | | |
| Normality Equivalent Acids (2N) | | | | | | | |
| Hydrochloric acid | PD: 1%, T: 48 h | 0.04 | 0.05 | | | | |
| Hydrochioric acid | PD: 2%, T: 48 h | 0.08 | 0.17 | | | | |
| | PD: 1%, T: 48 h | 0.38 | 0.31 | | | | |
| Sulfuric acid | PD: 2%, T: 48 h | 0.41 | 0.40 | | | | |
| NT*1* | PD: 1%, T: 48 h | 0.12 | 0.05 | | | | |
| Nitric acid | PD: 2%, T: 48 h | 0.11 | 0.11 | | | | |
| | PD: 1%, T: 48 h | 1.99 | 2.03 | | | | |
| Citric acid | PD: 2%, T: 48 h | 2.08 | 2.29 | | | | |
| | PD: 1%, T: 48 h | 0.77 | 1.48 | | | | |
| Oxalic acid | PD: 2%, T: 48 h | 0.80 | 2.19 | | | | |
| (Bio)leaching | | | | | | | |
| Growth medium (sterile) | PD: 1%, T: 21 days | 3.98 | 4.83 | | | | |
| | PD: 2%, T: 21 days | 3.88 | 4.65 | | | | |
| | PD: 3%, T: 21 days | 3.85 | 4.60 | | | | |
| | PD: 1%, T: 21 days | 0.90 | 0.62 | | | | |
| Growth medium + bacteria | PD: 2%, T: 21 days | 1.15 | 0.71 | | | | |
| | PD: 3%, T: 21 days | 1.43 | 0.98 | | | | |

Table 2. The final pH values in the leachates from executed treatments.

Abbreviations: PD—pulp density, T—treatment time.

2.3.2. Mineralogical Analyses

Scanning electron microscope observations were performed before and after the leaching experiments. Thin sections and/or slag grains were carbon-coated and observed using a scanning electron microscope (SEM-EDS JEOL JSM-IT100, JEOL, Tokyo, Japan) operating at high vacuum and in the 15–20 kV working mode.

X-ray powder diffraction analyses of pulverized slag samples (fraction 0.25–0.5 mm) were made using a Bruker D8 Advance diffractometer (Bruker, Billerica, MA, USA) with CuK α (1.54060 Å) radiation operating at 40 kV and 40 mA. The analyses were recorded in the range of 2-theta angles from 4° to 75° at a rate of 6° 20/min.

3. Results and Discussion

3.1. Effect of Sulfuric Acid Concentration

The analysis of how acid concentration and pulp density influence the extraction yield was performed using H_2SO_4 . This chemical agent was selected because it had previously been proven to perform well in the extraction process on various copper slags [20,21,30,36]. The literature reports a positive correlation between the concentration of acid used and extraction yield achieved [23,38].

However, an economically viable extraction process requires the amount of chemicals consumed to be minimized. Therefore, the acid concentration used in the present study ranged from 0.1 to 1 M (Figure 2). The pH values obtained in the final leachates are presented in Table 2.

3.1.1. Crystalline Slag

In the case of crystalline slag (CS), the results demonstrated that maximal extraction for most elements studied (with the exception of Cu) was generally achieved when $1 \text{ M H}_2\text{SO}_4$ and 1% slag pulp density conditions were used (Figure 2). Such operating conditions enabled the extraction of as much as 59.9% of Zn (2173 mg kg⁻¹) and 52.5% of Fe (181 g kg⁻¹), whereas the extraction efficiency for Cu was surprisingly low at 1.4% (53.1 mg kg⁻¹). A similar observation occurred with the study of Stuurman et al. (2014), who demonstrated decreasing Cu extraction from Cu/Co ores once the H₂SO₄ concentration used surpassed 0.8 M [45]. Thus, it remains to be elucidated what secondary precipitation process is responsible for such low Cu leaching. It has to be emphasized that Cu leachability from CS is generally high, as proven by several previous studies (e.g., [40]), therefore it is clear that an additional factor must have played a role in the leaching system studied here (discussed in detail in Section 3.3).

Furthermore, the results demonstrated that an increase of acid molarity from 0.1 to 1 M notably enhanced the extraction of Zn and Si. This difference was especially pronounced when 1% of CS pulp was used in the extraction process. In this case, a higher acid molarity (1 M) enabled 6.1 times more Zn (nearly 60%) to be extracted as compared to the extraction reached when using 0.1 M acid (only 9.8%). Likewise, the extraction of Si was enhanced by a factor of 3.3 once the acid molarity increased from 0.1 to 1 M. Both Si and Zn are elements incorporated in glass and fayalite, therefore no conclusion can be made concerning which phase is responsible for Zn input to the leachate. The effect of normality equivalent acids is discussed in Section 3.2 (Figure 3).

Undoubtedly, an improvement of Cu leaching from CS could be achieved when a higher temperature is applied, because thermal activation improves phase dissolution (in this case Cu-sulfides) [46,47]. According to literature reports, high Cu-recovery rates from slags could be achieved when leaching was performed at higher temperatures ([20] and references therein). For example, Sukla et al. (1986) extracted 95% of Cu within 1 hour of leaching at 150 °C [31]. Likewise, Beşe (2007) accomplished an 80% Cu removal from slags at 65 °C [48]. On the other hand, it has to be remembered that a higher slag dissolution is associated with a higher content of Si in the solution and, therefore, a higher risk of silica colloid formation may be an important process shortcoming [49] (discussed in detail in Section 3.3).

3.1.2. Amorphous Slag

Amorphous slag (AS) subjected to extraction with sulfuric acid appeared to have a higher susceptibility to extraction than CS, especially when Cu is considered. For example, as much as 63.3% of Cu (12,500 mg kg⁻¹) was extracted after 48 h with 1 M H₂SO₄ at 1% PD (Figure 4). However, an important observation concerning the behavior of AS in the leaching system is that the metal amount extracted in 1 M acid was nearly the same as the amount extracted with 0.5 M acid. For example, Cu extraction with 0.5 M H₂SO₄ varied in the range of 15.4% to 65.6% (depending on the pulp density used), whereas the amounts achieved using 1 M acid ranged between 24.7% to 63.3%. This observation is valid for all the metals studied (Figure 4). In contrast, the difference between 0.1 M and 0.5 M acid used for AS extraction was more pronounced and it was especially notable when AS was treated at the 1% pulp density. For example, an increase of acid concentration from 0.1 to 0.5 M enabled extraction yields to be improved by a factor of at least 1.8 (for Cu and Zn), and up to 2.7 (for Pb). Amorphous slag was found to release the highest quantities of metals when leached with HCl, as up to 98.8% of Cu (18,211 mg kg⁻¹) and 81.3 % of Zn (478 mg kg⁻¹) could be extracted (Figure 5).



Figure 2. Chemical extraction of metals from crystalline slag treated with sulfuric acid at different concentrations (0.1–1 M) and various pulp densities (1–10%).



Figure 3. Chemical extraction of metals from crystalline slag treated with normality equivalent (2 N) acids at various pulp densities (1–2%).



Figure 4. Chemical extraction of metals from amorphous slag treated with sulfuric acid at different concentrations (0.1–1 M) and various pulp densities (1–10%).



Figure 5. Chemical extraction of metals from amorphous slag treated with normality equivalent (2 N) acids at various pulp densities (1-2%).

A screening study of leaching efficiency with H_2SO_4 showed that CS is treated more efficiently with 1 M acid. Thus, 1 M acid was selected for equ-normal acid extraction in order to enable a comparison of the leaching susceptibility of crystalline and amorphous slags.

Among the organic extractants studied, citric acid was found to have better performance as compared to oxalic acid and additionally, AS susceptibility to leach metals in the presence of citric acid was higher than that observed for CS. For example, even 69.5% of Cu (13,708 mg kg⁻¹) and 84.3% of Zn (495 mg kg⁻¹) was extracted from AS with citric acid with 1% PD. This indicates that the susceptibility of AS to organic solution is higher than the susceptibility recorded for crystalline slag. This observation is in accordance with previous studies concerning the leaching of CS and AS in organic solutions (a mixture of various organic acids) [43,50]. A prime advantage of the use of AS in chemical treatment is the fact that it contains a lower amount of Fe. This point is crucial when selective recovery (e.g., Cu) is targeted, because Fe purification from a pregnant leachate is such a challenging aspect [51–53]. Iron extraction in organic leaching media (citric and oxalic acid) was relatively high (up to 87.5%) in the case of AS leaching at 1% PD, whereas the amount of Fe decreased to 22% when 2% PD was used. Such a change may not only be related to a higher pulp density but in fact be due to Fe(III) citrate formation, which is relatively stable and dissolves slowly [54].

3.2. Effect of Pulp Density

Pulp density (PD) is an important economic driver of the extraction process because, for instance, the use of a 2% pulp density instead of 1% enables the consumption of chemical agents to be reduced by a factor of two [55]. A wide range of pulp densities (1%, 5%, and 10%) used for H_2SO_4 extraction revealed the latter as being the least favorable for extraction. For example, over 60% of Zn (2184 mg kg⁻¹) was extracted from CS using 1% PD and 1 M H_2SO_4 , whereas an increase of PD to 10% allowed for the extraction of Zn in an amount not exceeding 1% (28.5 mg kg⁻¹). Thus, using a 10-fold higher pulp density affected the extraction such that the yield was over 75 times lower. One can assume that a higher PD is associated with a higher neutralizing capacity of the slag. As shown in Table 2, a pH recorded in the reactors of 1% to 10% PD showed some variations, however, the main factor that determined the lower slag extraction rate at 10% PD is the limited phase exposure to the leaching solution.

A similar observation applies to AS that released even 63.3% of Cu (12,500 mg kg⁻¹) during extraction at conditions 1% PD and 1 M H₂SO₄, whereas only 31.7% of Cu (6248 mg kg⁻¹) was extracted when PD increased from 1% to 10%, while pH variations were also rather marginal (Table 2). Thus, the extraction efficiency decreased by a factor of 2, which indicated a much lower impact of AS pulp density than in the case of CS. This supports the conclusion that AS reveals a higher susceptibility to leaching with H₂SO₄ than CS does. A greater leachability of amorphous materials than crystalline ones has already been mentioned in the literature [56].

A study on pulp densities (1% and 2%) using various chemical agents (Figures 3 and 5) revealed that even a narrow range of PD of 1% to 2% slightly affects the process's efficiency. For example, Cu extraction from CS using HNO₃ solution at 1% PD was 33.5% (1259 mg kg⁻¹), whereas extraction achieved at 2% PD was 27.3% (1025 mg kg⁻¹). Such results have also been shown in the case of AS; however, the difference between PD 1% and 2% was more pronounced there than in case of CS. For example, Cu extraction in AS with HNO₃ reached 93.8% (15,634 mg kg⁻¹), while the use of 2% PD enabled extraction of only 25.3% (4123 mg kg⁻¹). This highlights the importance of a deep study of simple leaching parameters since even a narrow change of operating conditions may significantly affect the leaching efficiency. In the case of AS, the use of 1% PD in chemical treatment (Figures 4 and 5) appears to be more reasonable, because it increases the yield by factor of 3.7, while it does not show relevance in the case of CS. Decreased metal extraction efficiencies along with increasing pulp density have already been observed [22]. Thus, the amount of extractant per slag volume is more important for AS despite its generally higher susceptibility to leaching as compared to CS.

Crystalline slag subjected to 24- to 48-h extraction procedures using normality equivalent acids resulted in relatively high extraction yields (Figure 3). In particular, Fe and Zn were easily leachable

elements since up to 68.6% of Fe (236 g kg⁻¹) and 72.1% of Zn (2617 mg kg⁻¹) were extracted when 2 M HCl was used as a leaching agent in conjunction with 1% pulp density. A high leachability of Fe and Zn again confirms the general fayalite susceptibility to dissolution. Although, Fe and Zn are also incorporated in glass, fayalite is a primary Fe and Zn carrier in this slag [41]. In addition, extraction rates of Si were also exceptionally high, reaching up to 97.8%. Therefore, it can be stated that not only was fayalite a highly soluble phase under such conditions but glass also was, and silica gel formation likely did not occur as it did in the case of H_2SO_4 leaching. That resulted in an improved Cu extraction yield (compared to H_2SO_4), reaching 30.5% (1149 mg kg⁻¹). Copper extraction in inorganic leaching conditions was maximally 33.5% (1259 mg kg⁻¹) using HNO₃ as an extracting agent. A high Cu leachability using HNO₃ has already been demonstrated [57]. Extraction achieved in organic solutions was lower (up to 17.2% Cu) compared to leaching reached using inorganic leaching agents (Figure 3). For instance, maximal extraction achieved in the case of citric acid was 17.2% of Cu (646 mg kg⁻¹) and 13.9% of Zn (503 mg kg⁻¹) from CS. The extraction yield achieved for oxalic acid did not exceed 4.4% (15.3 g kg⁻¹ Fe). The better removal potential of citric acid over oxalic acid has also already been demonstrated [54,58,59]. Generally, the extracting agents used revealed the following CS extraction efficiency in decreasing order: $HCl > HNO_3 > H_2SO_4 > citric > oxalic acid (Figure 3)$. The reason for such behavior of slags in the presence of these extractants is that HCl is the strongest acid among the acids studied. A similarly high efficiency of HCl has already been noted during red mud extraction [60].

3.3. Silica Gel Formation

The reason for the relatively low Cu extraction rates with H_2SO_4 can be the potential formation of silica gel in a highly acidic leaching system (Equation (1)). The generation of such gel can entrap metals, including copper [21,35,61]. In detail, the leaching medium (H_2SO_4) was enriched in sulfates. Under such conditions, Si dominates in the form of monomeric Si(OH)₄ and once the supersaturation phase is reached, this species polymerizes to a colloidal species, forming a gel [61–63]. Apart from affecting the metal content in the leachate, silica gel also makes the leachate filtration process difficult, as was observed in our case. A similar observation applies to the study of Davris et al. (2017), who reported difficulty in the vacuum pressure filtration process in the presence of silica gel [64]:

$$2\text{MeO} \cdot \text{SiO}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{MeSO}_4 + \text{H}_4\text{SiO}_4 \text{ (Me: Fe, Co, Zn, Cu etc.)}.$$
(1)

The occurrence of silica gel in this leaching system is proven by a relatively low Si concentration in the leachate (maximum of 33.6%) with a simultaneously high concentration of Fe (up to 52.5%; Figure 2). Silicon and iron are incorporated in two primary phases, fayalite and glass [65], thus it would be expected that these two elements are leached at similar rates. The occurrence of an Si-rich surface layer composed of amorphous silica on a fayalite surface has already been reported [66]. However, incomplete Fe solubilization (maximally 68.6%) from solid to liquid may either suggest that the leaching reaction was not completed during the 48 h or was due to the formation of precipitates, such as schwertmannite and jarosite, known to form in sulfate-rich solutions [11,67].

Furthermore, an increase of H_2SO_4 molarity had an adverse effect on the Cu extraction efficiency. This serves as an additional argument for the involvement of silica gel as a mechanism inhibiting the presence of dissolved Cu in the leachate. A similar observation was made by Basir and Rabah (1999), who demonstrated higher Zn leachability than Cu from slags [34]. Likewise, Altundogan et al. (2004) observed an over three times lower Cu extraction rate than Zn when 1 M H₂SO₄ was employed as an extractant [38]. Despite the similarities of our results with the previous study, we find that the most plausible reason for a low content of Cu in the H₂SO₄ leachate is Cu entrapment in silica gel as explained above. In order to reach a higher extraction rate in the future, the reactor can either be supplemented with K₂Cr₂O₇ [38] or alternatively, H₂O₂ can be added in order to prevent silica gel formation [21]. Additionally, the supplementation of the leaching reactor with H₂O₂ could avoid the

formation of metal complexes and therefore maintain a high metal content in the dissolved form of the solution [68].

3.4. Bioleaching Efficiency

Bioleaching is a cutting-edge technology for metal extraction being studied by numerous research groups dealing with biohydrometallurgy [11,13,15,69]. It is known that the chemical process is generally unsurpassed for its shorter duration as compared to a biological process; however, the latter has a "green" connotation, which is seen as highly desirable given current trends in waste management [10]. Both types of slags were subjected to abiotic leaching with a sterile medium (control) and biotic extraction with *A. thiooxidans*. The work of these bacteria in a bioleaching system relies on the production of sulfuric acid as the result of elemental sulfur metabolic oxidation (Equation (2)). The elemental sulfur source in biotic incubations was provided by its initial supplementation to the growth medium. In addition, sulfur originating from sulfidic phases can also be a source (Equation (3)) (for an extended description of sulfur oxidation, see [70,71]). However, based on literature data, negative growth of *Acidithiobacillus thiooxidans* on sulfide minerals has been highlighted [72]. For example, Kaksonen et al. (2016) pointed out that an increase of bioleaching efficiency by 20% could be observed in biotic incubations when elemental sulfur was supplemented [72]:

$$S + 3/2O_2 + H_2O \rightarrow H_2SO_4 \rightarrow SO_4^{2-} + 2H^+,$$
 (2)

$$MeS_2 + 7/2O_2 + H_2O \rightarrow Me^+ + SO_4^{2-} + 2H^+.$$
 (3)

The leaching trends were alike in the case of both slag types (Figure 6). Dissolution of the slags is governed by: (i) Solution chemistry, mainly the type of extracting agent and its pH; (ii) the phase composition of the slag, because individual phases may dissolve at different rates; and (iii) the type of microorganism acting in the bioleaching system [10]. The kinetics of Si, Fe, and Zn (relative %) dissolution from both studied slags was nearly the same. However, concerning the different chemical composition of these materials, the values (mg kg⁻¹) of the elements in the leachates were different (Figure 6). This trend indicates that at extremely low pH levels (<1), dissolution of both slags is governed by pH rather than by the phase composition of the slag itself and bulk slag is dissolved, with a slight preference for Cu bearing phases of AS. Furthermore, the most significant increase of leaching rates occurred between 4 and 7 days of treatment. It has to be emphasized that these experiments run in parallel and therefore one can assume that at this stage of the experiment the biological activity of *A. thiooxidans* was alike in both the CS- and AS-containing reactors, implying that: (i) Until the seventh day of the experiment, bacteria remained in an exponential phase; [73] and (ii) bacterial performance was not affected by the metal content in the pregnant leachate [74].

3.4.1. Crystalline Slag

As shown in Figure 6, for all the elements studied, higher extraction rates were achieved under biotic conditions as compared to the respective abiotic control. This is undoubtedly related to a lower pH value in biotic incubation as compared to abiotic conditions (Table 2). The reduction of pH was due to sulfur oxidation by bacteria *A. thiooxidans*. In addition, dissolution features observed on CS originating from abiotic treatment (Figure 7A,B) were less pronounced as compared to features on CS treated with bacteria (Figure 7C–F). As can be seen in Figure 7A,B, fayalite and glass remained not dissolved, whereas Figure 7C–F demonstrate complete fayalite dissolution. Glass and sulfides remained dissolved to a lower degree as compared to fayalite crystals, however, dissolution features on these grains were clearly more pronounced as compared to grains resulting from abiotic leaching.

As the result of the 21-day extractions, the leaching yield was improved by a factor of 43 (CS treated at 5% PD) and 31 (AS treated at 1% PD) under biotic conditions (GMB) as compared to abiotic conditions (GM). Generally, biotic treatment of CS resulted in a notably high Cu and Zn extraction

yield when 1% PD was used. Given such conditions, as much as 52.7% of Cu (1981 mg kg⁻¹) and 68.4% of Zn (2482) were extracted. Incomplete Zn extraction refers to the stability of hercynite (Zn-bearing phase, Figure 7) that was surely responsible for the maintenance of this element in the solid phase. The incomplete dissolution of Cu also indicates that Cu-bearing sulfides (the primary Cu carriers) were not completely dissolved. Likewise, the extraction of Fe from CS reached 90.6% (312 mg kg⁻¹). According to scanning electron microscope observations, an exposure of CS to biotic conditions revealed more notable dissolution features (Figure 7C–F) as compared to signs observed on CS exposed to abiotic conditions (Figure 7A,B). Particularly, fayalite was significantly deteriorated (Figure 7C–F), while the glass matrix, despite being altered, still remained distinguishable (Figure 7). A greater degree of fayalite dissolution in bioleaching systems than glass has already been reported [75]. Copper release from CS was related with sulfide (mainly bornite) dissolution as proven by SEM observations (Figure 7D,F). The dissolution of such a mineral phase under exposure to the work of acidophilic bacteria has already been demonstrated [76].



Figure 6. (Bio)extraction of metals from crystalline and amorphous slags treated with growth medium and growth medium with bacteria *Acidithiobacillus thioxidans*. Values indicated in: (i) red-colored line and rectangle present bulk metal content in CS, (ii) blue-colored line and rectangle indicate bulk metal content in AS.



Figure 7. Scanning electron microscope images of CS leached during 21 days in abiotic growth medium and biotic solution with *A. thiooxidans*. Abbreviations: Fa: fayalite, Gl: glass, Hc: hercynite, Bn: bornite, Chp: chalcopyrite. (**A**,**B**): Crystalline slag exposed to abiotic growth medium; (**C**–**F**): Crystalline slag exposed to *Acidithiobacillus thiooxidans*.

3.4.2. Amorphous Slag

Similarly, AS treated with growth medium remained slightly dissolved (Figure 8A,B), whereas more significant changes were observed after treatment with biotic solution (Figure 8C–F). In the case of AS, dissolution appeared to be even more significant than with CS, because the AS was not only dissolved but appeared to be a residue with a contrasting composition and structure to that observed in the original sample. AS residue was characterized by the presence of gypsum and amorphous silica, both significantly depleted in metals.



Figure 8. Scanning electron microscope images of AS leached during 21 days in abiotic growth medium and biotic solution with *A. thiooxidans*. Abbreviations: GI: glass, Cu: metallic copper, Gp: gypsum. (**A**,**B**): Amorphous slag exposed to abiotic growth medium; (**C**–**F**): Amorphous slag exposed to *Acidithiobacillus thiooxidans*.

An application of 1% PD during biotic extraction of AS resulted in a clearly higher efficiency as compared to efficiencies achieved for the 2% and 5% treatments. Amorphous slag was highly susceptible to bioleaching, being able to release 98.7% of Cu (19,461 mg kg⁻¹) and 73.0% of Zn (428 mg kg⁻¹) during the 21-day treatments. For instance, Kaksonen et al. (2016) accomplished extractions of 73% to 83% of Cu and 23% to 27% of Zn during Cu-slag bioleaching with mixed cultures during 47-day treatments at 10% PD [72]. Thus, it can be assumed that in our case, an application of mixed microbial consortia in the future could be a way to improve extraction yield, especially if Fe-bearing phases are targeted for dissolution. The application of a higher pulp density for bioleaching does not appear to be optimal, since even the use of 5% PD enabled the extraction of only 10.9% (Cu) and 13.8% (Zn) in the case of CS and 10% (Cu) and 13.4% (Zn) in the case of AS. According to SEM observations, the dissolution of AS under biotic conditions resulted in the generation of gypsum-rich residue (Figure 8C–F) importantly depleted in metals, whereas the dissolution of AS under abiotic conditions resulted in less pronounced dissolution and material remained dissolved but not as much changed due to the biotic conditions in which it took place (Figure 8A,B).

3.4.3. Comparison of Slag Behavior

A comparison made between CS and AS shows that when a single metal is targeted for recovery, a suitable material can be chosen. Specifically, as shown in Figure 6, when Cu extraction is targeted, AS appears to be more suitable, because in order to extract 2257 mg kg⁻¹ (the value achieved during CS treatment at 1% PD over 21 days), only 24 h of biotic treatment of AS is required in the same operating conditions. Conversely, CS appears to be more efficient for Zn and Fe recovery. For example, a 4-day biotic extraction of CS provides higher Zn and Fe leaching yields as compared to a 21-day treatment of AS in the same operating conditions of 1% PD (Figure 6).

It is important to highlight that in spite of the high metal extraction rate that occurred in biotic incubations, the metals did not pose a notable toxicity threat to the bacteria. Based on the activity test performed after bioleaching, it was found that the bacteria remained active in all biotic incubations. In contrast, no bacterial activity occurred in the test tubes, with abiotic leachate additionally proving that the control conditions remained sterile during the run of the experiment.

Furthermore, it is evident that biotic extraction is longer (Figure 6) as compared to 48-h long, 1 M, and normality equivalent acids (chemical) extractions (Figures 3 and 5). However, the advantage of a biotic process is a lower consumption rate of chemicals as only a mineral salt medium is required for the maintenance of microbial growth [77].

3.5. Phase Dissolution in Bioleaching System

Calculating the molar ratios of the most easily released element versus other elements specific for individual slag phases is a useful geochemical tool for tracking a phase's dissolution fingerprint [43]. In the case of this study, iron was found to be highly leachable, thus Fe was used as a reference element (Figure 9). Furthermore, Mg was used to distinguish fayalite dissolution, whereas Ca, Al, and K were used to indicate glass dissolution. The molar ratios calculated for Cu and Zn aimed to decipher the biodissolution sequence of Cu- and Zn-bearing phases. Fe/Si molar ratios calculated for slags exposed to bacteria demonstrated that Fe is clearly more leachable from crystalline slag, as Fe/Si ratios were far from the theoretical ratios calculated for congruent slag dissolution (Figure 9). In contrast, Fe/Si experimental ratios achieved for AS were close to the theoretical ratio, indicating that there was no preference for bioleaching between these two elements. What this implies is that fayalite is more susceptible to dissolution than the glass of crystalline slag. A greater dissolution of crystalline phases as compared to glass under extremely low pH conditions has also been demonstrated by other authors [78,79]. Furthermore, Mg being incorporated in the fayalite structure has shown a slight preference towards release at the initial stages (24 h) of the biotic experiment. It is important to note that leaching of Fe and Mg was preferential with respect to Si in a bioleaching system. Such behavior of fayalite has already been reported [66,80]. As the experiment progressed, Fe/Mg ratios were close to those calculated for congruent dissolution. An additional argument for fayalite dissolution is the trend observed for Zn occurring in fayalite as an impurity. There was a slight preference for Fe release compared to Zn, likely due to the fact that some Zn is also incorporated in hercynite and glass. The elements Al, Ca, and K are contained in a higher quantity in glass; therefore, these are good indicators for fingerprinting this phase's biodissolution. Al and Ca were bioleached with a clear preference of Fe, whereas this preference was less pronounced in the case of K. The preferential release of network-modifying elements (alkali and alkaline-earth metals) from glass surfaces usually occurs due to metal/proton exchange reactions [81], while preference for Fe release in the present study is due to: (i) Higher fayalite dissolution than glass in the case of CS, and (ii) slag conversion to a newly

formed Ca-rich residue in the case of AS. It is noteworthy that there was a clear preference for Cu release as compared to Fe, implying that Cu-bearing sulfides are also highly susceptible to leaching as has already been demonstrated [14,78]. However, a higher leachability of Cu from AS (up to 98.7%) than CS (up to 52.1%) suggests that metallic Cu is more susceptible to dissolution than Cu-sulfides, which is in accordance with other findings [75].



Figure 9. Molar ratios of metal versus Fe in biotic system with slags at various pulp densities.

In the case of amorphous slag, most elements were bioleached in a rather congruent manner, because the ratios achieved experimentally and those calculated for theoretical dissolution were close to overlapping. However, there was a clear preference for Fe release with respect to Ca from this slag and maximal release of Ca was assessed at 14.2% (AS treated at 1% PD for 21 days). Solution chemistry, which indicated such a low content of Ca with a simultaneously high content of other elements in the solution, made it necessary to elucidate a mechanism responsible for low Ca content in the solution. As demonstrated by SEM observations, the main phase identified in the leach residue was gypsum

(CaSO₄·2H₂O), therefore explaining the Ca presence in the solid. The conversion of amorphous slag to gypsum-rich residue has already been demonstrated [14]. There is no clear preference for any phase to dissolve preferentially when amorphous slag is present in the bioleaching system. In addition, the high release of Ca led to the formation of gypsum in the biotic system, which is congruent with previous findings on other amorphous copper slags [14]. The generation of gypsum as the result of this process potentially allows for the further use of this residue; for example, gypsum is known to reduce exposure of plants to saline stress in soil [82].

It has been shown that in the case of amorphous slag, a 7-day bioleaching treatment seems to be optimal to achieve a satisfactory yield of metals. The use of a 1% pulp density was found to leach especially well when the experiment progressed onward from the 7-day mark. Similar observations can be made when the behavior of crystalline slag is considered. For pulp densities of 2% and 5%, the optimal leaching yield was obtained after 7 days, whereas the use of a 1% pulp density enabled the bioleaching reaction to continue as shown in Figure 6.

3.6. Economic Potential for Treatment of Historical Slags

The economic driver is undoubtedly an advantage for specific process developments on a larger scale [83]. Without doubt, when compared to traditional hydrometallurgical processes, the leaching yields obtained in the treatment of historical slags have to be markedly high in order to ensure process profitability. This is mainly connected to the need for slag to be collected from its disposal area and subsequently transferred to a treatment plant; both management activities are inherently associated with extra expenses. However, the additional environmental benefit that could be achieved by removing these wastes from soils is that any future metallic pollution potentially rendered by these slags [50] will then be eliminated, the additional economic value of which is difficult to quantify.

The economic estimation addressed in this study is a theoretical calculation used to present potential differences between the specific treatments (Table 3). It has been made based on average metal values specified on the market in 2019. A complete estimation concerning each element studied is included in Table 1. Depending on the treatment implemented and level of extraction achieved, it has been demonstrated that a gain of up to \$35 (CS) and \$127 (AS) (per ton) can be made when treating the slags with HCl for 48 hours. Biological treatment, despite its longer duration, can bring a slightly higher profit of \$47 (CS) and \$135 (AS) per ton of slag treated. However, it is important to point out that in the present study, only selected elements were considered, while profit could presumably be increased when other critical metals are also included. As demonstrated recently, up to an additional \$512 of profit can be made during biological treatment of one ton of Cu slags if critical and rare earth elements are taken into consideration too [44].

The commercial applications of bioleaching remain in their infancy at present and are the subject of lukewarm opinions from representatives of the industrial sector. Thus, the data contained here aims to show the preliminary results on extraction efficiency and to convince skeptics about the suitability of slag for metal extraction and potential recovery to be developed in the future management of these wastes. Thus, all leaching studies presented in the literature can be considered as a step from the experimental laboratory stage towards commercial exploitation. Currently, it is known that the primary advantage of chemical treatment is its shorter duration as compared to biotic treatment, as the latter usually requires some time for a bacterial culture to develop and act. On the other hand, chemical treatment consumes extracting agents, which increases the processing expenses incurred and generates chemical wastes that are not environmentally inert. A key advantage of bioleaching is its lack of toxic, highly concentrated acids (e.g., HCl) in the procedure. However, it has to be noted that the bioleaching process does require careful consideration of a larger number of variables in order to optimize the process (Table 4).

| | | Crystalline Slag | | | | Amorphous Slag | | | | | |
|--------------------------------------|---|--|----------------------------------|----------------------------------|----------------------------------|----------------|-----------------------------------|----------------------------------|----------------------------------|----------------------------------|-----------------------------------|
| Solution Used as Extracting Agent | Treatment with the Best Operating Parameters | Fe 0.09 \$ kg ⁻¹ | Cu 6.5 \$ kg ⁻¹ | Zn 2.8 \$ kg ⁻¹ | Pb 2.1 \$ kg ⁻¹ | Sum | Fe 0.09 \$ kg ⁻¹ | Cu 6.5 \$ kg ⁻¹ | Zn 2.8 \$ kg ⁻¹ | Pb 2.1 \$ kg ⁻¹ | Fe 0.09 \$ kg ⁻¹ |
| | | Economic Profit Dollars [\$] Per Ton of Slag Treated | | | | | | | | | |
| Hydrochloric acid | PD: 1%, T: 48 h | 20.23 | 7.47 | 7.33 | 0.07 | 35.10 | 6.88 | 118.48 | 1.33 | 0.10 | 126.80 |
| Sulfuric acid | PD: 1%, T: 48 h | 15.49 | 0.35 | 6.09 | 0.03 | 21.95 | 4.42 | 81.19 | 0.88 | 0.02 | 86.51 |
| Nitric acid | PD: 1%, T: 48 h | 16.28 | 8.19 | 5.62 | 0.07 | 30.16 | 5.51 | 101.68 | 1.36 | 0.10 | 108.66 |
| Citric acid | PD: 1%, T: 48 h | 2.76 | 4.20 | 1.41 | 0.05 | 8.42 | 7.04 | 109.51 | 1.39 | 0.11 | 118.05 |
| Oxalic acid | PD: 1%, T: 48 h | 0.51 | 0.36 | 0.01 | 0.02 | 0.89 | 6.12 | 16.75 | 0.64 | 0.00 | 23.52 |
| Growth medium (sterile) | PD: 1%, T: 21 days | 0.00 | 0.42 | 0.35 | 0.00 | 0.77 | 0.00 | 40.58 | 0.30 | 0.00 | 40.89 |
| Growth medium + bacteria | PD: 1%, T: 21 days | 27.00 | 12.88 | 6.95 | 0.00 | 46.84 | 6.89 | 126.57 | 1.20 | 0.01 | 134.67 |

Table 3. Estimated economic potential of chemical and biological treatment of slags.

Abbreviations: PD—pulp density, T—treatment time. Metal prices taken from https://markets.businessinsider.com/commodities.

| Evaluated Parameter | Chemical Treatment | Biological Treatment | |
|---|--------------------|-----------------------------|--|
| Chemicals consumption during extraction | high | low | |
| Processing time | short | long | |
| Metal yield | comparable | | |
| Environmental impact | high | low | |

Table 4. Comparison of chemical and biological treatment of metallurgical slags.

4. Conclusions

Metallurgical slags are susceptible to dissolution in inorganic and organic solutions; therefore, these wastes should be considered as prospective candidates for metal extraction and recovery processes rather than simply being disposed of and forgotten. Suitable and efficient treatment depends on the metal(s) targeted and conditions set. Given the right circumstances, amorphous slag was found to be highly susceptible to dissolution. In addition, as a result of the bio-assisted extraction of AS, metal-depleted residue can be generated in the form of gypsum and silica residue, rendering it suitable for even further applications. Crystalline slag subjected to bioleaching resulted in more pronounced fayalite biodissolution as compared to glass, showing it to be a particularly promising candidate for the Fe-recovery process. Chemical treatment is unrivaled in the brevity of its duration as compared to a biological process. Theoretical calculations made based on leachate compositions revealed that the chemical treatment of slags can bring as many as \$35 and \$127 of profit (per ton of slag material) in the case of crystalline and amorphous slag, respectively. Additionally, as a result of biologically assisted treatment, a gain of \$47 and \$135 can also be made for each ton of CS and AS, respectively.

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