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(Bio)dissolution of Glassy and Diopside-Bearing Metallurgical Slags: Experimental and Economic Aspects

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Abstract: Dissolution of diopside-bearing slag and its amorphous counterpart was investigated to decipher recovery potential of these slags. The contribution of direct slag phase dissolution was investigated using a biotic solution with *Acidithiobacillus thiooxidans* versus sterile growth medium, whereas citric acid was applied to demonstrate slags dissolution in organic medium. Potential metal donor slag phases and easily released elements were identified by comparing theoretical and experimental dissolution ratios. It was shown that K and Na were the most mobile elements leaching from glassy and diopside slag (up to 99%). Recovery targeted metals were released in the quantities of 56% (Cu)–96% (Zn) from glassy slag and 27% (Cu)–98% (Zn) from diopside slag. Results demonstrated that studied slags are good candidates for Zn recovery during short-term treatment, whereas extension of time would be required for efficient Cu extraction. Abiotic growth medium had little effect on metal leaching (up to 53% versus only 3% for the glassy and diopside slags, respectively). Glassy slag revealed greater susceptibility to dissolution as compared to diopside slag. Further studies improving recovery conditions are expected to improve environmental soundness of proposed treatments and to generate residues depleted in toxic elements. This study highlights the importance of evaluation of individual slags in terms of metal and major elements leachability.

Keywords: slag; diopside; glass; bioleaching; *Acidithiobacillus thiooxidans*; citric acid



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1. Introduction

The metallurgical industry holds a great economic and societal importance; this sector is key for meeting supply demands of various industrial branches. Currently, metals enable the development of human living conditions. However, the role of metals was already acknowledged in ancient times. Definitely, development of society would not have been possible without investigating metal properties and their applicability [1].

Metal production is mainly achieved by pyrometallurgy, however this industrial sector generates various types of wastes, including slags. Additionally, it is important to note that the pyrometallurgical industry is associated with metal losses; a large number of reports have proven this based on mineralogical analysis of slags. The slags usually carry phases enriched in metals indicating that achieving complete process efficiency is not possible [2]. The problem applies in both ferrous and non-ferrous industries.

The increasingly large volumes of slag being produced combined with the rapid growth of industrialization worldwide raise concerns about the decreasing availability of land suitable for landfills and, as a result, slag disposal costs are rising ever higher. Limited space for disposal and mounting evidence on the adverse environmental impacts of slag [3–6] has resulted in urgency in the search for alternative uses for slag. Although slag landfilling is at present the least suitable management option, a vast amount of material is present at numerous dump sites worldwide [7–10]. Disposal sites are known to encounter a broad array of chemical and biological processes and environmental factors

(e.g., pH variations, the presence of inorganic and organic acids, microbial communities) termed “weathering” [7,11]. A slag with long-term exposure to weathering may undergo the dissolution and subsequently may lead to metal being released into the environment leaving a fingerprint on the slag surface and contamination consequences in its immediate surroundings [9,12,13]. As a result, elevated concentrations of potentially toxic metals in the vicinities of slag piles is an alarming environmental issue for numerous disposal sites. The environmentally persistent metal contaminants may find their way into living organisms, causing various impairments. Current understanding of how slag impacts on ecosystems have earned these wastes a spot on the list of emerging environmental concerns and the search for alternative management routes has become increasingly urgent to decrease slag’s footprint on the environment.

The discovery of the role of microorganisms in minerals dissolution provides a basis for a whole new technology, known as secondary metal recovery from metallurgical slags. Today this approach is one of the main study chains being pursued towards sustainable slag management. Generally, extractive leaching can be defined as the treatment under specific conditions influencing the solubility of the metallurgical slag. As the result of extraction, the transfer of metals from the solid (slag) to the liquid phase (leachate) takes place. The extraction can be carried out by chemical leaching (using inorganic or organic chemical agents) or bioleaching (using a solution with microorganisms). The mechanism involved depends on agent applied. Acidolysis promotes the dissociation of phases by interaction with hydrogen ions leading to the metal transfer from solid to liquid, whereas complexolysis relies on metal binding to organic molecules.

Application of (bio)leaching on an industrial scale is currently limited, because suitable conditions proven efficient to recover metals have not yet been defined in spite of numerous evaluative approaches undertaken to do so [14,15]. Currently, metal extraction and recovery processes are evaluated at the laboratory scale. Testing a variety of leaching agents enables researchers to determine reagent efficiency, its suitable concentration, and phases that are the most prone to dissolution. The advancement of the current state of optimal protocol definitions is undoubtedly influenced by the number of publications dedicated thereto, but an accurate and universal “how to” does not exist thus far. Additionally, it is important to point out that traditional metal reserves (raw, metal-bearing ores) are finite and non-renewable, thus unreasonable wasting of the metal incorporated in the slags is seen as suboptimal and needs to be definitely avoided.

The chemical composition of the slags is variable. It depends on the type of process in which the metal is smelted, the materials used as fluxes, the type of smelted ore, and the material that was used in the furnace. Slags are composed of diverse phases that are present in various volumetric proportions. Each phase generally exhibits different susceptibility to dissolution depending on the conditions to which the slag is exposed [16]. Specific metals targeted in recovery may be incorporated in different phases, whereby sulfides and intermetallic phases are known to be main metal carriers. However, sulfides and intermetallic phases cannot be treated as individual particles, but together with silicates and oxides are an inseparable whole in spite of the existence of some approaches for sulfide separation such as flotation [17]. In addition, silicate and oxide phases may host significant amounts of various trace elements [18–20]. The dissolution behavior of silicate slag phases under the influence of acidic and basic conditions varies from one specific silicate to another [21–23], therefore, the knowledge of conditions promoting individual phase dissolution is fundamental to designing a suitable recovery method. Furthermore, glassy slags are known for greater susceptibility to dissolution as compared to crystalline slag, although some exceptions from this rule have also been observed. The content of SiO_2 plays an important role since slags exhibiting higher content of silica have a denser silica network. Therefore, comparing crystalline and amorphous slags susceptibility to dissolution is reasonable provided that both types owe similar content of SiO_2 . Thus, the feasibility of extracting metals by implementing different (bio)hydrometallurgical approaches will be assessed in the frame of this study. This interdisciplinary subject is presented towards

the prime objective of achieving an efficient, environmentally friendly and economically profitable slag recycling method. Shaft furnace diopside-bearing slag and its glassy counterpart are compared in respect to dissolution under biotic, abiotic and organic conditions. It is hypothesized that these slags reveal different susceptibility to dissolution and various elements are released preferentially depending on the conditions to which the slags are exposed. We aimed to delineate the dissolution sequence of slag phases including diopside, glass, sulfides and intermetallic phases.

2. Materials and Methods

2.1. Metallurgical Slags

Two types of Cu-slags, crystalline diopside-bearing slag (Di-slag) and its amorphous glassy slag counterpart (Gl-slag) were selected for this study (Table 1, Figure 1). Major and minor elements were determined through inductively coupled plasma emission spectrometry (ICP-ES) after the fusion of the samples by $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$ and dissolving the residue with nitric acid in the Bureau Veritas Mineral Laboratories (Vancouver, Canada). Identification of phases present in the slags was done using X-ray powder diffraction (XRD), scanning electron microscopy equipped with energy dispersive spectrometer (SEM-EDS) and electron microprobe analyzer (EMPA). Detailed methodology is given elsewhere [24,25].

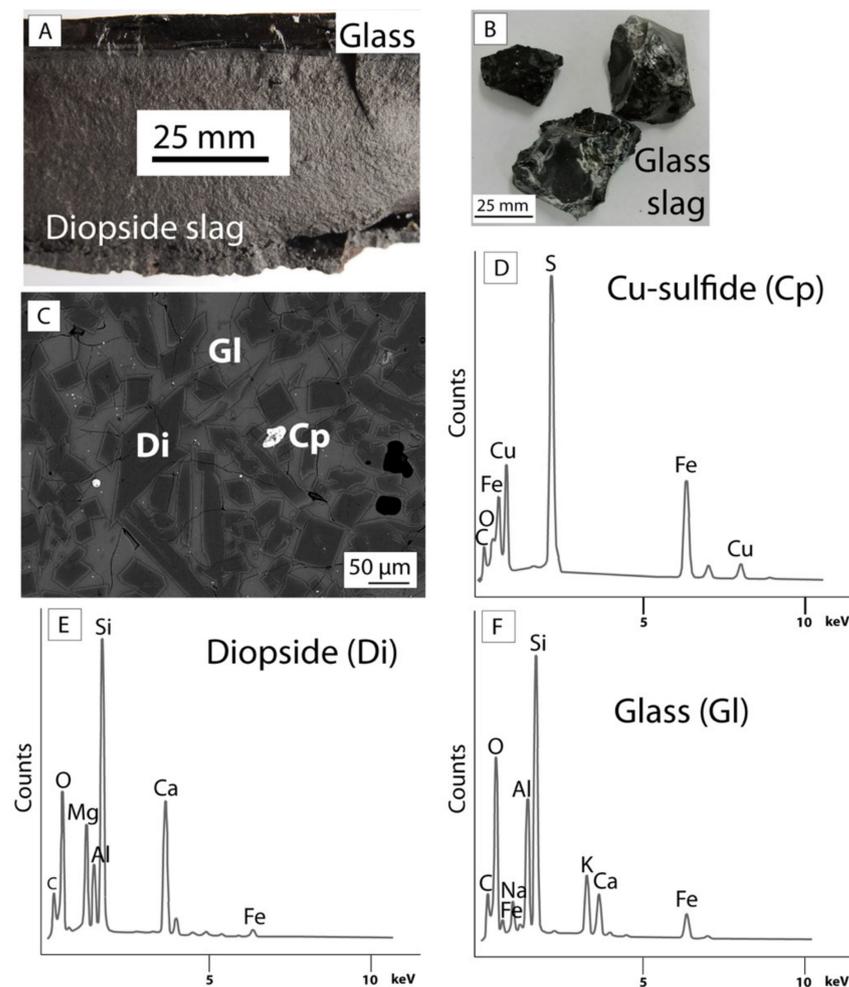


Figure 1. Macroscopic images of crystalline slag (A) and amorphous slag (B) and scanning electron microscopic images of phases identified in studied crystalline slag (C) and energy dispersive spectrometer (EDS) spectra of Cu-sulfide (D), diopside (E) and glass (F).

Table 1. Chemical composition of studied slags.

	Glassy Slag (GI-Slag)	Crystalline Slag (Di-Slag)
	Primary slag from shaft furnace	
	Surface glassy part of slag	Bulk slag with a crystalline part
Bulk Chemical Composition *	Major Oxides [wt. %] vs. (Major Element [wt. %])	
Fe ₂ O ₃ (Fe)	33.4 (23.4)	10.7 (7.5)
SiO ₂ (Si)	33.0 (15.4)	44.9 (21.0)
CaO (Ca)	10.4 (7.4)	17.6 (12.6)
Al ₂ O ₃ (Al)	5.73 (3.0)	13.1 (6.9)
MgO (Mg)	4.99 (3.0)	6.31 (3.8)
K ₂ O (K)	3.45 (2.9)	3.57 (3.0)
Na ₂ O (Na)	0.80 (0.6)	1.54 (1.1)
	Metals (mg kg ⁻¹)	
Cu	2795	2687
Zn	15,407	3832
Pb	2950	1559

* Composition reported in [24,25].

2.2. Experimental Leaching

This study applied experimental leaching for a preliminary evaluation of the slag (fraction < 0.3 mm) potential to serve as a Fe, Cu and Zn resource. Three types of agents were used: citric acid (CA 1 mol L⁻¹), growth medium inoculated with bacteria *Acidithiobacillus thiooxidans* (GM + B) and sterile growth medium (GM – C) as a control experiment representing abiotic acidic leaching. Parameters such as pulp density (PD 1%, 5% and 10%) and leaching time (1, 7 and 14 days) were varied. A short experiment duration was applied, because an integral objective of the biohydrometallurgy branch is to extract metals in as short a time as possible. Citric acid was used as leaching agent in order to mimic fungi-mediated (e.g., *Aspergillus niger*) bioleaching conditions. Bacterium *A. thiooxidans* was selected due to its proven ability to generate strongly acidic conditions. *A. thiooxidans* (strain number DSM 9463) was purchased from Deutsche Sammlung von Mikroorganismen und Zellkulturen (Braunschweig, Germany).

The growth medium (initial pH = 2.5) used for bioleaching was composed of: 2 g ammonium sulfate ([NH₄]₂SO₄), 0.25 g magnesium sulfate (MgSO₄ × 7H₂O), 0.1 g dipotassium hydrogen phosphate (K₂HPO₄), 0.1 g potassium chloride (KCl) and 3% (wt./v) elemental sulfur (S⁰) per 1 L of ultrapure water. The incubation flasks were placed on an incubator shaker set at 100 rpm and 30 °C.

The sample aliquot was filtered through 0.22 µm polytetrafluoroethylene (PTFE) filters and acidified with 65% HNO₃ (2% v/v., Suprapur, Merck). The concentrations of major (Si, Fe, Al) and minor (Cu, Zn, Pb) elements in the solutions were analyzed using Atomic Absorption Spectrometer (AAS 200 Perkin Elmer, Waltham, MA, USA). Quality control included systematic analysis of calibration standards. The procedure was repeated at least once for every 10 samples analyzed. The quantities of metals in the solutions were recalculated to express the values in mg of element released per kilogram of the slag by multiplying the metal concentration in the solution (mg L⁻¹) by the liquid to solid ratio.

3. Results

3.1. Characterization of Metallurgical Slags

The investigated copper slag (Di-slag) is mainly composed of minerals from the pyroxene group (diopside) surrounded by the interstitial glass (Figure 1). Sulfide inclusions as bornite, chalcopyrite, chalcocite and sphalerite as well as metallic lead inclusions are also found [26]. Locally, the sample is characterized by a hypo-crystalline structure, in these spots the basic component of the slag is surface glass (GI-slag). Diopside has a skeletal form and often forms crystals with a size of 50 µm to 500 µm. Smaller crystals sized at less than

30 μm were also observed. The sulfides are opaque with spherical shapes and sizes ranging 10–100 μm . Detailed characterization of slags has been described elsewhere [25,26].

3.2. Elements Extraction from Studied Slags

The slags subjected to the leaching tests revealed similar general trends in terms of element release. They showed high extraction efficiencies in citric acid conditions and biotic conditions with bacteria *A. thiooxidans* (Figures 2–5). Conversely, as growth medium alone was used as extracting agent, the leaching of the elements (Si, Fe, Al, Mg, Ca, Cu and Zn) was notably poorer. Leaching efficiency obtained in studied treatments are expressed as relative values as %.

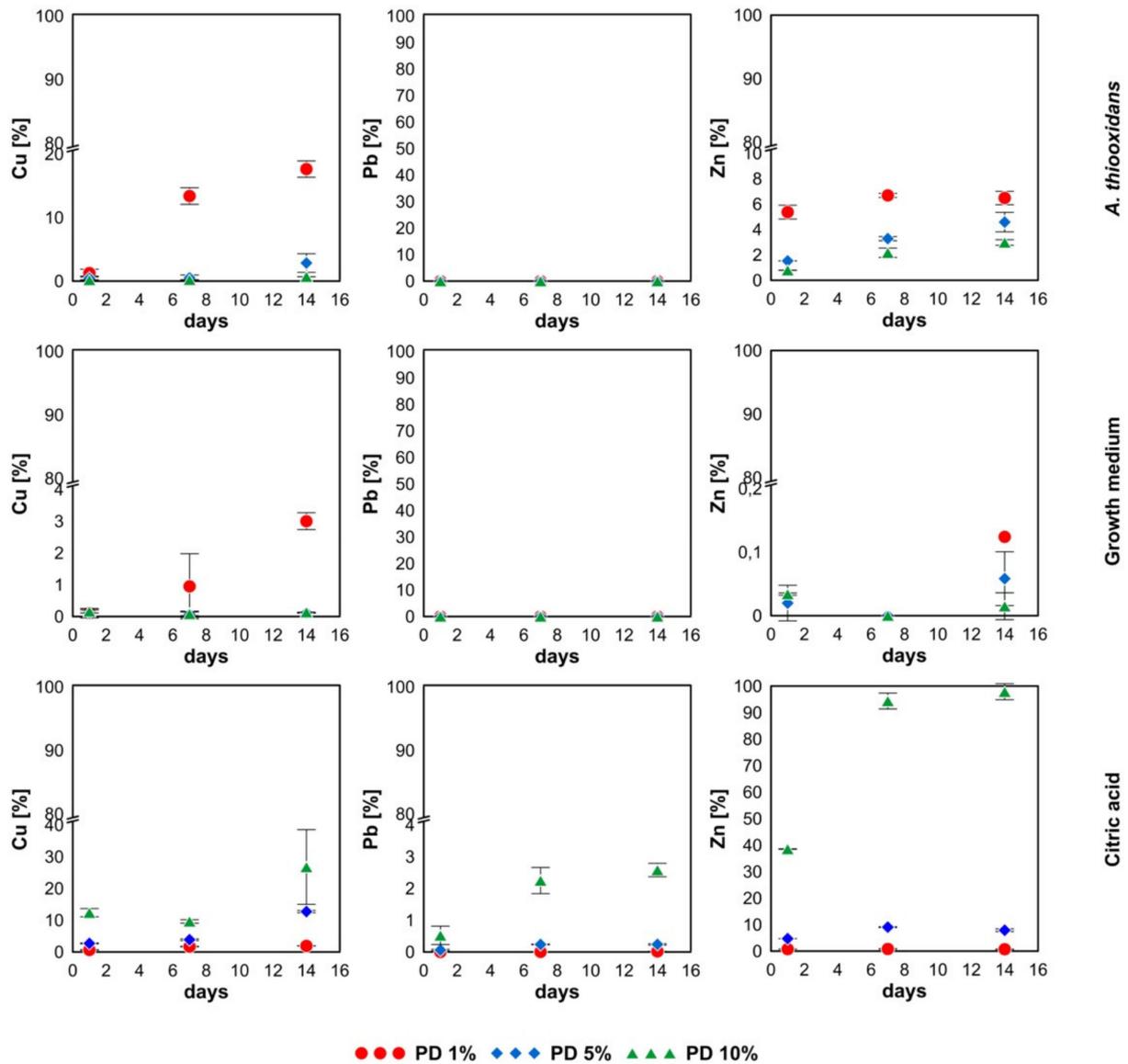


Figure 2. Extraction efficiency of recovery-targeted elements from studied diopside-bearing slag.

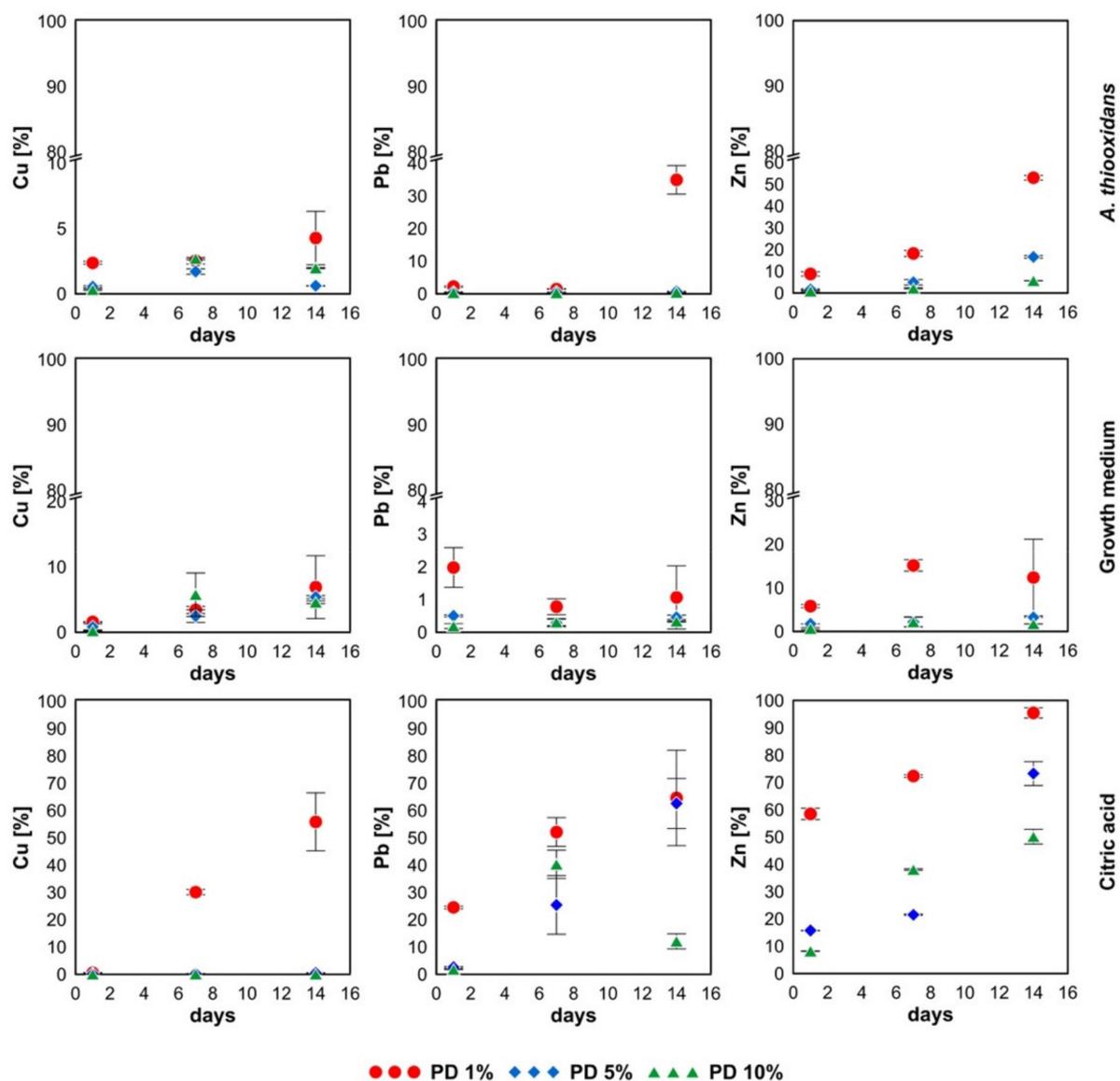


Figure 3. Extraction efficiency of recovery-targeted elements from studied glassy slag.

Under biotic GM+B and CA conditions with Di-Slag, the release of metals (Cu and Zn) increased slightly from the initial stages of incubation (1 day) to the end of experiment (14 days). The most pronounced increase was observed for PD 5% and 10%. For example, Zn extraction from Di-slag in GM+B conditions increased from 0.8% (1 day) to 3% (14 days) at PD 10%, whereas in the case of Gl-slag exposed to the same leaching conditions the observed increase was more pronounced; from 0.8% (1 day) to 5.7% (14 days). In contrast, leaching time had minor effect during Di-Slag leaching at PD 1% as extension of leaching time from 1 day to 14 days in GM+B, increased Zn extraction from 5.4% to 6.5% only. This is contrary to Gl-Slag that released only 8.8% of Zn during 1 day and as much as 53% of Zn during 14 days. Furthermore, Cu behavior was opposite to that of Zn and in order to achieve higher Cu extraction yield, an extension of time was required for Di-slag, whereas for Gl-Slag extension of time played a less important role. A detailed track of leaching trends is presented in Figures 2 and 3.

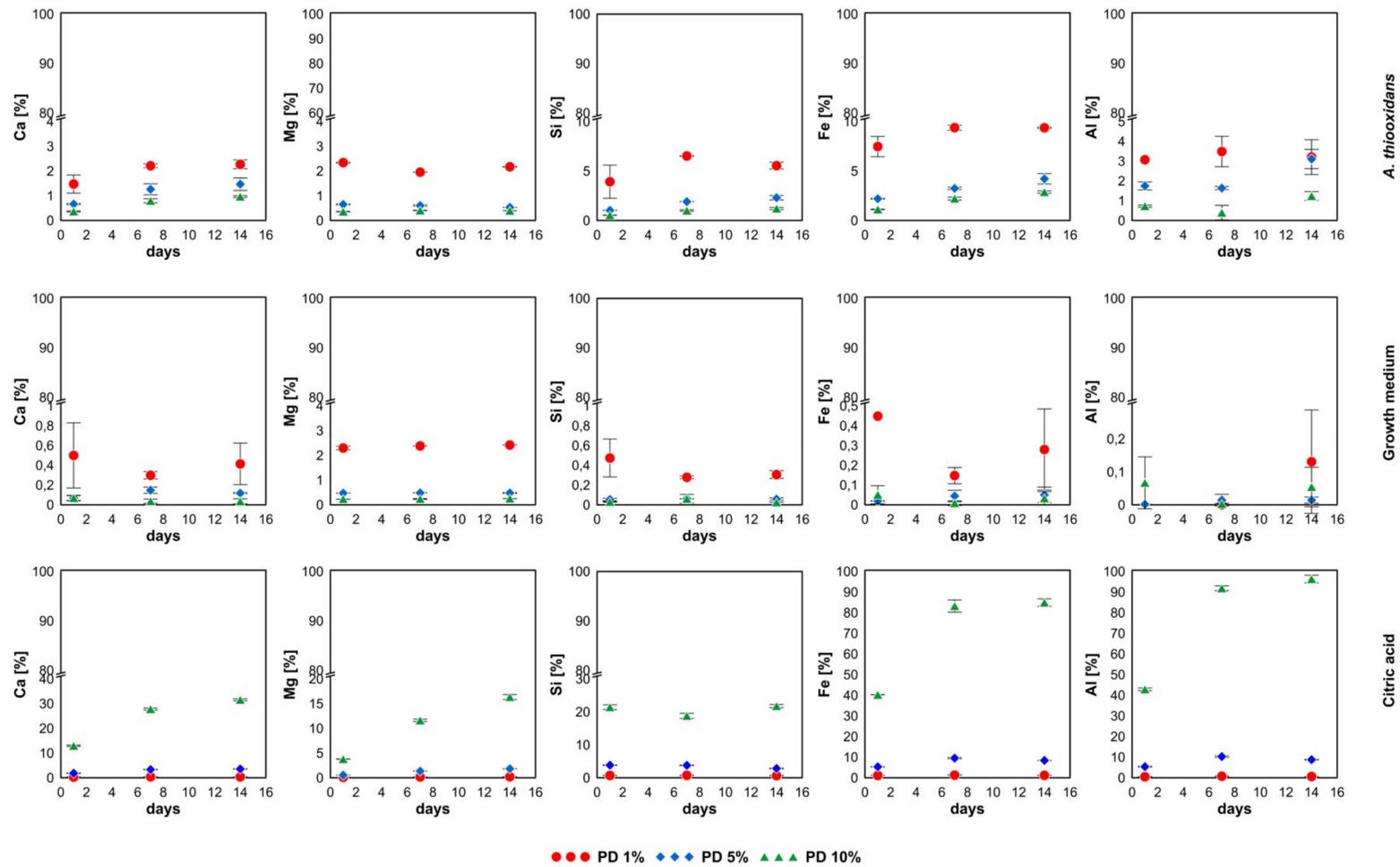


Figure 4. Extraction efficiency of major elements from studied diopside-bearing slag.

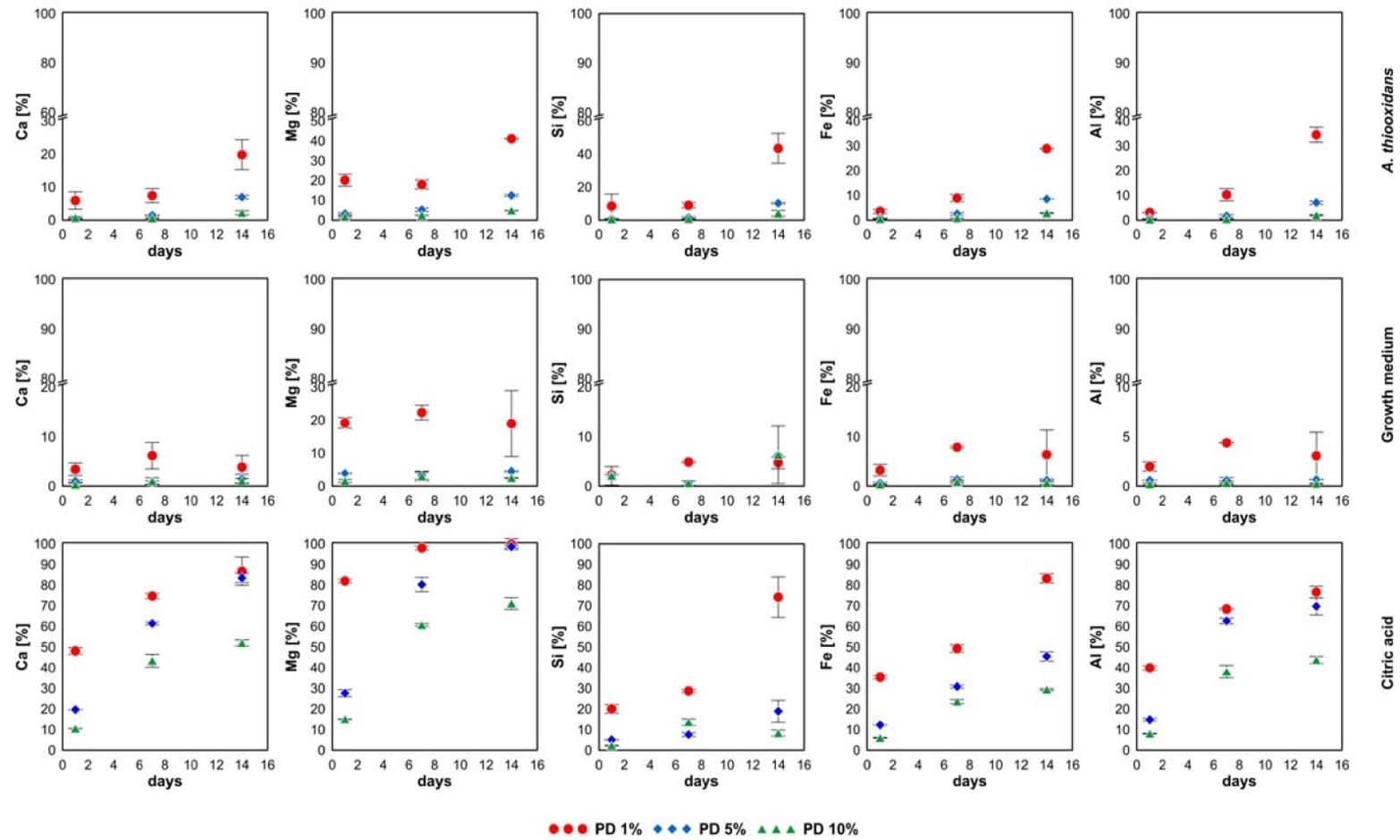


Figure 5. Extraction efficiency of major elements from studied glassy slag.

Under CA conditions, the extraction of Cu and Zn from Di-slag was better than under biotic GM+B conditions and reached a maximum of 26.8% (Cu) and 97.9% of (Zn) at PD 10% instead of PD 1% as observed for GM+B. At the same incubation conditions (CA, PD 1%), only 0.1% (Cu) and 50.1% (Zn) were released from Gl-Slag. Thus, to improve extraction to 55.9% (Cu) and 95.5% (Zn), incubation of Gl-slag at lower pulp density (PD 1%) was required (Figures 4 and 5).

The inoculation of *A. thiooxidans* in growth medium had a significant effect on extraction efficiency. The GM+B improved leaching by factors 25.5 (Cu)–200 (Zn) for Di-slag and by factor up to 5.1 (Zn) for Gl-slag when compared to abiotic GM-S conditions.

Furthermore, different trends of Pb leaching were observed depending on the type of slag leached. Gl-slag exposed to CA conditions released up to 64.6% (Pb), at a 1% pulp density at the end of the experiment. A much lower extraction efficiency was achieved when the Di-Slag was treated reaching a maximum of 2.6% (Pb) during CA extraction. It may be associated with the quite long duration of this experiment.

In these experiments, apart from metals, major elements were also analyzed (Figures 4 and 5). The values of extracted elements were relatively low for high pulp density (PD 10%) reaching up to 3.3% (Na) and 12.6% (K) for Di-slag and Gl-slag, respectively considering GM+B and GM treatments. Leaching of major elements from Di-slag in CA solution at PD 10% was much higher and reached up to 99% (K), whereas similar extraction yield (96% of K) for Gl-slag was achieved at PD 1%. Generally, bacteria *A. thiooxidans* improved major elements extraction from Di-slag by factors up to 47 (Si), 87 (Fe) and 219 (Al), whereas extraction from Gl-slag was improved by factor 9 (Si), 7 (Fe) and 11 (Al). Bacterially-mediated extraction had less pronounced influence on leaching of K, Na, Mg and Ca improving their leachability by factors up to 27 and 5 for Di-slag and Gl-slag, respectively, as compared to experiments performed in the (GM-S) sterile growth medium (Figures 4 and 5). Ca leaching in CA solution was the highest, however it was already reported in the literature that an even lower concentration of CA (0.1 M) can readily mobilize Ca [27].

4. Discussion

Literature reports on the dissolution of slag phases allow the indication of the general susceptibility of individual phases under specific conditions. However, the overall complexity of slag phase composition means that different dissolution sequences can be delineated for individual slags. Discrepancies in phase dissolution order depend on dissolution conditions, volumetric proportion of individual phases and how long the slag is exposed to certain conditions. The solubility property can better be observed when applying a laboratory leaching test, demonstrating trend curves for specific elements released as a function of time [28–30]. Based on gathered results, we found that crystalline diopside-bearing slag and its amorphous counterpart undergo dissolution, however, overall dissolution manner varied depending on slag incubated and conditions tested.

4.1. Effect of Leaching Agent

One factor influencing dissolution cannot be treated as a separate entity nor fully understood without considering the others. An adequate choice of leaching solution should be primarily dictated by the slag's composition and therefore the main phase targeted as a metal releasing phase. For this reason, different leaching agents were tested in this study.

The most effective leaching agent among treatments applied was citric acid (1 mol L⁻¹). Previously, the researchers reported that the leaching of elements tends to be better under highly acidic conditions (pH 2–4) [31], which is confirmed in the conducted experiments. The pH conditions for the chemical treatment with citric acid (CA) oscillated between 1.5–2.2, in the biological method (GM+B) with *Acidithiobacillus thiooxidans* (pH 1.5–3.5) and in abiotic medium (pH 5.5–8.0). The general efficiency of the experiments followed the trend CA > GM+B > GM-C. Thus, citric acid was found to be crucial in elements extraction from studied slags. Organic compounds affect slag dissolution rates through acidification

and/or complexation mechanisms. The specific strength of dissolution results from the organic acids' affinity towards individual metals incorporated in the mineral phase and the subsequent stability of the metal-complex formed. Since pH conditions in studied biotic medium (GM+B) were nearly the same as that in CA medium, while leaching yield was lower in the former and higher in the latter solution it can be stated that complexation was the main mechanism driving the CA-mediated dissolution process. In addition, Castro et al. [32] showed that efficiency of CA is determined by the compilation of factors including the type of mineral subjected to leaching, acid concentration, growth medium composition and pH. One could question whether efficiency of leaching would also be efficient for studied slags when applying fungi to produce citric acid and whether any toxicity effect posed by high metal load could occur. As demonstrated by Strigáč [33], Cu slags revealed low antifungal properties. This indicates a potential to involve fungi in future citric acid mediated bioleaching of our slags. In addition, Mehta et al. [34] pointed out that CA chemical leaching was less efficient as compared to bioleaching involving CA producing fungi. A similar suggestion was made by Castro et al. [32] showing that indirect and direct CA bioleaching is more efficient than chemically mediated extraction. Furthermore, Sukla et al. [35] demonstrated that the addition of hydrochloric acid to *A. niger* culture filtrate can facilitate extraction. Likewise, Mulligan and Kamali [36] noticed that the addition of small quantities of sulfuric acid improved leaching; that is also in accordance with the observation of Anjum et al. [37]. Observations made in the above-mentioned studies reveal a prospective for fungi-mediated bioleaching to be developed.

The leaching of the elements in the control medium GM-C resulted in much lower leaching; the efficiency was impoverished relative to GM+B by factors up to 33 (Pb) and up to 200 (Zn), in the cases of GI-slag and Di-slag, respectively. This was due to the higher pH of the GM-S solution. Given the fact that both GM-S and GM+B solution had the same initial pH, the results demonstrated that the neutralization potential of slag accounted for pH increase in GM-S. In contrast, under biotic conditions (GM+B) neutralization capacity of the slag was conquered by bacterial activity that was prevailing and resulted in generation of sulfuric acid and subsequent pH depletion. However, it is important to point out that overall efficiency of bacterially-mediated leaching at PD 1% was low as only up to 6.5% (Zn) and 53% (Zn) was released from Di-slag and GI-slag respectively. The release of Cu was 17% and 4.3% for Di-slag and GI-slag respectively. Previously, it was demonstrated that at similar bioleaching conditions over 60% (Zn) and over 40% (Cu) can be released from crystalline and amorphous copper slags [38]. This effect can be assigned to the overall mineralogical characteristic of studied slag. Sulfides in Di-slag are hidden between the crystals of diopside known to dissolve at lower rates than fayalite [39]—the main crystalline phase protecting sulfides in the previous study [38].

A plurality of factors affecting the process proves how important the exploration of each one is, by reflecting the slags phase preference to specific conditions at which metals are efficiently dissolved. The more optimal factors that are introduced into the treatment, the more positive the response of slags in terms of metal release.

4.2. Effect of Pulp Density

Incubating slags with various pulp densities is well known to affect the final chemical and biotic leaching results [40]. An increase of surface area exposed to (bio)leaching solution can be attained by a reduction of the pulp density [41–44] and consequently higher leaching rates can be expected. On the other hand, a reduction of pulp density is not always desired considering the bioleaching system as a whole. Lower pulp density means that higher leaching rates can be expected not only to metal bearing phases but also to silicates. The Si-bearing phases are responsible for the release of Si which may be problematic under acidic conditions due to formation of silica gel [17]. This study revealed that Si release from Di-slag in CA solution increased as PD increased (up to 0.74% for PD 1% and up to 21.8% for PD 10%) as opposed to GI-slag for which Si release increased as PD decreased (up to 74% for PD 1% versus up to 8% for PD 10%). Given the same conditions applied to both

slags, it can be stated that their phase composition likely accounted for these discrepancies. Glass being the only one and volumetrically major Si-bearing phase in Gl-slag revealed unrestricted exposure towards extracting solution, therefore, smaller PD enhanced Si leaching. In contrast, Di-slag is characterized by two Si-bearing phases; the interstitial glass located between the crystals of diopside is less exposed to leaching solution as compared to glass of Gl-slag. Thus, the most plausible explanation of why Di-slag extraction yielded a better result at higher pulp density (PD 10%) is that the higher amount of material contained in the incubation flask accounted for a higher number of surface zones exposing glass as compared to the flask where slag at PD 1% was contained. Therefore, we state that glass was the main phase that accounted for Si release from both slags in citric acid solution. The complexing strength of the reactant is able to increase the rates of silicate dissolution [45–47]. Increased PD was already found to be a beneficial factor to enhance CA-mediated leaching of slags and ores [48–50]. Similarly, Gargul et al. noted a decreasing trend of Pb leaching as PD decreased from 20% to 10%, whereas further decrease of PD to 5% caused an increase of Pb leaching [51]. Even if Si input in major extent comes from glass, diopside dissolution also took place under organic-rich conditions. It has already been shown that organic solutions even at concentration level of 0.01–0.1 M enhance diopside dissolution [52].

Furthermore, the release of Si from Di-slag under abiotic GM-C conditions was much lower (up to 0.5%) as compared to CA conditions. In addition, increased PD caused decreased Si leaching; the Si leaching yield of 0.5% was achieved at PD 1% and <0.1% at PD 10%. This opposite trend to that observed in CA conditions may indicate that under inorganic leaching conditions (GM-S), Si release from Di-slag dominantly originated from diopside. This is in accordance with another study demonstrating higher susceptibility of pyroxene than glass under inorganic acidic conditions [53]. This trend has also been confirmed by the biotic acidic leaching (GM+B), where 6.5% Si was extracted at PD 1% and 1.2% at PD 10%.

Of particular importance to the analysis of slag stability is the extraction of metals that can be targeted in recovery processes. Generally, Cu and Zn leaching was higher at PD 1% as compared to higher PDs. This behavior of metals can be explained by the better exposure of the slag particles at lower PD and subsequent better exposure of metal-bearing phases. An exception was observed in CA for Di-slag as the most efficient element, where leaching was achieved at PD 10% reaching up to 26.8% (Cu) and 97.9% (Zn). This is likely due to the important incorporation of Zn in glass and diopside [26]. As pointed out by Santhiya and Ting [54] pulp density and particle size are the main drivers of the CA leaching, whereas our study highlights that pulp density reveals different influence in CA leaching of crystalline and glassy slags. Thus, phase composition is an important variable determining the efficiency of CA leaching.

The effect of PD on Cu and Zn leaching from Gl-slag incubated with CA followed the opposite trend of promoting leaching at PD 1% reaching 95.5% (Zn) and 55.9 (Cu). In contrast, at GM+B conditions, both slags followed the same trend, in spite of different efficiencies observed. Leaching of Cu varied from 0.70% (PD 10%) to 17.6% (PD 1%) for Di-slag and 2.0% (PD 10%)–4.3% (PD 1%) for Gl-slag. The effect of PD was even more pronounced for Zn leached at 3.0% (PD 10%) and 6.5% (PD 1%) for Di-slag and 5.7% (PD 10%) and 53.0% (PD 1%) for Gl-slag. These results also show that Di-slag appears to be a better candidate for Cu leaching than Gl-slag, whereas both slags appeared to be very good Zn contributors in extractive leaching. Overall leaching efficiency achieved after 14 days long slag incubation is displayed in Figures S1 and S2 included in the Supplementary Materials.

Based on our observations, we state that preliminary tests addressing the effect of pulp density are highly relevant for (bio)leaching systems in order to operate under optimal conditions. On the other hand, an optimal bioleaching system may require a high pulp density, because less (bio)leaching solution may be necessary for the whole process [55].

4.3. Effect of Phase Composition

Silicates are common slag phases occurring as volumetrically major components [7,10,56,57]. Primary silicate present in studied slags is pyroxene surrounded by silicate glass. These volumetrically major phases differ in dissolution susceptibility and dissolution rates [58]. Generally, the simplified model of silicate dissolution can be described as the removal of Si and metal cations from ortho-, pyro- and cyclosilicates. During partial dissolution a silicate's reaction with the acid causes a disturbance of the slags framework which leads to metal removal and a remnant siliceous residue.

Due to the comparison of theoretical slags dissolution with experimental data obtained in the present study (Figures 6 and 7) it was possible to delineate how Di-slag and its amorphous counterpart (Gl-slag) dissolve under the same incubating conditions. First, it was possible to delineate the dissolution sequence of phases present in slags. Second, it was possible to delineate the preferential release of elements (Figures 6 and 7). This study demonstrated that up to 22% and 74% of Si can be released from Di-slag and Gl-slag, respectively. The release of Ca and Mg from Di-slag did not exceed 32%, whereas nearly complete removal of these elements was observed for Gl-slag. Under biotic conditions Si from Gl-slag revealed preferential release in respect to Cu (Figure 7). This preference is slightly less pronounced under abiotic conditions GM-S and CA (with an exception observed for CA PD 5%). In contrast, Cu was found to leach preferentially from Di-slag (with an exception observed for GM+B at PD 10%) and this preference was more pronounced at lower PDs (Figure 6). This indicates that Gl-slag is generally more prone to dissolution than Di-Slag with the latter exhibiting promoted release of Cu rather than Si (Figure 6). The Fe, Al and K were released to a greater extent from Di-Slag as compared to the above-mentioned elements (Ca and Mg). However, where preference to release of these elements is concerned, Gl-slag mostly appeared to preferentially release these elements rather than Cu, likely due to generally lower mobilization of the latter element (Figure 7). Also, the behavior of Di-slag indicated that dissolution of phase other than glass took place and undoubtedly diopside dissolution accounted for Fe and Al input to the leachate (Figure 6).

Furthermore, CA was also found to enhance Zn leaching from Di-Slag incubated at high PD. Since relevant Zn content is incorporated in diopside and glass when taking into account its volumetric relation with sulfides, undoubtedly these phases accounted for Zn release in CA. However, diopside dissolution may vary from one specific diopside to another [59]. Furthermore, the Zn carrier in Di-Slag is also sphalerite, even if this phase occurs at lower volumetric proportion than diopside. The Zn release from slags was better in GM+B than GM-C. The presence of sulfur-oxidizing bacteria is relevant when the metal targeted is hosted in a sulfide and may facilitate leaching. For example, a biologically leached sphalerite dissolved more effectively compared to a chemically mediated dissolution; the improved effectiveness was attributed to the lack of a sulfur surface layer on the biologically leached sphalerite compared to the chemically treated sphalerite [60]. Thus, it was the main reason why bacterially mediated dissolution of slags improved Zn leaching relative to GM-C.

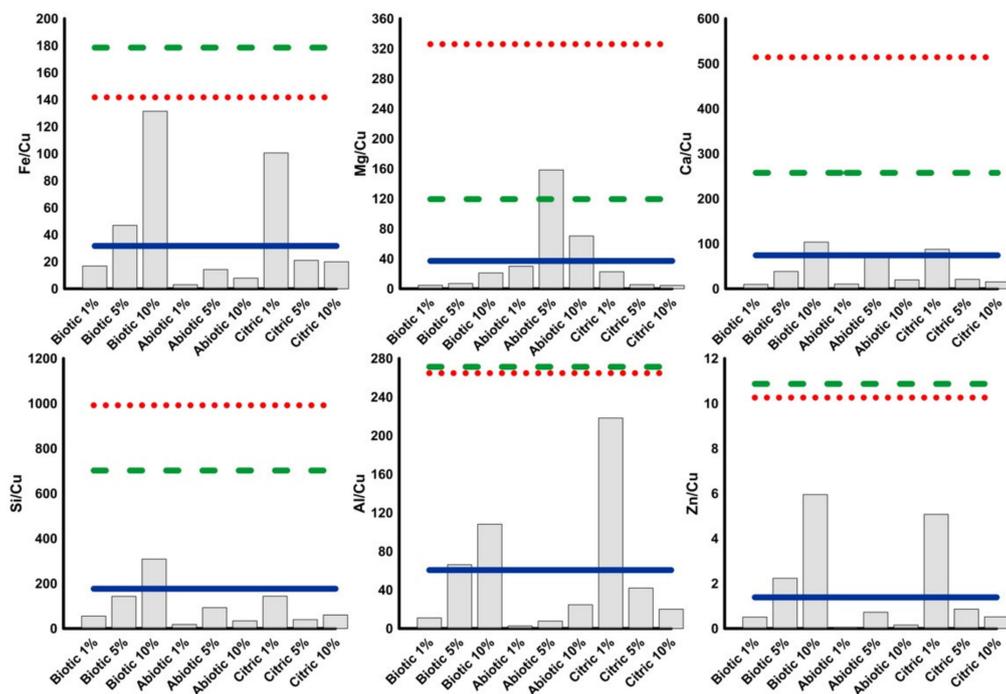


Figure 6. Theoretical and experimentally achieved element ratios with respect to Cu observed for diopside-bearing slag. Solid blue line indicates theoretical molar ratios for bulk slag, dotted red line indicates theoretical molar ratios for glass, dashed green line indicates theoretical molar ratio for diopside, bars show dissolution ratios achieved experimentally.

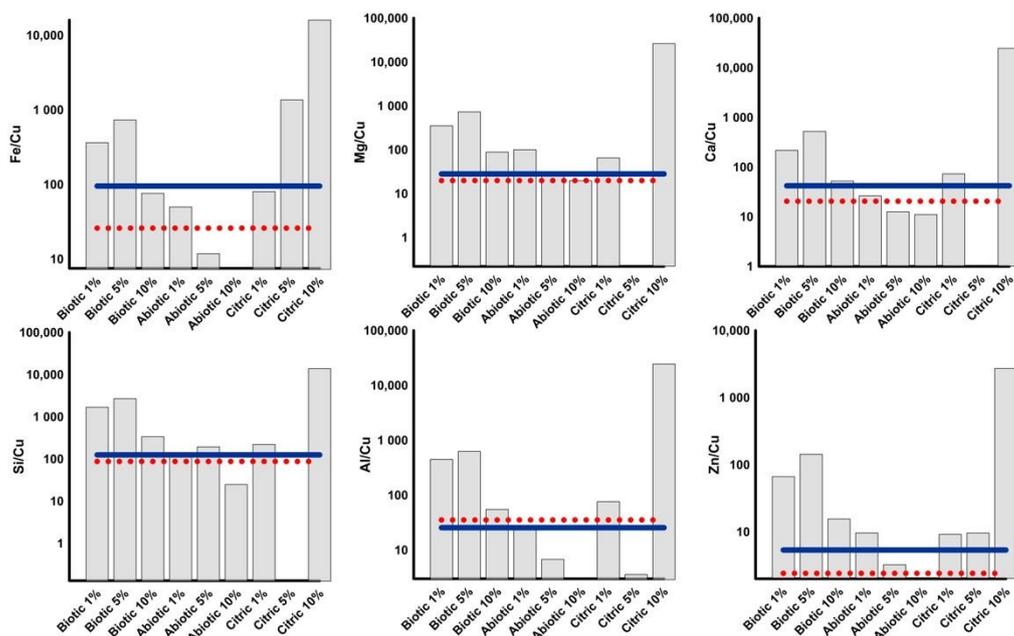


Figure 7. Theoretical and experimentally achieved element ratios with respect to Cu observed for glassy slag. Solid blue line indicates theoretical molar ratios for bulk slag, dotted red line indicates theoretical molar ratios for glass, bars show dissolution ratios achieved experimentally.

Copper is mainly associated with sulfides (chalcocite, chalcopyrite, bornite) and with intermetallic phases. After 14 days, 26.7% Cu was leached from Di-slag, whereas the extraction of Pb was surprisingly low; after 2 weeks, only 2.6% of Pb was leached. In addition, the ratios calculated reveal that Cu is preferably released relative to other elements for all the treatments performed for Di-slag at PD 1%, while this preference

is less pronounced for higher PDs indicating that elements are transferred from solid phase (i.e., slag) to liquid phase at different rates under individual conditions (Figure 6). It is not entirely clear what the reason for such Pb behavior in our leaching system was. Probably the oxides and Pb-containing phases are much more resistant to leaching processes. There were numerous inclusions of metallic Pb and Pb-Cu phases, Pb oxides and Pb-Cu oxides within the Cu-sulfides [26], therefore stronger sulfides dissolution would be required to enhance Pb release. As noted by Gargul et al., Pb mobilization from Cu slag was rapid at the initial stages of the experiment, whereas the trend depleted as the experiment progressed [51]. This trend was not observed in our study as leaching time had a rather positive effect on Pb extraction efficiency. On the other hand, it is important to note that pH-dependent leaching of Di-slag at pH 2–4 demonstrated Pb release at approximately 30% (data not shown in this study). Therefore, it becomes clear that surface glass is the main carrier responsible for Pb release since the pH dependent leaching study contained bulk samples (including crystalline and glassy part), while the sample used in our study contained either crystalline part of slag (devoid of surface glass) or surface glass alone. The Gl-slag released up to 60% of Pb.

A prime issue in the development of hydrometallurgical slag processing is the dissolution sequence of slag components, because these phases being the most important metal carriers are expected to dissolve first. Other components, less important regarding the metal content incorporated within on one hand, but more important volumetrically on the other, also dissolve and affect the extraction process. However, it has to be highlighted that occurrence of these elements in crystalline phases (in this case diopside) and glassy phases causes interpretation of the dissolution sequences for major phases to be counterintuitive and difficult to decipher. Regardless of this, the general phase leachability sequence obtained in our study is arranged as follows: sulfides (sphalerite > chalcopyrite) > intermetallic phases > glass > diopside.

Given observed discrepancies in leaching behavior of individual elements from studied slags, we conclude that complete analysis of element mobilization in the leaching system is required in order to properly design extractive leaching conditions. Even if extraction of recovery targeted elements such as Cu and Zn can be achieved under well-adjusted reactor configuration, it must be kept in mind that other elements, particularly major ones may cause strong interferences during the final recovery stage [61]. The metal recovery from pregnant leachates may be complicated by the dissolution of silicate phases under acidic conditions causing increased solution viscosity [62,63]. In acidic solutions, silicates prevail as monomeric $\text{Si}(\text{OH})_4$ that reaches supersaturation conditions when the monomer concentration increases, leading to high levels of dissolved and colloidal silica in the pregnant leach solutions that may finally impact the metal recovery step [62]. Likewise, other elements present in pregnant leachate may also cause interferences mainly due to much higher concentrations as compared to recovery-targeted metals.

4.4. Future Considerations in Economic and Environmental Context

Bioleaching is a cutting-edge technology with an ecological component. Although its economic advantages are a matter of course, undoubtedly its environmental benefit is of primary importance [64]. For this reason, current trends in waste management are moving towards the advancement of this technique. A review of the studied approaches is given in Table 2.

Table 2. Comparison of treatment efficiencies obtained in this study with examples of efficiencies obtained in other works. Abbreviations: d: duration, T: temperature, LS: liquid to solid ratio.

Slag Treated and Agent/Conditions Tested	Results	Economic Potential Estimated [\$ tonne ⁻¹]	Reference
Shaft furnace slag (Di-Slag) CA, <i>A. thiooxidans</i>	Cu: 27% (719 mg kg ⁻¹) Zn: 98% (3751 mg kg ⁻¹)	Cu: 4.7	This study
Shaft furnace slag (Gl-Slag) CA, <i>A. thiooxidans</i>	Cu: 56% (1561 mg kg ⁻¹) Zn: 96% (14,711 mg kg ⁻¹)	Cu: 10.2	This study
Cu flash smelting slag Citric acid (1 mol dm ⁻³)	LS = 5, T: 70 °C Pb: 85% Cu: 26% (32,360 mg kg ⁻¹)	Cu: 211	[51]
Cu converter slag Citric acid (0.5 mol dm ⁻³)	CA from <i>Aspergillus niger</i> filtrate, d: 4h, LS = 20, T: 30 °C Cu: 23% (9269 mg kg ⁻¹) Ni: 4%, Co: 5.7%, Fe: 1.5%	Cu: 60.3	[35]
Cu converter slag Citric acid (2 mol dm ⁻³)	LS: 6.66 (PD 15%), d: 15 h, T: 35 °C Cu: 99% (14,157 mg kg ⁻¹) Ni: 89.2%, Co: 94%, Fe: 99.2%	Cu: 92.1	[48]
Cu converter slag <i>A. ferrooxidans</i>	LS: 20, d: 80 days, T: 35 °C Cu: 99% (16,830 mg kg ⁻¹) Ni: 22%, Co: 30%	Cu: 110	[65]
Cu slags <i>A. thiooxidans</i>	LS: 100, d: 21 days, T: 30 °C Crystalline fayalite slag (CS) Cu: 79% (4469 mg kg ⁻¹), Zn: 76% (3011 mg kg ⁻¹) Amorphous glassy (AS) Cu: 81% (9254 mg kg ⁻¹) Zn: 79% (6170 mg kg ⁻¹)	CS Cu: 29.1 AS Cu: 60.2	[66]
Cu slags <i>A. thiooxidans</i>	LS: 100, d: 21 days, T: 30 °C Crystalline fayalite slag Cu: 52% (1981 mg kg ⁻¹), Zn: 68% (2482 mg kg ⁻¹) Amorphous glassy Cu: 99% (19,461 mg kg ⁻¹) Zn: 73% (428 mg kg ⁻¹)	CS Cu: 12.9 AS Cu: 126.6	[38]

* Economic potential was calculated by multiplying the amount of individual elements recovered by the price of metal. Metal prices taken from: <https://markets.businessinsider.com/commodities> (2020).

Since the composition of metallurgical slags may be unique between producers, studies carried out thus far have been based on specific materials having specific chemical and phase compositions, perfectly adjusted processes would require conditions defined such that its applicability to all slags would be increasingly possible. Although, laboratory treatment appears to be a cost intensive operation; only 5–127 \$ per ton of slag can potentially be gained (see Table 2). However, taking into account processing expenses, the process is rather uneconomic [67,68]. Thus, its development should be considered in the context of environmental profits instead. The reasons for further evaluation of metallurgical slags as secondary metal resources are the following: (i) a reduction of the space consumed for disposal, (ii) an increase of the availability of secondary metal resources and (iii) technological development in a way that residues are safe for further use or disposal.

Most of the literature data reports acid driven dissolution as the most promising prospect for metal recovery from slags [69–71]. However, given the relatively high suscep-

tibility of silicates under alkaline conditions; this introduces the option of implementing a double step slag treatment. The identification of these dissolution features can only be relevant when two step slag dissolution is intended. One can assume that if sulfides do not dissolve easily under alkaline conditions then two step dissolution should be evaluated. Once at least partial dissolution of silicates under alkaline conditions is completed then the second step of acid dissolution will generate less silica in the system. Such an approach has hardly ever been tested thus far, however according to current dissolution theory it appears to be a promising direction to explore. Thus, the exclusion of at least a partial volume of silicates may increase the efficiency of the second step. Such a hypothesis still requires thorough experimental evaluation, however, and will be the objective of our next study. Furthermore, the bioleaching process represents a lower ecological risk as compared to chemical treatments, and the overall economic cost of such a process would probably be more attractive. Thus, a deeper study comparing chemical and biotic CA leaching would be interesting to pursue, especially given a high citric acid efficiency at high PD 10% in case of Di-slag. Undoubtedly, factors such as medium composition and acid addition should be evaluated in the context of bioleaching with biologically produced citric acid. It also highlights that the interaction among several disciplines, such as environmental/chemical engineering, biotechnology, mineralogy, chemistry and microbial ecology lays the foundation for a new type of approach for solving problems through efficient recovery solutions.

5. Conclusions

This study evaluated the biological and chemical possibilities regarding the extraction of metals from crystalline diopside-bearing slag and its amorphous counterpart. The elements bound in sulfides, intermetallic compounds and glass were extracted much easier than those contained in diopside. The leaching sequence delineated here can be stated as follows: sulfides (sphalerite > chalcopyrite) > intermetallic phases > glass > diopside. Citric acid was found to improve extraction rates as compared to *A. thiooxidans*-mediated leaching. If the use of a bacterially-mediated method is intended, it is evident that either lower pulp density or extension of bioleaching time has to be considered. Slags eventually revealed a potential for Zn recovery, whereas recovery of Cu and Pb from this material is rather unsuitable.

The use of the proposed methods for this material at an industrial scale would be economically unprofitable. The original material after treatment was partially depleted in metals, but it was not possible to remove Pb completely from this waste that disqualifies its potential for use in construction or agriculture sectors. This study provides important insight into the dissolution of diopside bearing and glassy slags and is relevant to development of suitable treatment of slags to mitigate their environmental fingerprint.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2075-163X/11/3/262/s1>, Figure S1: Two weeks long leaching of elements from diopside-bearing slag as a function of pulp density, Figure S2: Two weeks long leaching of elements from glassy slag as a function of pulp density.

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References

1. Radetzki, M. Seven thousand years in the service of humanity—the history of copper, the red metal. *Resour. Policy* **2009**, *34*, 176–184. [[CrossRef](#)]
2. Bellemans, I.; De Wilde, E.; Moelans, N.; Verbeken, K. Metal losses in pyrometallurgical operations—A review. *Adv. Colloid Interface Sci.* **2018**, *255*, 47–63. [[CrossRef](#)] [[PubMed](#)]
3. Ettler, V. Soil contamination near non-ferrous metal smelters: A review. *Appl. Geochem.* **2016**, *64*, 56–74. [[CrossRef](#)]
4. Tyszka, R.; Pietranik, A.; Kierczak, J.; Ettler, V.; Mihaljević, M.; Weber, J. Anthropogenic and lithogenic sources of lead in Lower Silesia (Southwest Poland): An isotope study of soils, basement rocks and anthropogenic materials. *Appl. Geochem.* **2012**, *27*, 1089–1100. [[CrossRef](#)]
5. Tyszka, R.; Pietranik, A.; Kierczak, J.; Zieliński, G.; Darling, J. Cadmium distribution in Pb-Zn slags from Upper Silesia, Poland: Implications for cadmium mobility from slag phases to the environment. *J. Geochem. Explor.* **2018**, *186*, 215–224. [[CrossRef](#)]
6. Piatak, N.M.; Seal, R.R. Mineralogy and environmental geochemistry of historical iron slag, Hopewell Furnace National Historic Site, Pennsylvania, USA. *Appl. Geochem.* **2012**, *27*, 623–643. [[CrossRef](#)]
7. Ettler, V.; Legendre, O.; Bodenan, F.; Touray, J.-C. Primary Phases and Natural Weathering of Old Lead Zinc Pyrometallurgical Slag from Příbram, Czech Republic. *Can. Mineral.* **2001**, *39*, 873–888. [[CrossRef](#)]
8. Parsons, M.B.; Bird, D.K.; Einaudi, M.T.; Alpers, C.N. Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California. *Appl. Geochem.* **2001**, *16*, 1567–1593. [[CrossRef](#)]
9. Piatak, N.M.; Seal, R.R. Mineralogy and the release of trace elements from slag from the Hegeler Zinc smelter, Illinois (USA). *Appl. Geochemistry* **2010**, *25*, 302–320. [[CrossRef](#)]
10. Kierczak, J.; Pietranik, A. Mineralogy and composition of historical Cu slags from the rudawy janowickie mountains, Southwestern Poland. *Can. Mineral.* **2011**, *49*, 1281–1296. [[CrossRef](#)]
11. Tyszka, R.; Kierczak, J.; Pietranik, A.; Ettler, V.; Mihaljević, M. Extensive weathering of zinc smelting slag in a heap in Upper Silesia (Poland): Potential environmental risks posed by mechanical disturbance of slag deposits. *Appl. Geochem.* **2014**, *40*, 70–81. [[CrossRef](#)]
12. Lottermoser, B.G. Mobilization of heavy metals from historical smelting slag dumps, north Queensland, Australia. *Mineral. Mag.* **2002**, *66*, 475–490. [[CrossRef](#)]
13. Ettler, V.; Johan, Z.; Kříbek, B.; Šebek, O.; Mihaljević, M. Mineralogy and environmental stability of slags from the Tsumeb smelter, Namibia. *Appl. Geochem.* **2009**, *24*, 1–15. [[CrossRef](#)]
14. Fomchenko, N.; Uvarova, T.; Muravyov, M. Effect of mineral composition of sulfidic polymetallic concentrates on non-ferrous metals bioleaching. *Miner. Eng.* **2019**, *138*, 1–6. [[CrossRef](#)]
15. Kaksonen, A.H.; Lavonen, L.; Kuusenaho, M.; Kolli, A.; Närhi, H.; Vestola, E.; Puhakka, J.A.; Tuovinen, O.H. Bioleaching and recovery of metals from final slag waste of the copper smelting industry. *Miner. Eng.* **2011**, *24*, 1113–1121. [[CrossRef](#)]
16. Liu, R.; Mao, Z.; Liu, W.; Wang, Y.; Cheng, H.; Zhou, H.; Zhao, K. Selective removal of cobalt and copper from Fe (III)-enriched high-pressure acid leach residue using the hybrid bioleaching technique. *J. Hazard. Mater.* **2020**, 121462. [[CrossRef](#)] [[PubMed](#)]
17. Muravyov, M.I.; Fomchenko, N.V.; Usoltsev, A.V.; Vasilyev, E.A.; Kondrat'eva, T.F. Leaching of copper and zinc from copper converter slag flotation tailings using H₂SO₄ and biologically generated Fe₂(SO₄)₃. *Hydrometallurgy* **2012**, *119*, 40–46. [[CrossRef](#)]
18. Warchulski, R.; Gawęda, A.; Kaździółka-Gawęł, M.; Szopa, K. Composition and element mobilization in pyrometallurgical slags from the Orzeł Biały smelting plant in the Bytom–Piekary Śląskie area, Poland. *Mineral. Mag.* **2015**, *79*, 459–483. [[CrossRef](#)]
19. Kupczak, K.; Warchulski, R.; Dulski, M.; Środek, D. Chemical and phase reactions on the contact between refractory materials and slags, a case from the 19th century zn-pb smelter in ruda Śląska, Poland. *Minerals* **2020**, *10*, 1006. [[CrossRef](#)]
20. Warchulski, R.; Mendecki, M.; Gawęda, A.; Sołtysiak, M.; Gadowski, M. Rainwater-induced migration of potentially toxic elements from a Zn–Pb slag dump in Ruda Śląska in light of mineralogical, geochemical and geophysical investigations. *Appl. Geochem.* **2019**, *109*, 104369. [[CrossRef](#)]
21. Crundwell, F. The mechanism of dissolution of minerals in acidic and alkaline solutions: Part III. Application to oxide, hydroxide and sulfide minerals. *Hydrometallurgy* **2014**, *149*, 71–81. [[CrossRef](#)]
22. Kouassi, S.S.; Andji, J.; Bonnet, J.P.; Rossignol, S. Dissolution of waste glasses in high alkaline solutions. *Ceram. Silikaty* **2010**, *54*, 235–240.
23. Oelkers, E.H.; Declercq, J.; Saldi, G.D.; Gislason, S.R.; Schott, J. Olivine dissolution rates: A critical review. *Chem. Geol.* **2018**, *500*, 1–19. [[CrossRef](#)]
24. Potysz, A.; Kierczak, J.; Fuchs, Y.; Grybos, M.; Guibaud, G.; Lens, P.N.L.; van Hullebusch, E.D. Characterization and pH-dependent leaching behaviour of historical and modern copper slags. *J. Geochem. Explor.* **2016**, *160*, 1–15. [[CrossRef](#)]
25. Mikoda, B.; Kucha, H.; Potysz, A.; Kmiecik, E. Metallurgical slags from Cu production and Pb recovery in Poland—Their environmental stability and resource potential. *Appl. Geochem.* **2019**, *101*, 67–74. [[CrossRef](#)]
26. Napieraj, M. *Recovery of Metals from Metallurgical Slags by Using Chemical and Biological Techniques (Odzysk Metali z Żużli Hutniczych Przy Zastosowaniu Technik Chemicznych Oraz Biologicznych)*; University of Wrocław: Wrocław, Poland, 2018.
27. Seo, S.K.; Kwon, C.M.; Kim, F.S.; Lee, C.J. Experiment and kinetic modeling for leaching of blast furnace slag using ligand. *J. CO₂ Util.* **2018**, *27*, 188–195. [[CrossRef](#)]
28. Jarošíková, A.; Ettler, V.; Mihaljević, M.; Drahotka, P.; Culka, A.; Racek, M. Characterization and pH-dependent environmental stability of arsenic trioxide-containing copper smelter flue dust. *J. Environ. Manag.* **2018**, *209*, 71–80. [[CrossRef](#)] [[PubMed](#)]

29. Jarošíková, A.; Ettler, V.; Mihaljevič, M.; Kříbek, B.; Mapani, B. The pH-dependent leaching behavior of slags from various stages of a copper smelting process: Environmental implications. *J. Environ. Manag.* **2017**, *187*, 178–186. [[CrossRef](#)]
30. Król, A.; Mizerna, K.; Bożym, M. An assessment of pH-dependent release and mobility of heavy metals from metallurgical slag. *J. Hazard. Mater.* **2020**, *384*, 121502. [[CrossRef](#)] [[PubMed](#)]
31. Ettler, V.; Piantone, P.; Touray, J.-C. Mineralogical control on inorganic contaminant mobility in leachate from lead-zinc metallurgical slag: Experimental approach and long-term assessment. *Miner. Mag.* **2003**, *67*, 1269–1283. [[CrossRef](#)]
32. Castro, I.M.; Fietto, J.L.R.; Vieira, R.X.; Trópia, M.J.M.; Campos, L.M.M.; Paniago, E.B.; Brandão, R.L. Bioleaching of zinc and nickel from silicates using *Aspergillus niger* cultures. *Hydrometallurgy* **2000**, *57*, 39–49. [[CrossRef](#)]
33. Strigáč, J.; Številová, N.; Mikušinec, J.; Varečka, L.; Hudcová, D. Antimicrobial efficiency of metallurgical slags for application in building materials and products. *Buildings* **2018**, *8*, 33. [[CrossRef](#)]
34. Mehta, K.D.; Das, C.; Pandey, B.D. Leaching of copper, nickel and cobalt from Indian Ocean manganese nodules by *Aspergillus niger*. *Hydrometallurgy* **2010**, *105*, 89–95. [[CrossRef](#)]
35. Sukla, L.B.; Kar, R.N.; Panchanadikar, V. Leaching of copper converter slag with *Aspergillus niger* culture filtrate. *BioMetals* **1992**, *5*, 169–172. [[CrossRef](#)]
36. Mulligan, C.N.; Kamali, M. Bioleaching of copper and other metals from low-grade oxidized mining ores by *Aspergillus niger*. *J. Chem. Technol. Biotechnol.* **2003**, *78*, 497–503. [[CrossRef](#)]
37. Anjum, F.; Bhatti, H.N.; Asgher, M.; Shahid, M. Leaching of metal ions from black shale by organic acids produced by *Aspergillus niger*. *Appl. Clay Sci.* **2010**, *47*, 356–361. [[CrossRef](#)]
38. Potysz, A.; Kierczak, J. Prospective (Bio)leaching of Historical Copper Slags as an Alternative to Their Disposal. *Minerals* **2019**, *9*, 542. [[CrossRef](#)]
39. Hausrath, E.M.; Navarre-Sitchler, A.K.; Sak, P.B.; Steefel, C.I.; Brantley, S.L. Basalt weathering rates on Earth and the duration of liquid water on the plains of Gusev Crater, Mars. *Geology* **2008**, *36*, 67. [[CrossRef](#)]
40. Sahni, A.; Kumar, A.; Kumar, S. Chemo-biohydrometallurgy—A hybrid technology to recover metals from obsolete mobile SIM cards. *Environ. Nanotechnol. Monit. Manag.* **2016**, *6*, 130–133. [[CrossRef](#)]
41. Carranza, F.; Romero, R.; Mazuelos, A.; Iglesias, N.; Forcat, O. Biorecovery of copper from converter slags: Slags characterization and exploratory ferric leaching tests. *Hydrometallurgy* **2009**, *97*, 39–45. [[CrossRef](#)]
42. Anand, S.; Sarveswara Rao, K.; Jena, P.K. Pressure leaching of copper converter slag using dilute sulphuric acid for the extraction of cobalt, nickel and copper values. *Hydrometallurgy* **1983**, *10*, 305–312. [[CrossRef](#)]
43. Sukla, L.B.; Panda, S.C.; Jena, P.K. Recovery of cobalt, nickel and copper from converter slag through roasting with ammonium sulphate and sulphuric acid. *Hydrometallurgy* **1986**, *16*, 153–165. [[CrossRef](#)]
44. Herreros, O.; Quiroz, R.; Manzano, E.; Bou, C.; Viñals, J. Copper extraction from reverberatory and flash furnace slags by chlorine leaching. *Hydrometallurgy* **1998**, *49*, 87–101. [[CrossRef](#)]
45. Drever, J.I.; Stillings, L.L. The role of organic acids in mineral weathering. *Colloids Surf. Physicochem. Eng. Asp.* **1997**, *120*, 167–181. [[CrossRef](#)]
46. Lazo, D.E.; Dyer, L.G.; Alorro, R.D. Silicate, phosphate and carbonate mineral dissolution behaviour in the presence of organic acids: A review. *Miner. Eng.* **2017**, *100*, 115–123. [[CrossRef](#)]
47. Terry, B. The acid decomposition of silicate minerals part I. Reactivities and modes of dissolution of silicates. *Hydrometallurgy* **1983**, *10*, 135–150. [[CrossRef](#)]
48. Meshram, P.; Prakash, U.; Bhagat, L.; Abhilash, D.; Zhao, H.; van Hullebusch, E.D. Processing of waste copper converter slag using organic acids for extraction of copper, nickel, and cobalt. *Minerals* **2020**, *10*, 290. [[CrossRef](#)]
49. Astuti, W.; Hirajima, T.; Sasaki, K.; Okibe, N. Comparison of atmospheric citric acid leaching kinetics of nickel from different Indonesian saprolitic ores. *Hydrometallurgy* **2016**, *161*, 138–151. [[CrossRef](#)]
50. Tang, J.A.; Valix, M. Leaching of low grade limonite and nontronite ores by fungi metabolic acids. *Miner. Eng.* **2006**, *19*, 1274–1279. [[CrossRef](#)]
51. Gargul, K.; Boryczko, B.; Bukowska, A.; Jarosz, P.; Matecki, S. Leaching of lead and copper from flash smelting slag by citric acid. *Arch. Civ. Mech. Eng.* **2019**, *19*, 648–656. [[CrossRef](#)]
52. Golubev, S.V.; Pokrovsky, O.S. Experimental study of the effect of organic ligands on diopside dissolution kinetics. *Chem. Geol.* **2006**, *235*, 377–389. [[CrossRef](#)]
53. Potysz, A.; Kierczak, J.; Pietranik, A.; Kądziołka, K. Mineralogical, geochemical, and leaching study of historical Cu-slugs issued from processing of the Zechstein formation (Old Copper Basin, southwestern Poland). *Appl. Geochem.* **2018**, *98*, 22–35. [[CrossRef](#)]
54. Santhiya, D.; Ting, Y.P. Bioleaching of spent refinery processing catalyst using *Aspergillus niger* with high-yield oxalic acid. *J. Biotechnol.* **2005**, *116*, 171–184. [[CrossRef](#)]
55. Tipre, D.R.; Dave, S.R. Bioleaching process for Cu-Pb-Zn bulk concentrate at high pulp density. *Hydrometallurgy* **2004**, *75*, 37–43. [[CrossRef](#)]
56. Piatak, N.M.; Parsons, M.B.; Seal, R.R. Characteristics and environmental aspects of slag: A review. *Appl. Geochem.* **2015**, *57*, 236–266. [[CrossRef](#)]
57. Vítková, M.; Ettler, V.; Johan, Z.; Kříbek, B.; Šebek, O.; Mihaljevič, M. Primary and secondary phases in copper-cobalt smelting slags from the Copperbelt Province, Zambia. *Mineral. Mag.* **2010**, *74*, 581–600. [[CrossRef](#)]

58. Ettler, V.; Mihaljevič, M.; Touray, J.-C.; Piantone, P. Leaching of polished sections: An integrated approach for studying the liberation of heavy metals from lead-zinc metallurgical slags. *Bull. Soc. Geol. Fr.* **2002**, *173*, 161–169. [[CrossRef](#)]
59. Schott, J.; Berner, R.A.; Sjöberg, E.L. Mechanism of pyroxene and amphibole weathering-I. Experimental studies of iron-free minerals. *Geochim. Cosmochim. Acta* **1981**, *45*, 2123–2135. [[CrossRef](#)]
60. Fowler, T.A.; Crundwell, F.K. Leaching of zinc sulfide by Thiobacillus ferrooxidans: Bacterial oxidation of the sulfur product layer increases the rate of zinc sulfide dissolution at high concentrations of ferrous ions. *Appl. Environ. Microbiol.* **1999**, *65*, 5285–5292. [[CrossRef](#)]
61. Lewis, A.E. Review of metal sulphide precipitation. *Hydrometallurgy* **2010**, *104*, 222–234. [[CrossRef](#)]
62. Queneau, P.B.; Berthole, C.E. Silica in hydrometallurgy: An overview. *Can. Metall. Q.* **1986**, *25*, 201–209. [[CrossRef](#)]
63. Kaksonen, A.H.; Särkijärvi, S.; Puhakka, J.A.; Peuraniemi, E.; Junnikkala, S.; Tuovinen, O.H. Chemical and bacterial leaching of metals from a smelter slag in acid solutions. *Hydrometallurgy* **2016**, *159*, 46–53. [[CrossRef](#)]
64. Mathieux, F.; Ardente, F.; Bobba, S.; Nuss, P.; Blengini, G.A.; Dias, P.A.; Blagoeva, D.; Torres De Matos, C.; Wittmer, D.; Pavel, C.; et al. *Critical Raw Materials and the Circular Economy. Background Report*; Report EUR 28832 EN; European Union: Brussels, Belgium, 2017.
65. Mehta, K.D.; Pandey, B.D. Premchand Bio-assisted leaching of copper, nickel and cobalt from copper converter slag. *Mater. Trans. JIM* **1999**, *40*, 214–221. [[CrossRef](#)]
66. Potysz, A.; Lens, P.N.L.; van de Vossenberg, J.; Rene, E.R.; Grybos, M.; Guibaud, G.; Kierczak, J.; van Hullebusch, E.D. Comparison of Cu, Zn and Fe bioleaching from Cu-metallurgical slags in the presence of *Pseudomonas fluorescens* and *Acidithiobacillus thiooxidans*. *Appl. Geochem.* **2016**, *68*, 39–52. [[CrossRef](#)]
67. Ettler, V.; Jarošíková, A.; Mihaljevič, M.; Křibek, B.; Nyambe, I.; Kamona, F.; Mapani, B. Vanadium in slags from smelting of African Pb-Zn vanadate ores: Mineralogy, extractability and potential recovery. *J. Geochem. Explor.* **2020**, *218*, 106631. [[CrossRef](#)]
68. Mikoda, B.; Potysz, A.; Kmiecik, E. Bacterial leaching of critical metal values from Polish copper metallurgical slags using *Acidithiobacillus thiooxidans*. *J. Environ. Manag.* **2019**, *236*, 436–445. [[CrossRef](#)]
69. Abdel Basir, S.M.; Rabah, M.A. Hydrometallurgical recovery of metal values from brass melting slag. *Hydrometallurgy* **1999**, *53*, 31–44. [[CrossRef](#)]
70. Banza, A.N.; Gock, E.; Kongolo, K. Base metals recovery from copper smelter slag by oxidising leaching and solvent extraction. *Hydrometallurgy* **2002**, *67*, 63–69. [[CrossRef](#)]
71. Tong, D.; Yunhan, L. Processing of copper converter slag for metal reclamation. Part I: Extraction and recovery of copper and cobalt. *Waste Manag. Res.* **2007**, *25*, 440–448. [[CrossRef](#)]