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Bioleaching and Selective Precipitation for Metal Recovery from Basic Oxygen Furnace Slag

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Abstract: Decreasing ore grades and an increasing consumption of metals has led to a shortage of important primary raw materials. Therefore, the urban mining of different deposits and anthropogenic stocks is of increasing interest. Basic oxygen furnace (BOF) slag is produced in huge quantities with the so-called Linz-Donawitz process and contains up to 5.2, 0.9, 0.1, and 0.07% of Mn, Al, Cr, and V, respectively. In the present study, sulfur-oxidizing *Acidithiobacillus thiooxidans* and iron- and sulfur-oxidizing *Acidithiobacillus ferridurans* were applied in batch and stirred tank experiments to investigate the biological extraction of metals from BOF slag. In the batch experiments, up to 96.6, 52.8, 41.6, and 29.3% of Cr, Al, Mn, and V, respectively, were recovered. The stirred tank experiments, with increasing slag concentrations from 10 to 75 g/L, resulted in higher extraction efficiencies for *A. ferridurans* and lower acid consumption. Selective metal precipitation was performed at pH values ranging between 2.5 and 5.0 to study the recovery of Mn, Al, Cr, and V from the biolixiviant. Selective precipitation of V and Cr was achieved at pH 4.0 from *A. thiooxidans* biolixiviant, while Fe and V could be selectively recovered from *A. ferridurans* biolixiviant at pH 3.0. This work revealed the potential of BOF slag as an artificial ore for urban mining and demonstrated that combining bioleaching and selective precipitation is an effective method for sustainable metal recovery.

Keywords: bioleaching; metal recovery; selective precipitation; semi-continuous setup; metallurgical slags

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1. Introduction

The use of non-renewable mineral resources is growing annually, reflecting the increase in gross domestic production (GDP) and population growth [1]. This increase leads to an estimated consumption of around 70 Gt of mineral resources per year [2]. As natural ore grades are declining and the production capacity of certain metals will consequently decrease [3–5], new alternatives for sustainable metal mining and recycling need to be developed.

Landfill mining and urban mining involve the recovery of valuable resources from all kinds of deposits and anthropogenic stocks [6]. The concept of using biological, chemical, or mechanical techniques to recover valuable metals from waste electrical and electronic equipment has already proven to be more cost-effective than original mining [7]. Furthermore, an evaluation of the economic potential of landfill mining in Europe has shown that resource recovery can become net profitable [8]. In recent years, various waste materials, such as fly ash and slag from waste incineration plants [9–11], sewage sludge [12–14], and metallurgical residues [15,16], have been investigated and revealed their potential in microbial metal recovery (bioleaching) for urban mining purposes [11,17,18]. Extremely acidophilic and chemolithotrophic bacteria, such as *Acidithiobacillus ferridurans* and *Acidithiobacillus thiooxidans*, are well known for their ability to dissolve metals directly via redoxolysis or indirectly via acidolysis and complexolysis [19,20]. The bacterial oxidation of ferrous iron and elemental sulfur generates ferric iron and sulfuric acid, facilitating the dissolution of oxide or sulfide minerals and releasing the incorporated metals.

The steelmaking process generates various by-products such as dusts, sludge, and slag. One type of steelmaking slag is the so-called Linz–Donawitz (LD) slag or, more generally, basic oxygen furnace (BOF) slag. BOF slag is produced during the downstream processing of pig iron with scrap into crude steel by injecting pure oxygen into the basic oxygen converter [21]. The main components of this slag are iron oxide, calcium oxide, and silicon dioxide, thereby making it an alkaline material. This type of slag also contains traces of potentially toxic elements, such as chromium (Cr) and vanadium (V) [22]. About 650,000 t of BOF slag is produced annually in Austria [21]. According to EUROSLAG, 18.4 Mt of steelmaking slag was produced in Europe in 2016, with a BOF slag share of 56.6% [23]. Part of the BOF slag can be recycled in the steelmaking process, but the main part is used for road construction and as an additive in the cement industry. There is no standardized regulation for the permitted application areas in Europe. BOF slag has been used as a road-building material in Austria since 1970. Based on the new legislation adopted in 2015, the conditions of its application as a road construction material have been tightened due to its V and Cr content [21,24]. The stricter regulation has led to more slag being landfilled. However, bioleaching allows for removing undesired metals from the slag and reusing it in different applications.

Many studies have mainly focused on the solubilization of valuable metals from various waste substrates using bioleaching [15,25,26], but only a few studies have addressed metal recovery from the biolixiviant [27]. Different metal recovery methods are available, such as chemical precipitation [17], biosorption [28], electrowinning [29], or bioelectrochemical systems [30]. In particular, chemical precipitation is a widely used treatment method for recovering dissolved metals [31]. Metals are removed from solutions by adjusting the pH to a value at which the solubility of the metal is minimal by adding sodium hydroxide, lime, or sodium carbonate [31]. Chemical precipitation with NaOH results in the formation of different metal hydroxides depending on the pH setting and has the advantages of cost-effectiveness and simple operation [32], which is suitable for automation, and thus, was chosen as the metal recovery method in this study.

This study aimed to evaluate the benefits of bioleaching of BOF slag from the steelmaking industry and recovery of dissolved metals by selective precipitation. Therefore, batch experiments were tested with either sulfur-oxidizing *A. thiooxidans* or iron- and sulfur-oxidizing *A. ferridurans*. Consequently, scale-up was performed in a continuously stirred tank reactor with increasing slag concentrations up to 75 g/L. A synthetic lixiviant was prepared and used for precipitation experiments to test the selective chemical precipitation of Fe, Al, Mn, V, and Cr. Combining both the processes of bioleaching and the selective precipitation of dissolved metals represents a novel biotechnological approach for urban mining of anthropogenic stocks, which was successfully demonstrated in this work.

2. Materials and Methods

2.1. Materials and Chemicals

BOF slag was obtained from an Austrian steelmaking company. The samples were dried at room temperature (22 °C), crushed in a jaw crusher (Model BB51, Retsch, Germany), and sieved through a sieve tower (Type 3D, Retsch, Germany). The fractions with particle sizes between 0.25 and 0.5 mm were used for bioleaching and control experiments. If not otherwise specified, all chemicals were of analytical grade, purchased from Sigma-Aldrich, and all solutions were prepared using deionized water.

2.2. Bacterial Strains and Growth Conditions

For bioleaching experiments, the sulfur-oxidizing bacterium *Acidithiobacillus thiooxidans* (DSM 504) and the iron- and sulfur-oxidizing *Acidithiobacillus ferridurans* (DSM 583) [33] were purchased from the German Collection of Microorganisms and Cell Culture (DSMZ, Braunschweig, Germany). *A. thiooxidans* was pre-cultivated at 30 °C and 150 rpm in a basal salt medium consisting of 3 g/L KH_2PO_4, 0.14 g/L $CaCl_2 \cdot 2H_2O$, 0.1 g/L NH_4Cl, and 0.1 g/L $MgCl_2 \cdot 6H_2O$, supplemented with 10 g/L elemental sulfur (S^0) (termed BSM-AT). The initial pH was 4.2. *A. ferridurans* was pre-cultivated at the same temperature and shaking rate in a basal salt medium containing 0.4 g/L $(NH_4)_2SO_4$, 0.4 g/L $MgSO_4 \cdot 7\,H_2O$, and 0.4 g/L KH_2PO_4, supplemented with 33.3 g/L $FeSO_4 \cdot 7\,H_2O$ (termed BSM-AF). The initial pH was adjusted to pH 1.4 with sulfuric acid.

2.3. Batch Mode Bioleaching

Bioleaching batch experiments were conducted in 250 mL Erlenmeyer flasks at 30 °C and 150 rpm for two weeks. To start the experiment, 10 mL (10% v/v) of the pre-cultivated bacterial cultures were added to 90 mL of the respective medium (BSM-AT or BSM-AF) in biological duplicates. Additionally, 1 g (10 g/L) of BOF slag (and 1 g of S^0 to the BSM-AF) were added to all the flasks. The abiotic control experiments were run with BSM-AT or BSM-AF (with 1 g of S^0). At the end of the experiments, 10 mL liquid samples were collected to determine the pH and metal concentration. The extraction efficiency was calculated as reported previously [11].

To minimize the effect of trace amounts of dissolved metals included in the culture media and inoculum, the leaching efficiency calculation was modified as follows:

$$L_{eff}[\%] = \frac{((c_L - c_M) * V_B) - (c_C * V_C)}{c_F * M_F} * 100$$

where c_L is the metal concentration in the leachate, c_M is the metal concentration in the culture media, V_B is total batch volume, c_C is the metal concentration in the inoculum, V_C is the inoculum volume, c_F metal concentration in the untreated BOF-slag, and M_F is the total mass used for the leaching experiments.

2.4. Semi-Continuous Mode Bioleaching

For scaling up, further bioleaching experiments were performed in a semi-continuous mode using a continuous stirred tank reactor (CSTR) with a working volume of 1.5 L. The CSTR consisted of 2 L glass vessels connected to an automatic pH control unit via a connected pH sensor and process control transmitter (Mettler Toledo, Vienna, Austria). Sulfuric acid (2 M) was used to control pH ($\leq$2.4) by two connected membrane pumps (ProMinent, Heidelberg, Germany). The temperature control (30 °C) and stirring (250 rpm) were provided by two hot plate stirrers (IKA, Staufen, Germany). Compressed air ($\approx$30 L/h) was used to sufficiently aerate the CSTR system (Figure 1).

Semi-continuous mode bioleaching was performed in two independent reactors containing *A. ferridurans* or *A. thiooxidans*. Prior to the bioleaching experiments, both reactors containing the respective medium (BSM-AF or BSM-AT) were inoculated with 150 mL (10% v/v) of pre-cultivated bacterial culture, achieving a sufficient cell density ($\approx 10^8$ cells/mL). First, 10 g/L of BOF slag was added to both of the bioleaching reactors, and bioleaching was performed for two weeks. After the first cycle, 1 L (2/3) of the spent medium with treated slag was removed from the reactors and replaced with respective fresh medium, 10 g/L of S^0 and 25 g/L of BOF slag. This was repeated for 50 and 75 g/L of BOF slag, resulting in a gradual increase in the converter slag and adaptation of the bacterial cultures over a total period of 8 weeks. The abiotic control experiment was performed under the same conditions using double distilled water and the same pH setpoint of 2.4.

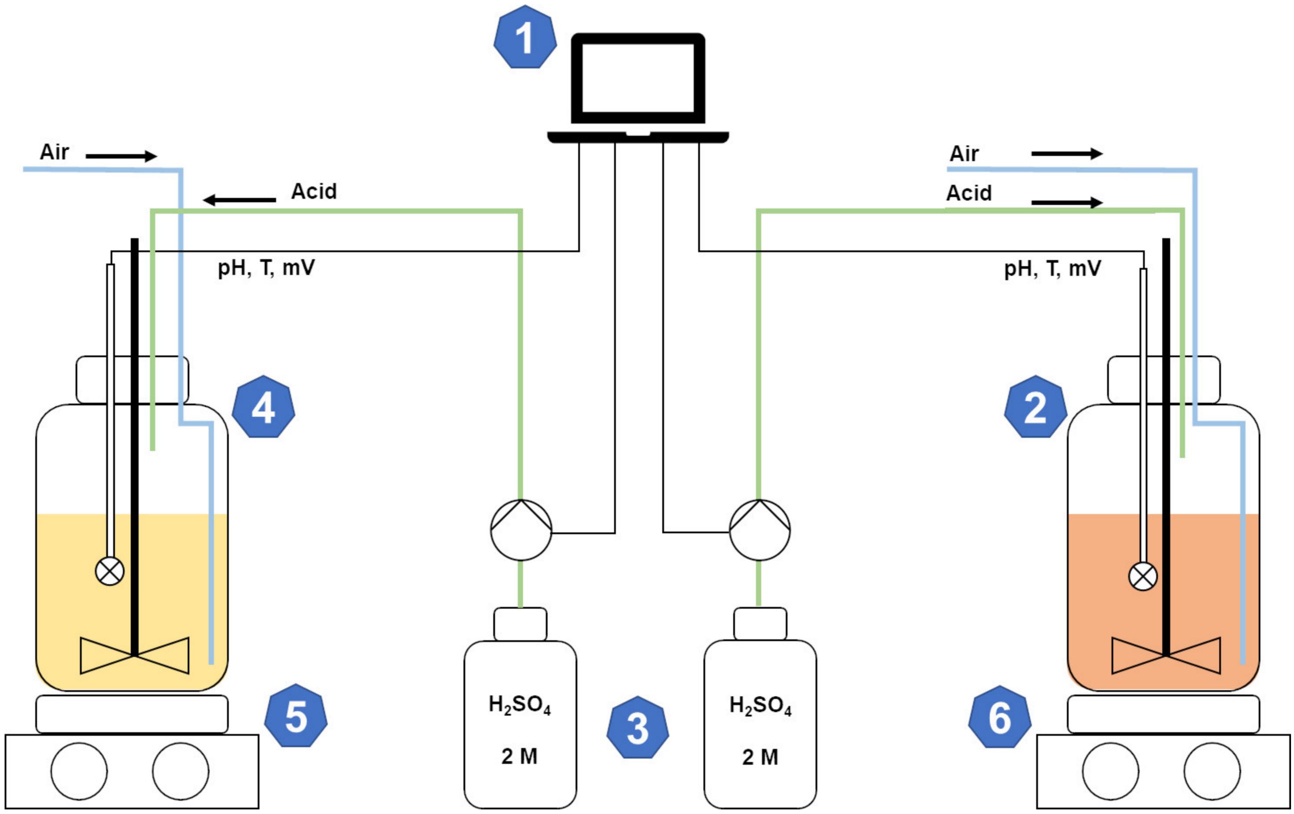

Figure 1. Continuous stirred tank reactor (CSTR) configuration. The CSTR consisted of a process control transmitter (1) controlling the pH value of two independent bioleaching cultures of *A. ferridurans* (2) and *A. thiooxidans* (4) using connected pH sensors and acid pumps (3). Temperature control and reactor stirring were done by two hot plate stirrers (5 and 6).

In all experiments, 5 mL samples were collected at the beginning (zero), middle (1 week), and end (2 weeks) of each cycle and used to measure the metal concentrations.

2.5. Chemical Analysis

The metal concentrations in the BOF slags, biolixiviants, and synthetic metal solutions were measured using inductively coupled plasma mass spectrometry (ICP-MS) as previously described [11]. Briefly, 1 g of BOF-slag was decomposed in a mixture of nitric acid and hydrogen peroxide and evaporated to dryness. Afterwards, the samples were decomposed in hydrofluoric acid, followed by leaching in perchloric acid, and evaporated to dryness. Finally, the samples were treated with hydrogen chloride and evaporated to dryness. ICP-MS was used to analyze the decomposed samples. To minimize the matrix effect and to get the best LOD, all samples were diluted with Milli Q water by a factor of 100, and a solution of Sc (400 $\mu g\ L^{-1}$) was used as an internal standard before analysis. Equally, microbial leachates were diluted with Milli Q water by a factor of 100 before ICP-MS analysis. Sc, as the internal standard (400 $\mu g\ L^{-1}$), was used to suppress the possible matrix effect. For quantification, a set of calibration solutions was prepared.

Mineral phase analysis was performed using X-ray diffraction (XRD) as previously described [11]. The samples were pulverized in a Retsch PM 100 planetary ball mill with an agate grinding jar and balls and homogenized with 10 wt.% of zincite (ZnO). Zincite was used as an internal standard for the quantification of the amorphous phase. Powder X-ray diffraction (XRD) analysis was conducted using a Panalytical X'Pert PRO MPD diffractometer with reflection geometry equipped with a cobalt tube ($\lambda K\alpha$ = 0.17903 nm), Fe filter, and 1-D RMTS (X'Celerator) detector. The step size was 0.017° 2Θ, the time per step was 320 s, the angular range was 4–100° 2Θ, and the total scan duration was 247 min. The acquired data were processed using Panalytical HighScore 4 plus and Bruker AXS

Topas 4 software. For the Rietveld refinement, crystal structure models from the ICSD database were used.

2.6. Kinetic Analysis

The cell numbers were determined by counting the bacteria cells in a Neubauer improved haemocytometer with a 0.01 mm depth (BRAND GmbH, Wertheim, Germany). The pH values were measured using a Mettler Toledo S220 pH meter with a combined glass electrode.

2.7. Preparation of the Synthetic Metal Solutions

For the selective chemical precipitation of metals from the biolixiviant produced by extreme acidophiles, two simplified synthetic metal solutions were prepared according to the ICP-MS results at the end of the semi-continuous modes in the CSTR with 75 g/L of BOF slag. Therefore, the corresponding chemicals were selected and dissolved in 1 L of ultrapure water to reach the desired concentrations of metals. To distinguish between the two bioleaching mechanisms, a synthetic metal solution similar to the biolixiviant produced by *A. ferridurans* (termed SMS-AF) was prepared with ferric chloride (Fe^{3+}), and a synthetic metal solution similar to the biolixiviant produced by *A. thiooxidans* (termed SMS-AT) was prepared with ferrous sulfate (Fe^{2+}). The SMS-AF consisted of 6.72 g/L $Al_2(SO_4)_3 \cdot H_2O$, 2.4 g/L $Fe(III)Cl_3$, 0.29 g/L $CrK(SO_4)_2 \cdot 12H_2O$, 0.04 g/L V_2O_5, and 6 g/L $MnSO_4 \cdot H_2O$. The SMS-AT was composed of 3.17 g/L $Al_2(SO_4)_3 \cdot H_2O$, 17.5 g/L $FeSO_4 \cdot 7H_2O$, 0.384 g/L $CrK(SO_4)_2 \cdot 12H_2O$, 0.093 g/L V_2O_5, and 2.74 g/L $MnSO_4 \cdot H_2O$. The pH values of both the synthetic metal solutions were adjusted to pH 2.2 and 2.3 with 1 M H_2SO_4, which corresponded to the pH values at the end of both bioleaching experiments.

2.8. Selective Chemical Precipitation

Selective metal precipitation was performed in duplicate by adjusting the pH levels to 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 under a 765 Laboratory pH Meter control (Knick Elektronische Messgeräte GmbH & Co. KG, Berlin, Germany). During the experiment, 25 mL of the synthetic metal solution was stirred continuously using an IKA® C-MAG HS7 plate stirrer (IKA, Staufen, Germany) at 500 rpm, while 1 M NaOH was added until the desired pH was reached. After 45 h, the supernatant was filtered (0.2 µm), and ICP-MS analyzed the metal concentrations in the filtrate.

3. Results and Discussion

3.1. Characterization of BOF Slag

The BOF slag samples were characterized based on the metal concentrations, mineral compositions, and pH values determined according to DIN EN 15933:2012-11. The BOF slag was mainly composed of metals such as Fe, Mn, Al, Cr, and V (Table 1). Compared to other metallurgical slags [15,34,35], V, Cr, and Mn were present in much higher concentrations in the investigated BOF slag, indicating its potential to be considered a valuable secondary resource.

Table 1. The metal concentration in BOF slag determined by ICP-MS analysis.

Elements (mg/g)	The Average Values and Standard Deviations (n = 3)
Fe	225.70 ± 4.97
Mn	51.46 ± 0.95
Al	9.21 ± 0.62
Cr	1.30 ± 0.00
V	0.67 ± 0.03

The results of XRD analysis (Figure 2) show that the main phases in the BOF slag were wüstite (FeO), larnite ($Ca_2[SiO_4]$), and srebrodolskite ($Ca_2Fe_2O_5$), which constituted >75 wt.%, in agreement with earlier findings [35]. In addition to the main phases, lime (CaO), portlandite (Ca[OH]$_2$), and merwinite (Ca$_3$Mg[SiO$_4$]$_3$) were present in small amounts. The high concentration of wüstite can be explained by the fact that it is an important intermediate product formed during the blowing of the molten blast furnace iron scrap with pure oxygen. However, oxide minerals, often present in other industrial ashes and slags, have a much poorer leachability of the incorporated metals compared to sulfide minerals [11]. Most of the metals investigated are in BOF slag in oxide mineral forms, making them more accessible for reductive rather than oxidative bioleaching [36]. Nevertheless, even operationally less demanding oxidative bioleaching can extract metals significantly using ferric iron in addition to biogenic sulfuric acid.

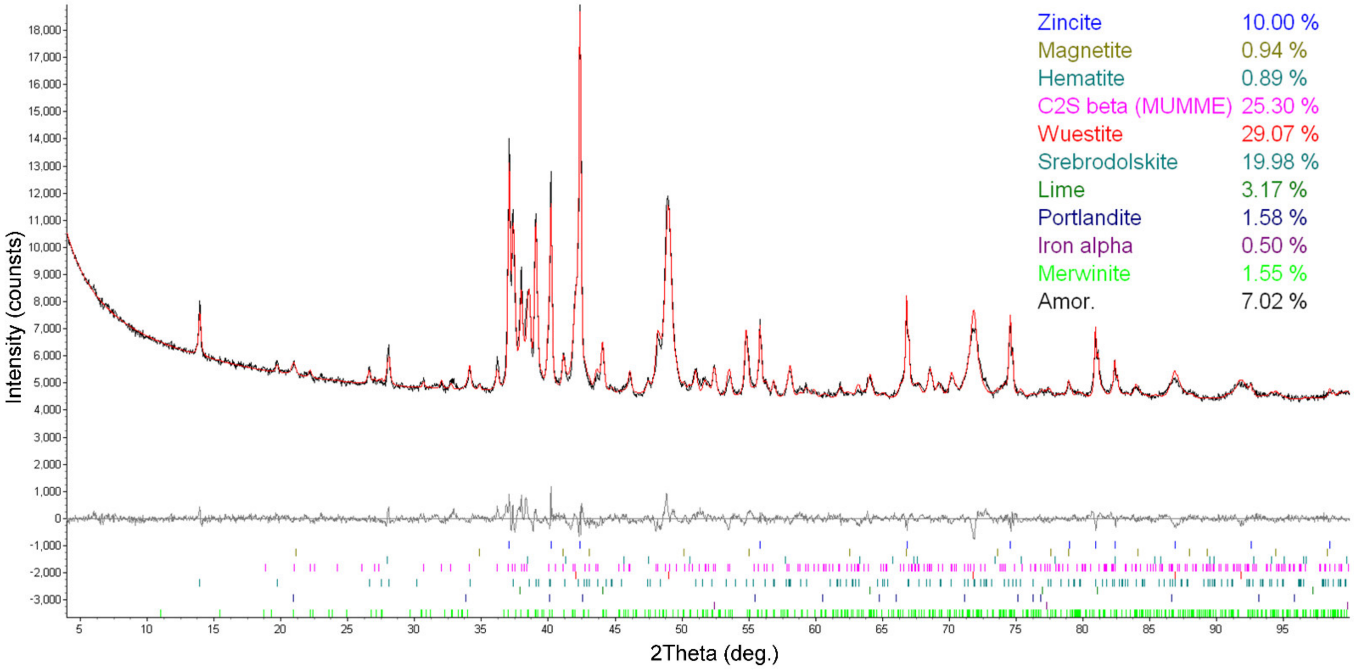

Figure 2. Results of XRD analysis of BOF slag. The main minerals are listed according to their concentration (wt.%). Zincite was used as an internal standard.

The particle size of the BOF slag ranged between 0.25 and 0.5 mm, and the determined pH value showed high alkalinity at around 12. The highly alkaline nature of these materials represents a challenging parameter for efficient bioleaching, as factors such as pulp density and high pH values have a severe impact on the extreme acidophiles employed in these processes [12,37]. On the other hand, a smaller particle size (<0.5 mm) promotes more efficient bioextraction, as more extractable metals have been reported in the fractions smaller than 4 mm in various waste ashes and slags, increasing the effective surface area for biooxidation [11,19,38].

3.2. Batch Mode Bioleaching of BOF Slag

The BOF slag was leached using two extremely acidophilic bacteria capable of oxidizing only S^0 to H_2SO_4 (*A. thiooxidans*) or oxidizing Fe^{2+} to Fe^{3+} and S^0 to H_2SO_4 (*A. ferridurans*). Both bacteria were able to extract metals more efficiently compared to the abiotic control experiments.

Sulfur-oxidizing *A. thiooxidans* leached V, Cr, Mn, and Al with efficiencies of approximately 30, 10, 37, and <1%, whereas iron- and sulfur-oxidizing *A. ferridurans* reached bioleaching efficiencies of approximately 2, 96, 42, and 53%, respectively (Figure 3). Significant differences in metal extraction were observed between the bioleaching mechanisms represented by two different *Acidithiobacillus* spp. By oxidizing Fe^{2+} to Fe^{3+}, *A. ferridurans* promoted a highly efficient Cr bioextraction of up to 100%, which may be related to its more effortless mobility and extractability under oxidative conditions compared to acid leaching [38]. Compared to other reports demonstrating the bioleaching of these waste types, this reflects one of the highest Cr recovery rates [9,36,39]. On the other hand, a negligible amount of V was recovered by bioleaching with *A. ferridurans*, contrary to previous studies [26,40]. One possible reason for this might be the higher pH value during the bioleaching experiments under Fe^{2+} oxidation compared to S^0 oxidation.

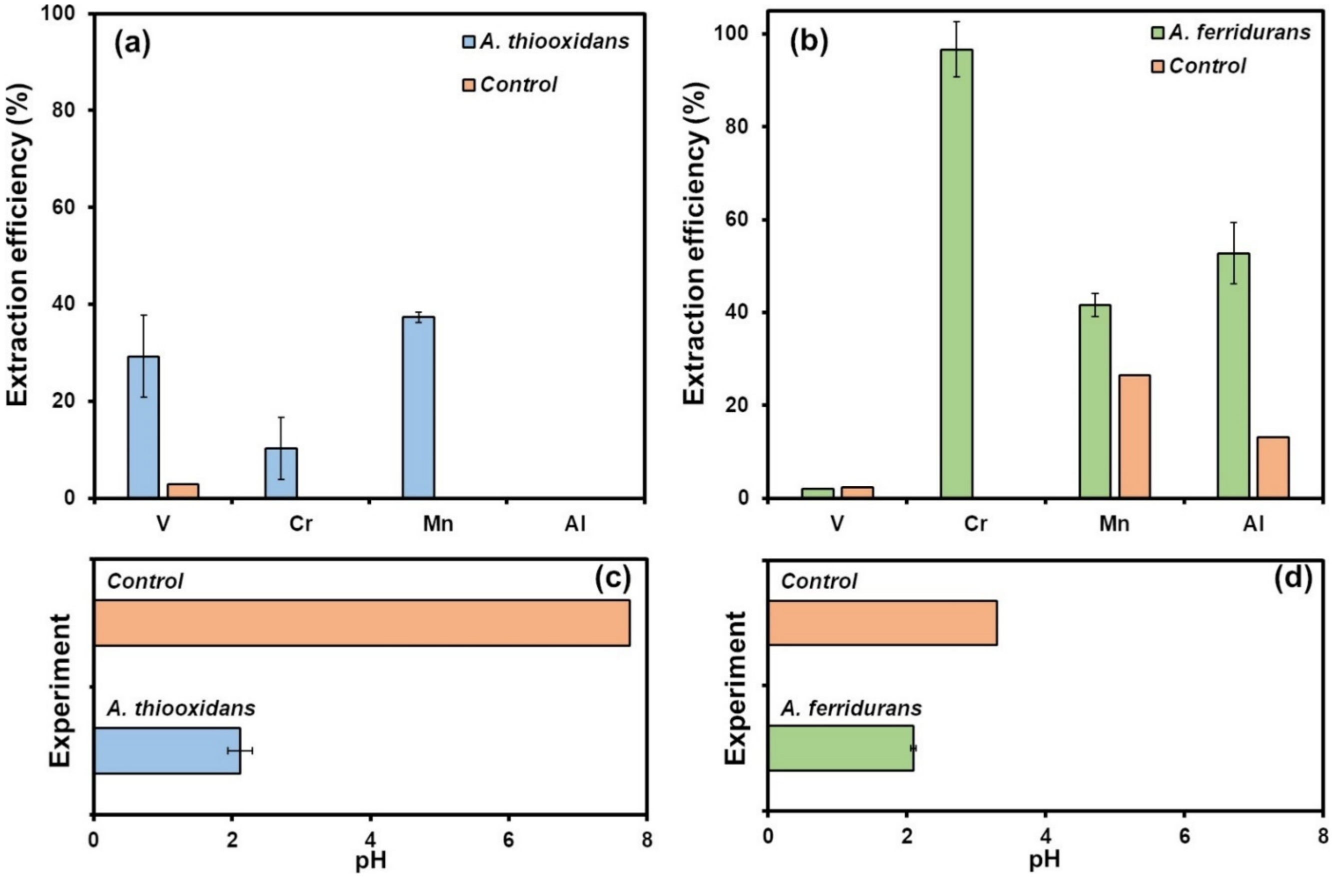

Figure 3. Bioleaching efficiency and pH values in batch modes. The metal extraction efficiency and pH values of *A. thiooxidans* (**a**,**c**) and *A. ferridurans* (**b**,**d**) and abiotic controls after two weeks. Error bars indicate the standard deviation ($n = 2$).

On the other hand, sulfur-oxidizing *A. thiooxidans* showed only low bioleaching efficiencies for Cr due to the absence of an oxidative environment, as this bacterial species cannot oxidize Fe^{2+} to Fe^{3+}. However, the high S^0 oxidation rate of *A. thiooxidans* corresponding to a distinct decrease in pH compared to the abiotic control (Figure 3c) led to strong acidification during bioleaching experiments, resulting in an enhanced extraction efficiency of V. The bioleaching efficiency of V tended to be within the percentages reported in previous studies [35,40]. In the case of Mn, bioleaching resulted in an extraction efficiency of approximately 40%, whereas in the control abiotic experiments, less than 1% was extracted using basal salt medium supplemented with S^0 and approximately 25% using basal salt medium supplemented with S^0 and Fe^{2+}. In investigating two different bioleaching mechanisms in batch mode, it seems that a combination of both might be suitable to dissolve various metals from BOF slag selectively. Cr and Al were more effectively removed by *A. ferridurans*, whereas the bioleaching of V occurred exclusively with *A. thiooxidans*.

3.3. Semi-Continuous Mode Bioleaching of BOF Slag

To increase the extraction efficiency and to gradually increase the slag concentration from 10 to 75 g/L, a semi-continuous mode in CSTR was operated. The bacteria were thus able to adapt to the increasing concentrations of heavy metals and the alkaline nature of the BOF slag.

At the lowest slag concentration of 10 g/L, both bacteria extracted Cr and Al with an efficiency of up to 100%, more than twice that of the abiotic controls (Figure 4). In addition, Mn and V were extracted more efficiently in both bioleaching experiments at a concentration of 10 g/L compared to the abiotic control. No further externally added acid was needed in the bioleaching processes, whereas the abiotic control required approximately 0.45 mL of 18 M sulfuric acid per gram of slag.

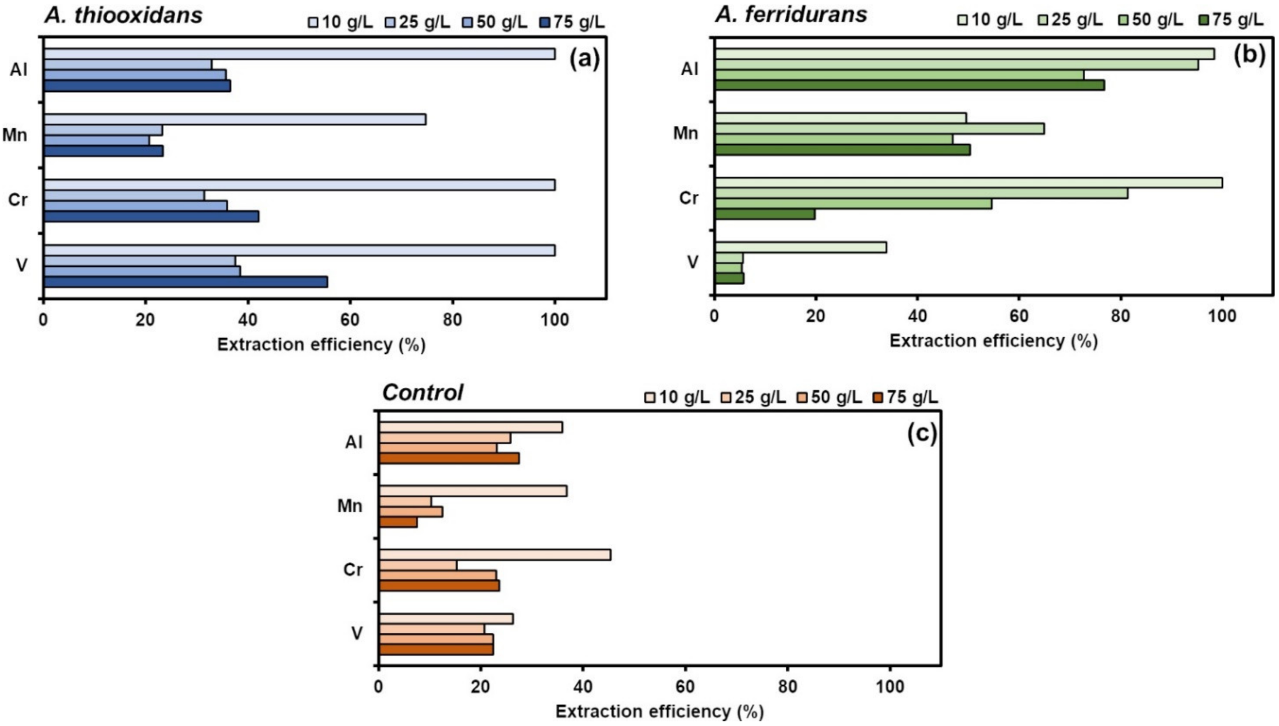

Figure 4. Bioleaching of BOF slag in a semi-continuous mode in CSTR. The metal extraction efficiency of *A. thiooxidans* (blue, **a**), *A. ferridurans* (green, **b**), abiotic control (orange, **c**) at increasing slag concentrations of 10–75 g/L.

With increasing slag concentrations, the metal extraction efficiency decreased, and the acid consumption increased for both bacteria, which is in agreement with previous studies [13,18,25]. Nevertheless, the Al and Mn bioleaching efficiencies remained consistently above 80 and 50% with *A. ferridurans*, decreasing to <40% with *A. thiooxidans* and <20% in the abiotic control. At the highest slag concentration tested (75 g/L), bioleaching with *A. thiooxidans* was more effective in extracting metals such as Cr and V, whereas bioleaching with *A. ferridurans* resulted in higher efficiency for Al and Mn, comparable to previous studies [40,41].

The acid consumption increased sharply during the bioleaching with *A. thiooxidans* at BOF slag concentrations of 50 and 75 g/L and attained higher values than *A. ferridurans* and the abiotic control experiments (Table 2). Therefore, the increased metal extractions at these slag concentrations were likely related to the external addition of sulfuric acid during the bioleaching with *A. thiooxidans*. In contrast, *A. ferridurans* required less externally added acid to maintain a low pH, probably due to the oxidation of Fe^{2+} to Fe^{3+}, which was further hydrolyzed, generating additional acidity, in addition to its higher metal tolerance [42,43]. At BOF slag concentrations between 10 and 50 g/L, *A. ferridurans* demonstrated the most promising results with (i) a bioleaching efficiency of >50% for Al, Mn, and Cr, and (ii) a lower acid consumption compared to *A. thiooxidans* and the abiotic control. Furthermore, similar results were observed regarding the selective dissolution of Mn, Cr, Al, and V at concentrations of 25–50 g/L compared to batch mode bioleaching. At 25 g/L, bioleaching with *A. ferridurans* could selectively dissolve Al and Cr, whereas the bioleaching efficiency with *A. thiooxidans* remained below 40%. The results indicate that the combined action of Fe^{3+} and biogenic H_2SO_4 led to higher acidity and even higher leaching efficiencies at elevated slag concentrations.

Table 2. Acid consumption during the CSTR bioleaching experiments compared to the chemical control for loading rates from 10 to 75 g/L.

Slag Concentration (g/L)	**Acid Consumption**		
	Acidithiobacillus thiooxidans	***Acidithiobacillus ferridurans***	**Control**
	(mL 18 M H_2SO_4/g Slag)		
10	-	-	0.44
25	0.05	-	0.27
50	0.31	0.07	0.25
75	0.49	0.19	0.23

3.4. Selective Chemical Precipitation for Metal Recovery

The selective chemical precipitation of Al, V, Cr, Mn, and Fe from the synthetic metal solutions (SMS-AT and SMS-AF) was tested by adjusting the pH from 2.5 to 5. Figure 5a shows the metals precipitation and the base consumption at each pH value of the SMS-AT. At pH 2.5, Al (4%) and Cr (2%) started to precipitate, and at pH 3, so did V (19%). At pH 4, 92% V and 75% Cr were precipitated from the solution, with 16% Al and 8% Fe. Thus, 24 mL/L 1 M NaOH was consumed. At pH 5, the entire V and Cr and 97% Al were recovered, whereas Mn (3%) and Fe (12%) remained nearly stable in the solution. These results prove that V and Cr could be selectively recovered from *A. thiooxidans* biolixiviant at pH 4, and Al at pH 5, whereas Mn and Fe remained in the solution. A previous study reported that >99% of Mn was removed at pH 11 [32]. However, it should be considered that adjusting to pH 11 is accompanied by a much higher base consumption.

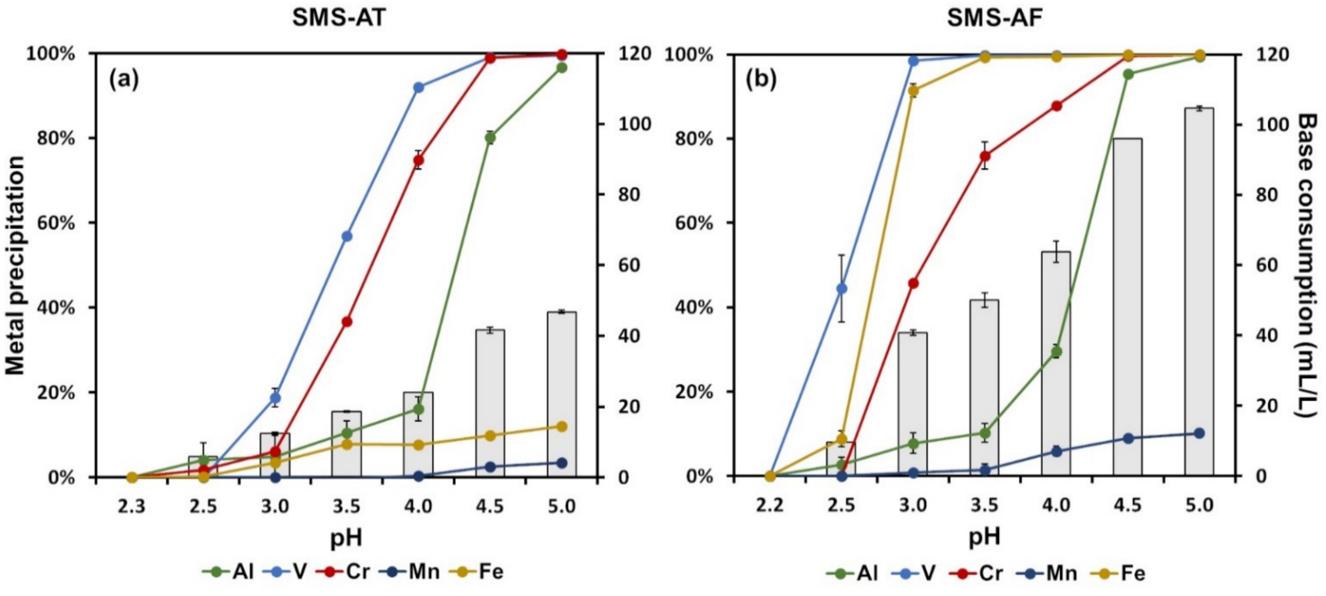

Figure 5. Selective metal precipitation from synthetic bioleachates. (**a**) Precipitation efficiency and base consumption of *A. thiooxidans* synthetic lixiviant (SMS-AT). (**b**) Precipitation efficiency and base consumption of *A. ferridurans* synthetic lixiviant (SMS-AF). Error bars indicate the standard deviation ($n = 2$).

Figure 5b shows the metal precipitation and the base consumption at each pH value of the SMS-AF. Significant differences were observed for Fe between the SMS-AT and SMS-AF (Figure 5a,b). At pH 3, 3% Fe from SMS-AT and 92% from SMS-AF were precipitated. This can be attributed to the oxidation state of Fe. SMS-AF was prepared with ferric chloride

(Fe^{3+}), whereas SMS-AT was prepared with ferrous sulfate (Fe^{2+}) to distinguish between the bioleaching mechanisms. Furthermore, V was precipitated from SMS-AF at pH 3 almost completely (98%), whereas only 19% V was removed from SMS-AT. In addition, Cr precipitation occurred faster in SMS-AF. At pH 3.5, 37% and 76% Cr was recovered from SMS-AT and SMS-AF. Similarly, 80% and 95% Al was precipitated from SMS-AT and SMS-AF at pH 4.5, respectively. However, the addition of base to adjust the required pH for precipitation was substantially higher for SMS-AF (to adjust to pH 5, 104.6 mL/L 1 M NaOH was consumed by SMS-AF, whereas SMS-AT consumed only 46.8 mL/L). At pH 3.5, V (100%), Fe (99%), and Cr (76%) could be selectively recovered from SMS-AF at a base consumption of 50 mL/L. At pH 4.5 and pH 5, Al was selectively precipitated at 95% and 100%, respectively. The obtained results show that it is possible to recover the selected metals from biolixiviant after slag bioleaching efficiently. Moreover, consuming large amounts of the base is unnecessary since selective metal precipitation is possible even at a lower pH than previously reported.

4. Conclusions

Novel concepts within a circular economy to recover economically critical raw materials, such as metals, are strongly required due to the depletion of natural mineral resources. This work demonstrated that chemolithotrophic acidophiles can effectively extract Al, Cr, Mn, and V from BOF slag up to a slag concentration of 75 g/L. In addition, the selective chemical precipitation of the dissolved metals from the biolixiviant using sodium hydroxide was proved to be a suitable method for metal recovery. Therefore, the combination of both methods represents a new biotechnological approach utilizing valuable secondary resources from low-grade steelmaking waste via bioleaching. Furthermore, combined bioleaching using ferric iron and biogenic sulfuric acid might lead to even higher extraction efficiency and needs to be investigated further.

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