A combined hydro-solvo-bio-leaching approach towards the valorization of a sulfidic copper mine tailing

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Abstract

Innovative and sustainable technologies are being developed to meet the demand for critical and economically important metals, and to minimize and valorize the increasing quantities of industrial waste streams. This study investigates a valorization route for the recovery of copper from a copper sulfide tailing (0.4 wt% Cu). Microwave-assisted roasting was used to transform the sulfidic fraction into a sulfate fraction, which increased the solubility of copper and other heavy metals during the following leaching steps. The roasted material was leached with an ammonia solution, and the effect on the leaching efficiency of varying the ammonia concentration was investigated. Simultaneous ammoniacal leaching and solvent extraction resulted in a high leaching efficiency of copper (nearly 100%) with a high selectivity against iron (less than 1% leaching efficiency). An indirect bio-leaching step with biogenic citric acid, supported by a compared leaching using purified organic acids, was applied to further decrease the concentration of residual metals (i.e, more than 40% leaching efficiency for Mn, around 20% leaching efficiency for Zn, and 5% leaching efficiency for Cu) and simultaneously neutralizing the pH of the substrate . A standardized environmental leaching test was performed on every leaching residue to evaluate the performance of the process.

Keywords: Ammoniacal leaching; Bioleaching; Microwave-assisted roasting; Solvent extraction; Environmental clean-up.

Introduction

The mining industry is vital for the supply of metals used in industry, consumer goods and for construction materials. However, extraction and processing of metallic ores generate large amounts of waste material, generally referred to as mine tailings. Although tailings are perceived as a residue stream, they often still contain relatively large concentrations of valuable metals, such as copper, zinc and nickel.[1] Sulfidic mine tailings, which are characteristic for their high content of sulfide minerals (mainly pyrite, FeS_2), are a common residue stream from the treatment of sulfidic ores. During the storage of sulfidic tailings, the oxidative weathering of sulfide minerals can cause acidification in the tailing deposits and, as a result, metals can leach from these deposits. This process, referred to as acid mine drainage (AMD), can cause severe damage to surface water, ground water reservoirs and soils.[2–4] Several treatments are available to minimize the risk of AMD, *e.g.* via the application of an alkaline source or organic material.[3,5] However, overall, the storage of sulfidic tailings is perceived as *i*) labour-intensive, *ii*) challenging in terms of environmental safety and *iii*) expensive.[6]

To minimize the accumulation of sulfidic tailings from copper production and their associated environmental risk, innovative technologies for re-use of these tailings are being explored. The main treatment strategies proposed for tailing recycling involve the recovery of metals (such as copper, cobalt or nickel for its economic value, and arsenic and lead for its environmental impact) and/or the use of tailings a secondary raw material for construction materials.[7] To improve the sustainability of existing mining practices and to contribute to a more circular use of materials, research in these domains is receiving a lot of attention from the research community.[8]

The recovery of valuable metals from fine-grained materials, including tailings, is typically based on a metallurgical leaching process, which aims at an efficient and selective dissolution of one or a few target metals. Many of these target elements are present in poorly-soluble sulfidic phases. It has been shown that oxidative pretreatments, *e.g.* based on roasting or oxidant addition,[9,10] can alter the mineral phase so that the subsequent leaching is enhanced. In this field, microwave-assisted roasting gained attention for heating selectively sulfidic phases inside the ores, promoting phase liberation and oxidation of sulfidic species to more amenable sulfate/oxide species.[11–13] Other studies obtained promising results with an oxidative leaching procedure.[14,15] Selectivity in the leaching process can be tuned by optimizing the leaching conditions (*e.g.* pH, complexing agent, temperature, etc.). Several leaching methods have been developed. Firstly, leaching with inorganic acids (*e.g.* HCl, H_2SO_4) is a conventional leaching method due to the high leaching efficiencies.[16] However, acid leaching typically has a poor selectivity, and co-dissolves large amounts of unwanted metals (e.g., iron).[17,18] Consequently, extensive downstream treatment of the acid leachate is required to separate metals of interest.[19] Secondly, ammoniacal leaching is a more selective leaching method, but for sulfidic materials it often requires high temperatures and pressure. The use of ammonia as a complexing agent in a mild alkaline medium can selectively extract copper, zinc, cobalt and nickel.[20] Finally, bio-leaching is a branch of biohydrometallurgy that is being increasingly studied, notably towards secondary materials. Microorganisms can facilitate redox reactions that mobilize metals and/or produce bio-molecules, including organic acids, that can act as lixiviant. Recent work has highlighted that pre-synthesized biogenic citric acid and its salt form can both be used to selectively extract metals from metallurgical residues in a ‘two step’ indirect leaching manner, showing great promise for integrated leaching and recovery technologies.[21,22]

A second important aspect in the processing of tailing materials is the development of secondary raw materials for construction out of the residues. A number of studies have investigated the direct application of copper tailings for preparation of cementitious binders [23–25] or road-base construction materials.[26] The environmental risk associated to heavy metal leaching from tailing-based construction materials can be mitigated by the fixation of the residual heavy metals in the matrix, as illustrated for tailing-based bricks.[27] However, the chemical conditions in these construction materials could change over time, *e.g.* due to weathering of the construction material or recycling of the construction material in other matrices, making it hard to guarantee the environmental safety over a longer period. Therefore, the most resilient approach is to reduce the heavy metal content to safe levels before use in construction applications.

In the past few years, the combination of different leaching methods for the treatment of tailings is receiving more attention, since this allows the sequential recovery of a range of target metals in a selective and systematic approach. For example, the potential of a bio-leaching step with a subsequent brine leaching step[28–30] and a synergistic combination of ammoniacal leaching with alkaline bacteria[31] were considered. The potential of this combination strategy justifies further investigation.

In this study, the combination of three technologies was tested for the valorization of a sulfidic copper mine tailing from the Cobre Las Cruces (CLC) mine in Sevilla, Spain. The process comprised the following steps *i*) microwave-assisted roasting (to increase the leachability of the target metals), *ii*) ammoniacal leaching with and without simultaneous solvent extraction (to selectively recover copper) and *iii*) indirect bioleaching (to clean the remaining residue). Throughout the process, the environmental properties of the material were assessed.

Experimental

Chemicals

The mineral tailings were obtained from the copper mine of Cobre Las Cruces (CLC; Sevilla, Spain; operated by First Quantum Minerals Ltd.). Ammonia (NH_3, 25 wt%), nitric acid (HNO_3, 65 %) and the ICP-OES standards were purchased from Chem-Lab NV (Zedelgem, Belgium). Petroleum ether, having a boiling range of ca. 180−280 °C, and malic acid (>99 %) were obtained from Acros Organics (Geel, Belgium). Solid citric acid (>99.5 %) and sodium citrate (>99 %) were purchased from Sigma-Aldrich (Overijse, Belgium). Biogenic citric acid solution (0.8 M) was obtained from Citrique Belge (Tienen, Belgium). The extractant LIX984 was obtained from BASF (Ludwigshafen, Germany). Titanium oxide (TiO_2, >94 %) was obtained from Kronos International.

Characterization of the material

In the CLC mine, copper is extracted from the ore through an iron(III) sulfate leaching process, followed by solvent extraction (SX) and electrowinning (EW). The tailings used in this work are the residue produced after the iron sulfate leaching. The received solid material was dried at 40 °C in a ventilated oven and homogenized before use. The mineralogical composition of the materials was investigated by X-ray diffraction (XRD, PANalytical Empyrean Diffractometer). The diffractometer operated at 40 kV and 45 mA, with cobalt anode material and equipped with a BBHD and a 3D detector (PIXcel 3D) with an active scanning length of 3.347° 2θ. Continuous mode scans with a scanning speed of 0.06° s^{-1} and step size of 0.013° were performed within a 2θ range of 5–120° 2θ. The diffractograms were qualitatively and quantitatively analyzed with the HighScore Plus software. Quantitative analyses by Rietveld refinement used an external standard

(TiO_2) as reference sample. The particle size distribution of the tailing was determined with a Malvern Mastersizer 3000, using water as suspension liquid.

The composition of the solid samples was determined via microwave digestion followed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis. The microwave digestion was performed using a Mars 6 iWave microwave digester with EasyPrep vessels. For the digestion, 100 mg of material was weighed and placed in the EasyPrep vessels and 4 mL of HCl, 5 mL of HNO_3 and 1 mL of HF were added (in this order). The vials were properly closed and digested following the US EPA 3052 method. After digestion, the vessels were opened, 10 mL of 4 vol% H_3BO_3 was added, and a second digestion with a standard neutralization method was performed. The digested sample was transferred to 50 mL volumetric flask and diluted with 2 vol% HNO_3. Each digestion was performed in triplicate and a blank sample was also digested to be used as reagent blank in the ICP-OES measurements. The metal content of the samples was determined via inductively coupled plasma optical emission spectroscopy (ICP-OES) using an Optima 8300 from PerkinElmer, with a 1-slot Hybrid XLT Ceramic-Quartz torch, also from PerkinElmer. For the ICP-OES measurements, the samples were prepared as follows: the samples were diluted in 2 vol% HNO_3, and scandium and indium (5 mg L^{-1}) were used as an internal standard. The dilution factor was chosen so the concentration of the metal of interest was lower than 50 mg L^{-1}.

Pre-treatment by microwave-assisted roasting

Microwave-assisted roasting was performed using a PYRO advanced microwave furnace (Milestone). The microwave was equipped with a silicon carbide (SiC) plate at the top of the heating chamber. This plate was installed to ensure the temperature inside the chamber stayed at the set temperature. The plate introduces the effect of a conventional furnace, by heating up under microwave irradiation and releasing heat to the sample chamber by convection and thermal radiation. Furthermore, pyrite, which is contained within the sulphidic tailing, is known to quickly heat to high temperatures in a MW field.[32] Therefore, convection and direct microwave-tailing (e.g. sulfides) dielectric heating of the tailings provided an hybrid heating system. The microwave-assisted roasting was performed at 500 °C (30 min ramp time, 60 min dwell time), which were conditions optimized in earlier work.[9] The mass losses were calculated by weighing the material before and after roasting.

Ammoniacal leaching and simultaneous solvent extraction

For the leaching experiments, the required amount of solid sample was added to a glass vial, the lixiviant was added, as well as the extractant if required, and the vial was closed and mixed using a Gerhardt THL500/1 thermoshaker. The lixiviants used in this work were aqueous ammoniacal solutions of different concentrations, and the extractant was LIX984 diluted in petroleum ether. After the leaching, all the liquid was filtered using syringe filters (PET, 0.45 μm). Each leaching experiment was performed in triplicate. The metal content of both the aqueous and organic phases was measured via ICP-OES. The metal concentrations in the aqueous samples were measured as described in the characterization section. The metal concentrations in the organic samples were measured using a Perkin Elmer Avio 500 spectrometer equipped with an axial/radial dual plasma view, a GemCone High Solids nebulizer, a baffled cyclonic spray chamber and a demountable quartz torch with a 2.0 mm internal diameter alumina injector. Petroleum ether was used as diluent for the sample preparation. Lanthanum (5 mg L^{-1}) was added as internal standard. After identification of optimal leaching conditions (*i.e.*, A/O/S ratio, temperature, time, etc.) a larger leaching experiment was performed to produce sufficient leaching residue for characterization and for the subsequent leaching steps. In this case, the solid-liquid separation was performed using a tared glass filter. The residue was rinsed in 5 steps (rinse 1: 65 mL of heptane; rinse 2: 65 mL of mQ water; rinse 3, 4 and 5: 65 mL of heptane). Each rinsing aliquot was kept separately and analyzed for its metal content. The solid residue was dried at 60 °C for 12 h. The dried material was weighted to quantify the mass losses associated to the simultaneous leaching and solvent extraction process.

Indirect bioleaching

An indirect ‘two step’ bioleaching approach was performed using a four-fold diluted biogenic citric acid solution (0.2 M) in deionized water as a lixiviant. To support the bioleaching experiments, solutions of malic acid, citric acid and sodium citrate were prepared by dissolution of the pure solid material into deionized water and dilution to the concentration of 0.2 M. To each Erlenmeyer flask, 4 g of residue and 40 mL of lixiviant solution were added, corresponding to a pulp density of 100 g L^{-1}. The suspensions were placed on an orbital shaker, shaking at 120 rpm, for 24 h at 28 °C. The solid-liquid separation was performed with a 0.45 µm Büchner filter. Afterwards, the residue was rinsed with demineralized water and dried at 70 °C for 48 h. The dried material was weighed to quantify the mass losses associated to the leaching process. All the experiments were performed in triplicate. The metal concentrations in the leachates were measured by radial ICP-OES (Varian MPX, Palo Alto, California) following dilution by 100-fold with 2 vol% HNO_3 in demineralized water. An external standard series was prepared freshly from individual stock solutions (TraceCERT, Sigma Aldrich) and the accuracy was verified by an independent quality control at the end of each sequence.

Environmental leaching tests

Environmental leaching tests were performed on the dried tailing material, and on the materials obtained after *i*) microwave-assisted roasting, *ii*) ammoniacal leaching and simultaneous SX and *iii*) bio-leaching. According to the EN 12457-2 standard, these materials were leached in MilliQ® water at a liquid to solid (L/S) ratio of 10 L kg^{-1} and a temperature of 20 ± 2 °C for 24 h. The suspensions were agitated using an overhead shaker. The samples were allowed to settle for 15 ± 5 minutes, before the pH values of the supernatants were measured. Subsequently, the leachates were filtered (Chromafil® RC-45/25 – 0.45 µm) and analyzed with ICP-OES.

Results and discussion

Chemical and mineralogical characterization of the initial mine tailings

Elemental analysis showed that the mine tailing obtained from the iron(III) sulfate leaching of the copper ore is mainly composed of silicon, sulfur and iron (Table 1). The remaining copper in the material was 0.4 wt%, while other heavy metals were present in low concentrations. The QXRD analysis (Table 2, Figure S1) showed that pyrite is the most abundant phase in the crystalline fraction, followed by quartz and calcium sulfate mineral phases. The XRD pattern is included in the Supplementary Data (Figure S2). It could not be determined via XRD in which mineral phases copper was present due to the low concentration of this element. However, in this type of tailings copper typically occurs in sulfidic minerals, such as chalcocite or chalcopyrite. Previous SEM-EDX measurements performed on the mine tailing showed strong associations between copper, iron and sulfur, suggesting that copper was present in the sulfidic form.[9] The particle size distribution of the tailing, showing a D_{50} of 22 µm and a D_{90} of 148 µm, is included in the Supplementary Data (Figure S3).

Table 1: Elemental composition (mg kg-1) of the: dry mine tailing; the roasted mine tailing; the dry leaching residue obtained after roasting and simultaneous leaching and solvent extraction (SX); and the dry leaching residue after roasting, simultaneous leaching and SX and bioleaching (determined via ICP-OES analysis). The standard deviation of triplicate experiments is included.

Element	**Mine tailing**[a]	**Roasted mine tailing**[b]	**Roasted, simultaneous leaching & SX**[c]	**Roasted, simultaneous leaching & SX & bioleached tailing**[d]
		mg kg^{-1} dry mass		
Al	3640	5201 ± 14	4804 ± 40	12628 ± 317
As	2270	3011 ± 77	3114 ± 48	2937 ± 68
Ca	8380	12364 ± 932	10224 ± 83	19557 ± 416
Cd	2.9	57 ± 17	48 ± 4	58 ± 5
Cr	17	9 ± 7	22 ± 5	42 ± 1
Cu	4370	6545 ± 100	1400 ± 24	2525 ± 42
Fe	305000	404995 ± 9588	484228 ± 6217	325246 ± 7915
Mn	102	131 ± 3	120 ± 2	394 ± 6
Ni	<10	15 ± 2	9 ± 2	19 ± 0
Pb	6700	9087 ± 161	7861 ± 100	16666 ± 496
S	348000	39332 ± 2783	25198 ± 318	21297 ± 362
Si	125150	124364 ± 4032	119950 ± 1767	142032 ± 510
Zn	1120	1533 ± 25	1089 ± 24	756 ± 5

[a] The estimated measurement uncertainty on this analysis method lies in the range 10-20% with a 95% confidence interval.

[b] Roasting conditions: T = 500 °C, t = 1 h

[c] Leaching and SX conditions: A/O/S (aqueous/organic/solid) = 0.5/2/1 L kg^{-1}, A= 6 M NH_3, O = 25 vol% LIX in petroleum ether, T = 60 °C, t = 2 h and 200 rpm

[d] Bioleaching conditions: citric acid solution 0.2 M, t = 24 h, L/S = 10 L kg^{-1}

Table 2: Quantification of the mineral phases present in the residues investigated in this work, calculated from the QXRD analysis

Mineral	**Mine tailing**	**Roasted mine tailing**[a]	**Mine tailing after roasting & simultaneous leaching & SX**[b]	**Mine tailing after roasting & simultaneous leaching & SX & bioleaching**[c]
Anglesite ($PbSO_4$)	-	1.1	-	-
Anhydrite ($CaSO_4$)	1.2	5.5	4.9	8.3
Calcite ($CaCO_3$)	0.2	-	-	-
Calciumsulfate hydrate ($CaSO_4 \cdot H_2O$)	5.6	-	-	-
Gypsum ($CaSO_4 \cdot 2H_2O$)	3.3	-	-	-
Hematite (Fe_2O_3)	-	47.9	53.2	29.9
Maghemite (Fe_2O_3)	-	10.0	15.0	24.4
Mikasaite ($Fe_2(SO_4)_3$)	-	6.6	-	-
Pyrite (FeS_2)	56.3	1.1	1.7	0.6
Quartz (SiO_2)	27.9	27.8	25.3	34.3
Rhomboclase ($H_5FeO_2(SO_4)_2 \cdot 2H_2O$)	1.5	-	-	-
Sulfur (S)	2.2	-	-	-

Szomolknite ($FeSO_4 \cdot H_2O$)	1.9	-	-	-
Total	100.1	100.0	100.1	99.9

[a] Roasting conditions: T = 500 °C, t = 1 h
[b] Leaching and SX conditions: A/O/S = 0.5/2/1 L kg^{-1}, A= 6 M NH_3, O = 25 vol% LIX in petroleum ether, T = 60 °C, t = 2 h and 200 rpm
[c] Bioleaching conditions: citric acid solution 0.2 M, t = 24 h, L/S = 10 L kg^{-1}

Roasting process

An oxidative roasting process was used to transform the sulfidic fraction, increasing the solubility of copper and other metals during the following leaching steps. The roasted samples were characterized by elemental analysis and QXRD. The elemental analysis showed an increase in the concentration of each metal (Table 1), which is explained by the mass losses associated to the oxidation of the pyrite and the formation of SO_2 gas during the roasting process. The mass losses were quantified by weighting the material before and after the roasted process and accounted for 21 wt%. The main changes in mineralogical composition were the transformation of the pyrite into iron oxides (hematite and maghemite) and iron sulfates (mikasaite), and the transformation of hydrated calcium sulfate into anhydrite (Table 2, Figure S1). The disappearance of the representative peaks of sulfidic phases is also shown in the Supplementary Data, Figure S2, where a comparison of the XRD diffractograms before and after roasting is shown.

Ammoniacal leaching

Ammoniacal leaching was investigated for the selective recovery of copper and other heavy metals from the mine tailing and the roasted-mine tailing. It is well known that copper(II) forms stable ammine complexes, while iron(III) is insoluble in ammonia solutions. The solubility of iron(II) in ammonia solutions is very low, although a certain amount of hexaammine iron(II) complex $[Fe(NH_3)_6]^{2+}$ can be formed under certain conditions.

The leaching of the non-roasted mine tailing with ammoniacal solutions was investigated. The material was also leached with water for comparison purposes. Figure 1 shows the effect of the ammonia concentration on the leaching efficiency and on the composition of the pregnant leach solution (PLS). Water could leach 30% of the copper, while ammoniacal solutions with a concentration >0.5 M could not leach more than 8% of the copper. This behavior can be attributed to the lower pH obtained for the water leaching when the sulfidic matrix was dissolved. Figure 1 also shows that water-leaching is much less selective against iron than ammoniacal leaching, *i.e.*, the water-PLS contained around 800 mg L^{-1} of iron, while it could not be detected on the ammonia-PLS. The leaching of calcium also decreases with an increasing concentration of ammonia, varying from ≈500 mg L^{-1} to ≈200 mg L^{-1}. It has been previously reported that ammonia prevents calcium solubility in the presence of carbonate or small amounts of sulfate.[33] The leachability of other heavy metals such as lead, zinc or arsenic was very low, although it was higher in water than in ammoniacal solutions.

The ammoniacal leaching of the roasted mine tailing was also investigated. Figure 1 shows the effect of the ammonia concentration on the leaching efficiency and on the composition of the PLS. The leaching efficiency of copper was higher with an increasing concentration of ammonia up to a 1 M concentration. The negligible effect of an increasing ammonia concentration on the copper leaching efficiency has been previously reported for systems with low copper content.[34] Both water (in Figure 1, 0 M NM_3) and ammoniacal leaching resulted in similar copper leaching efficiencies. However, ammoniacal leaching was much more selective against iron. The concentration of iron in the water PLS was *ca*. 2000 mg L^{-1}, while that obtained for the ammoniacal leaching was below the quantification limit of ICP-OES (Figure 1b). The much higher selectivity for copper against iron justified the use of ammonia over water. The leaching efficiency of zinc followed a trend similar to copper. The solubility of metals such as iron, lead, arsenic or calcium was inhibited by the presence of ammonia, and it decreased with the concentration of ammonia. This can be attributed to the higher pH of the ammoniacal solutions compared to water leaching.

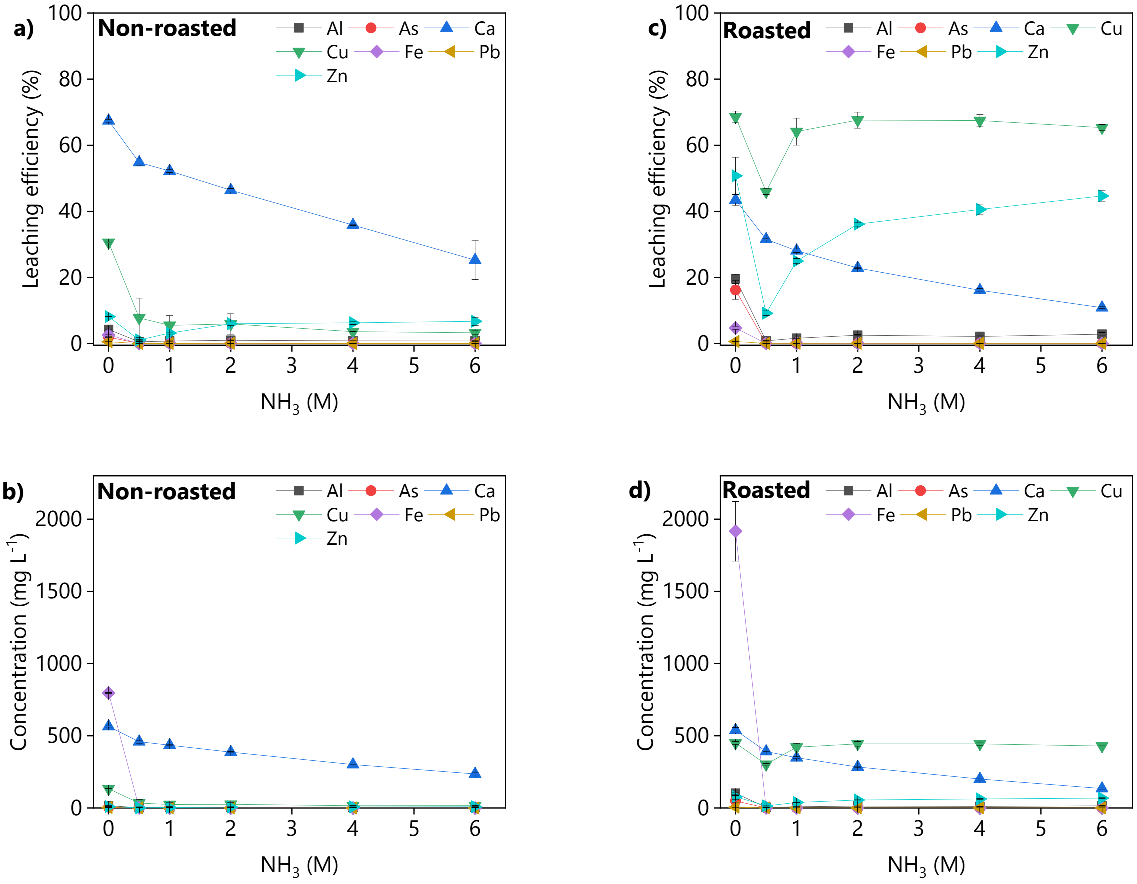

Figure 1: Effect of the ammonia concentration on the (a) leaching efficiency and (b) composition of the PLS for the non-roasted mine tailing, and the (c) leaching efficiency and (d) composition of the PLS for roasted mine tailing. Leaching conditions: T = 60 °C, t = 2 h; L/S = 10 L kg^{-1}, 200 rpm.

A comparison of the non-roasted ammoniacal metal extraction highlighted that the roasting drastically increased the solubility of copper and zinc and decreased that of calcium for both the water and the ammoniacal leaching. The roasting process also increased the solubility of aluminum, arsenic, iron and lead in water, but not in ammonia. Whilst roasting increased the leachability, less than 70% of the copper was leached via conventional ammoniacal leaching. To increase the efficiency of the process, a simultaneous leaching and solvent extraction (SX) was investigated.[35,36] In this process, the solid (S) is contacted with two immiscible liquid phases, *i.e.* the aqueous lixiviant phase (A) and the organic extractant phase (O). The solid is leached by the aqueous phase, but the leached metals are immediately extracted to the organic phase. Therefore, the lixiviant becomes again available for further leaching. This process intensification technique is particularly effective for several reasons: lower lixiviant requirements, increased leaching efficiency and reduced capital and operational costs.

The effect of the A/S ratio on the leaching efficiency of roasted mine tailing was studied (Figure 2). The organic phase was 25 vol% LIX984 in petroleum ether, and the organic-to-solid ratio (O/S) was kept constant at 10. Two different aqueous phases were considered: water and a 6 M ammonia solution. Independently of the type of aqueous phase, 100% copper leaching efficiency was achieved, which confirmed the superior performance of simultaneous leaching and SX over conventional ammoniacal leaching, where only 65% copper was leached. The A/S had little effect on the leaching efficiency of most metals for both aqueous and ammoniacal systems. A/S as low as 0.5 could fully leach 100% of the copper. Therefore, the aqueous phase acted merely as a catalyst for the SX. This is important because reducing the amount of lixiviant significantly reduces the operational costs of the process. Similarly to standard leaching experiments (Figure 1), the ammoniacal leaching was more selective against iron than the water leaching (Figure 2 b and d). Comparing the compositions of the PLSs, water leaching produced a PLS richer in iron than in copper. Figure 2 also shows that the ammoniacal system could leach more arsenic, zinc and lead than water. The removal of heavy metals is necessary for the valorization of the remaining residue as construction material. Therefore, based on the higher selectivity against iron and the higher heavy metal dissolution, ammoniacal leaching was preferred over water leaching. The direct leaching of the roasted material with the extractant phase (non-aqueous phase) was also tested (A/S = O). Only a small fraction of copper (≈25%) was leached, demonstrating that the aqueous phase is required to provide protons to the LIX984 extractant.

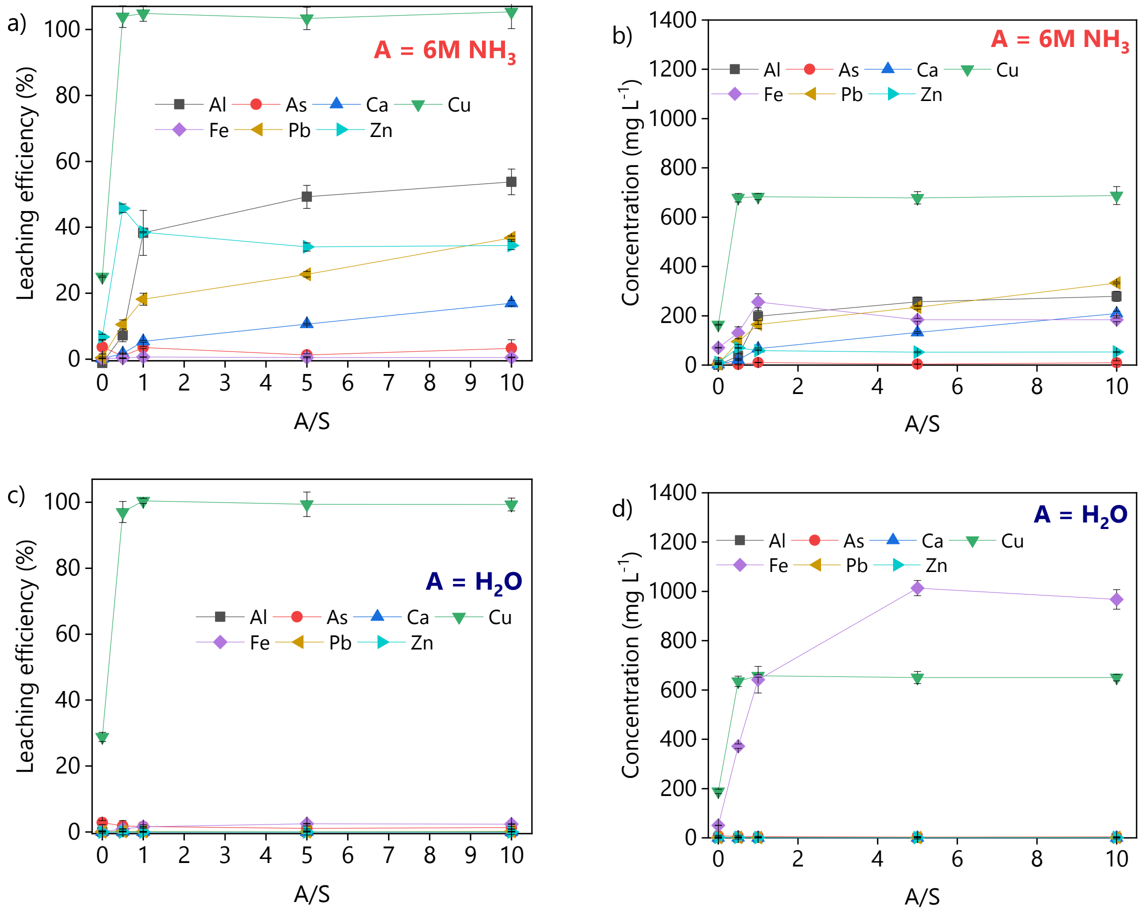

Figure 2: Effect of the aqueous-to-solid ratio on the leaching efficiency (a and c) and composition of the PLS (b and d) for the simultaneous ammoniacal leaching and solvent extraction of roasted mine tailing. The organic phase was LIX984 (25 vol%) diluted in petroleum ether, and the aqueous phase was 6 M ammonia (a and b) and water (c and d). The leaching conditions are: O/S = 10 L kg^{-1}, T = 60 °C, t = 2 h, 200 rpm.

The effect of the O/S on the leaching of the roasted sample was investigated for an A/S = 0.5 (Figure 3). Whilst a decrease of the O/S decreased the solubility of copper, zinc and lead, it also decreased the operational costs of the process. Therefore, the selection of an appropriate O/S is not a straightforward decision.

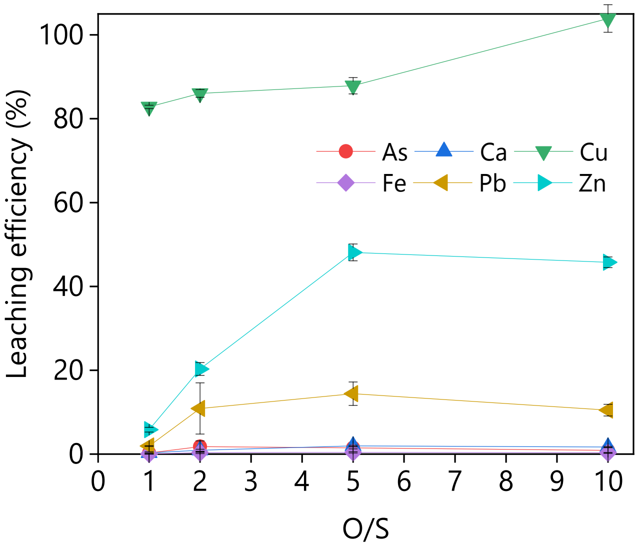

Figure 3: Effect of the organic-to-solid ratio on the leaching efficiency of the roasted mine tailing leached via ammoniacal leaching and simultaneous solvent extraction. The organic phase was LIX984 (25 vol%) diluted in petroleum ether, and the aqueous phase was 6 M ammonia. The leaching conditions are: A/S = 0.5 L kg^{-1}, T = 60 °C, t = 2 h, 200 rpm.

The simultaneous leaching and solvent extraction process was upscaled from 1 to 60 g of solid material. Two different conditions were tested: A/O/S = 0.5/2/1 L kg^{-1} and A/O/S = 0.5/10/1 L kg^{-1}, performed at A= 6 M NH_3, O = 25 vol% LIX984 in petroleum ether, T = 60 °C, t = 2 h and 200 rpm. The copper leaching efficiencies obtained for the upscaling of the process were 91 and 95%, respectively. The elemental analysis of the obtained leaching residues showed a remaining copper content of 1400 mg Kg^{-1} for A/O/S = 0.5/2/1 and of 1153 mg Kg^{-1} for A/O/S = 0.5/10/1. In this work, the A/O/S ratio of 0.5/2/1 was selected for further study due to the good compromise between process economics and copper recovery.

At the selected conditions, the mass losses associated with the leaching and solvent extraction process accounted for 9.4%. The obtained leaching residue was characterized by elemental analysis (Table 1) and QXRD (Table 2). The elemental analysis showed that the concentrations of all the elements that increase their leaching efficiency (i.e., Al, Ca, Cu, Pb, S, and Zn) decreased compared to the roasted tailing, whereas the opposite occurred to Fe which emphasizes the selectivity of the process. From the QXRD, apart from quartz (25.3%) and anhydrite (4.9%), only iron phases could be detected: hematite (53.1%), maghemite (15%) and pyrite (1.7%).

Indirect bioleaching

In attempt to further reduce the remaining heavy metal content, the leaching residue obtained from the simultaneous leaching and solvent extraction process subsequently reacted with a 0.2 M biogenic citric acid lixiviant. To support the leaching behavior, experiments were performed with biogenic citric acid, its salt form sodium citrate, and another identified by-product of fermentation, malic acid, against the bulk water matrix background control using ultrapure water (Figure 4).[21] When comparing the use of sodium citrate under more alkaline conditions (pH 8.4) with respect to citric acid (pH 2.1), the latter showed to be more effective towards metal leaching. It confirms that bio-leaching from a sulfur matrix is likely initiated by proton attack (Schippers and Sand, 1999). Whilst of lower leaching efficiency of initial target metals Cu and Zn, an improved selectivity against the bulk iron matrix was observed for biogenic citric acid in comparison to the purified form. The similar pH (2.8) but higher ionic strength, due to the presence of trace impurities in the biogenic form, resulted in the extraction of less iron (0.36 mg g^{-1}) as compared to leaching by pure citric acid (13.62 mg g^{-1}). It is plausible that the dissolution of Fe(III) may then drive the oxidation (and leaching) of other elements, which could account for the differences in leaching patterns. Efficient metal extraction is therefore entangled by an adverse selectivity against iron.

Nevertheless, such approach using heterotrophically produced biogenic acids has a marked advantage in operation over other commonly used autotrophic and acidophilic bioleaching approaches. Interestingly, an increased extraction efficiency was observed for lead by biogenic citric acid which may be attributed to the synergistic extraction of both citric acid and other metabolic by-products such as malic acid.

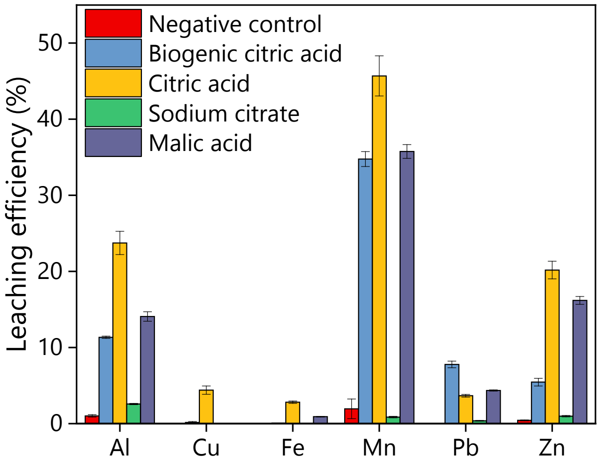

Figure 4: Extraction efficiency of various 0.2 M solutions of organic acids (*n* = 3). Leaching conditions: L/S = 10 L kg^{-1}, T = 28 °C, t = 24 h and 120 rpm.

To explore whether biogenic citric acid had an impact on the further extractability of the leaching residue, a further leaching test with ultrapure water was performed. The leaching residue obtained after this leaching step was characterized via elemental analysis following microwave digestion (Table 1) and QXRD (Table 2, Figure S1). Interestingly, citric acid had a marked impact on the extractability of iron, reducing the overall iron content from 48.4 to 32.5 wt%, whilst simultaneously up-concentrating the concentrations of copper (80% from 1400 and to 2525 mg kg^{-1}) and lead (112% from 7861 and to 16,666 mg kg^{-1}) . This is in contrast to the control with ultrapure water on the non-citric acid treated mineral residue (< 0.05 mg g^{-1}) (Figure 5), where very low metal concentrations were observed in the pregnant leachate solution. The QXRD analysis showed that hematite and pyrite were significantly reduced in the material, from 53 to 31% and from 1.6% to below the detection limit respectively (SI Figure 1). Citric acid has been demonstrated to cause mineralogical transformations of iron minerals,[37] thus provides an additional benefit for a more sustainable approach to mineral residue up-concentration for subsequent leaching steps.

Feasibility of the combination of technologies

The combination of technologies to 1) recover the remaining copper and 2) produce a clean residue suitable for safe landfilling or construction applications was investigated. The roasting increased the leachability of the copper and transform the sulfides into sulfates, reducing the AMD risk. The subsequent ammoniacal leaching and simultaneous SX could leach between 85 and 100 % of the copper depending on the experimental conditions and the leaching scale. The upscaling was performed at A/O/S = 0.5/2/1. A bioleaching step with biogenic citric acid was tested on the latter residue, resulting in additional extraction of transition metals with high selectivity towards the major competing metal, iron. The very high selectivity and the possibility to recover citric acid for reuse[21] gives provides a more sustainable approach for final step leaching approaches where target metal concentrations are low. The observation that citric acid could transform crystalline iron phases hematite and pyrite for the facile extraction with water also provides an additional benefit for greener mineral residue up-concentrations for subsequent leaching steps. A simplified flowsheet of the combination of the three technologies, including the composition of all the solid residues is included in Figure 5. Based on the obtained results the best path towards valorization of extracted metals seems to be a combination of roasting and simultaneous ammoniacal leaching and SX, with a low O/S ratio.

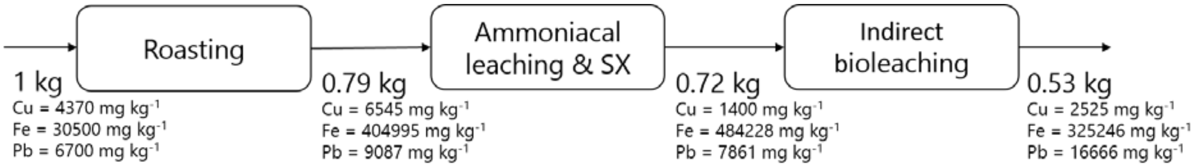

Figure 5: Combined process for the valorization of the mine tailing, analysis of the leaching residues.

Environmental leaching tests

In order to evaluate the environmental impact of the solid streams, a standardized environmental leaching test (EN12457-2) was performed (Table 3). The roasting process increased the leachability of the metals due to the transformation of stable sulfides into more soluble sulfate and/or oxide phases. After the ammoniacal leaching and simultaneous solvent extraction step, the leachability of heavy metals in water drastically diminished. However, the indirect bioleaching step increased the leachability of most heavy metals, consistent with the previous observations in the XRD and residue digest analysis towards citric acid mediated mineralogical transformations following an additional water leaching step.

Table 3: Results of the environmmental leaching tests of the residues used in this work, expressed in mg of dissolved metal per kg of dry residue

	Mine tailing	Roasted mine tailing[a]	Mine tailing after roasting & simultaneous SX + leaching[b]	Mine tailing after roasting + simultaneous SX + leaching + bioleaching[c]	Proposed Flemish limit	Spanish limit	Italian limit
	mg kg^{-1}	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
As	327	718	0.17	199	0.8	2	0.5
Cd	0.38	1.56	0.07	0.26	0.03	1	0.05
Cr	5.82	2.39	<0.01	0.99	2.6	10	0.5
Cu	1700	4340	0.17	118	0.8	50	0.5
Hg	<0.5	<0.5	<0.5	<1	0.02	0.2	0.01
Pb	36.2	33	1.79	218	1.3	10	0.5
Ni	5.8	14.4	0.5	2.87	0.75	10	0.1
Zn	137	642	7.87	29.9	2.8	50	30

Sb	9.27	1.94	0.052	16.7	1	0.7	
Ba	0.018	0.03	0.27	0.11	20		10
Co	36.6	231	0.37	2.56	0.5		2.5
Mo	0.57	0.17	<0.01	0.43	55	10	
Se	0.79	0.72	0.3	0.062	2		0.1
Sn	0.42	1.23	<0.01	1.09	1	0.5	
V	1.28	0.8	<0.01	0.85	2.5		2.5
pH	2.245	2.483	4.804	3.116			
Cond. (mS cm^{-1})	6.835	6.5	2.815	4.27			
Redox (mV vs. SHE)	435.8	463.3	349.5	361.1			

[a] Roasting conditions: T = 500 °C, t = 1 h

[b] Leaching and SX conditions: A/O/S = 0.5/2/1 L kg^{-1}, A= 6 M NH_3, O = 25 vol% LIX in petroleum ether, T = 60 °C, t = 2 h and 200 rpm

[c] Bioleaching conditions: citric acid solution 0.2 M, t = 24 h, L/S = 10 L kg^{-1}

We have compared the results of the environmental leaching tests to various existing legislations: 1) Spanish limit values for waste storage in landfills (to evaluate the environmental impact of the treated residue according with the legislation of the country in which the residue is produced)[38], 2) Flemish leachability limit for construction applications[39] and 3) Italian leachability limits for construction applications (for comparison purposes)[40]. Unfortunately, in Spain the legislation regarding leachability of construction applications has been transferred to the Autonomous Regions and a national leaching limit value does not apply. The limit leachability values according to the aforementioned legislations are also included in Table 3 for comparison purposes.

The obtained results showed that only the solid residue produced after the ammoniacal leaching and simultaneous solvent extraction complied with the Spanish leaching values required for landfilling as a non-dangerous material. Therefore, the roasting and ammoniacal leaching process not only recovered a significant fraction of the copper (>90%), but also produced a clean material which can be safely disposed. Furthermore, it was observed that this material complied with most of the leaching limits to be used as construction material in Belgium and Italy. Only the leachability of cadmium and lead were slightly over the limits in both Italy and Flanders. However, it should be considered that the residue can be blended with other materials, or immobilized prior use. It is worth noticing that the environmental leachability limits show a large variability from country to country, making it difficult to assess the true environmental impact of the remaining solid residue, as evidenced by the following JRC report.[41]

Conclusion

A combination of innovative metallurgical processes was evaluated to valorize metals within a sulfidic copper mine tailing material. The objective was the recovery of the remaining copper, together with other metals while producing a clean solid residue that can be safely landfilled or used as a construction material. Microwave-assisted roasting successfully enhanced the metal leachability of the tailing via the oxidation of the sulfidic phases. Ammoniacal leaching of the roasted material revealed that increasing the ammonia concentration above 1 M did not have a significant effect on the copper leaching efficiency. However, a higher ammonia concentration did increase the selectivity towards iron. The lixiviant requirements could be reduced by combining leaching and solvent extraction in a single-step. Furthermore, this method also increased the copper leaching efficiency from 60% to 100% at certain conditions. Subsequent indirect bio-leaching using a 0.2 M biogenic citric acid lixiviant facilitated the further selective extraction of metals, including manganese, zinc and lead, and could transform iron minerals into more extractable forms, which offers a greener alternative to mineral up-concentrations and activation for further leaching steps. This work is of particular relevance to establish an economic treatment process for the millions of tons of CuS bearing mine tailings produced globally each year.

Associated content

Supporting information: QXRD difractograms of all solid samples, mineralogical composition of all solid samples and particle size distribution of the sulfidic tailing.

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Conflict of interest

There are no conflicts to declare.

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