



# A New Application of Solvent Extraction to Separate Copper from Extreme Acid Mine Drainage Producing Solutions for Electrochemical and Biological Recovery Processes

Amir Nobahar<sup>1,2</sup> · Alemu Bejiga Melka<sup>1,2</sup> · Alexandra Pusta<sup>1</sup> · João Paulo Lourenço<sup>2,3</sup> · Jorge Dias Carlier<sup>1</sup> · Maria Clara Costa<sup>1,2</sup>

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## Abstract

Over the last decade, AMD waters have gained more attention as a potential source of metals due to the emerging need to recover or recycle metals from secondary resources. Metals recovery supports sustainability and the development of a circular economy with benefits for resource conservation and the environment. In this study, five extractants (Acorga M5640, LIX 54, LIX 622, LIX 622 N, and LIX 864) diluted (15% (v/v)) in Shell GTL with 2.5% (v/v) octanol were compared and evaluated for Cu recovery from an extreme AMD sample ( $5.3 \pm 0.3$  g/L Cu) collected at the inactive São Domingos Mine in the Iberian Pyrite Belt of Portugal. Of the five extractants, Acorga M5640 showed the best selective efficiency. Further tests showed that 30% (v/v) of this extractant was able to selectively extract  $\approx 96.0\%$  of the Cu from the AMD in one extraction step and all of the remaining Cu (to below detection) in three steps. Among the different stripping agents tested, 2 M sulfuric acid was the most efficient, with  $\approx 99\%$  of the Cu stripped, and the recyclability of the organic phase was confirmed in five successive cycles of extraction and stripping. Furthermore, contact time tests revealed that the extraction kinetics allows the transfer of  $\approx 97\%$  of the Cu in 15 min, and aqueous to organic phase ratios tests demonstrated a maximum loading capacity of  $\approx 16$  g/L Cu in the organic phase. Raising the concentration of Cu in the stripping solution (2 M sulfuric acid) to  $\approx 46$  g/L through successive stripping steps showed the potential to recover elemental Cu using traditional electrowinning. Finally, a biological approach for Cu recovery from the stripping solution was evaluated by adding the supernatant of a sulfate-reducing bacteria culture to make different molar ratios of biogenic sulfide to copper; ratios over 1.75 resulted in precipitation of more than 95% of the Cu as covellite nanoparticles.

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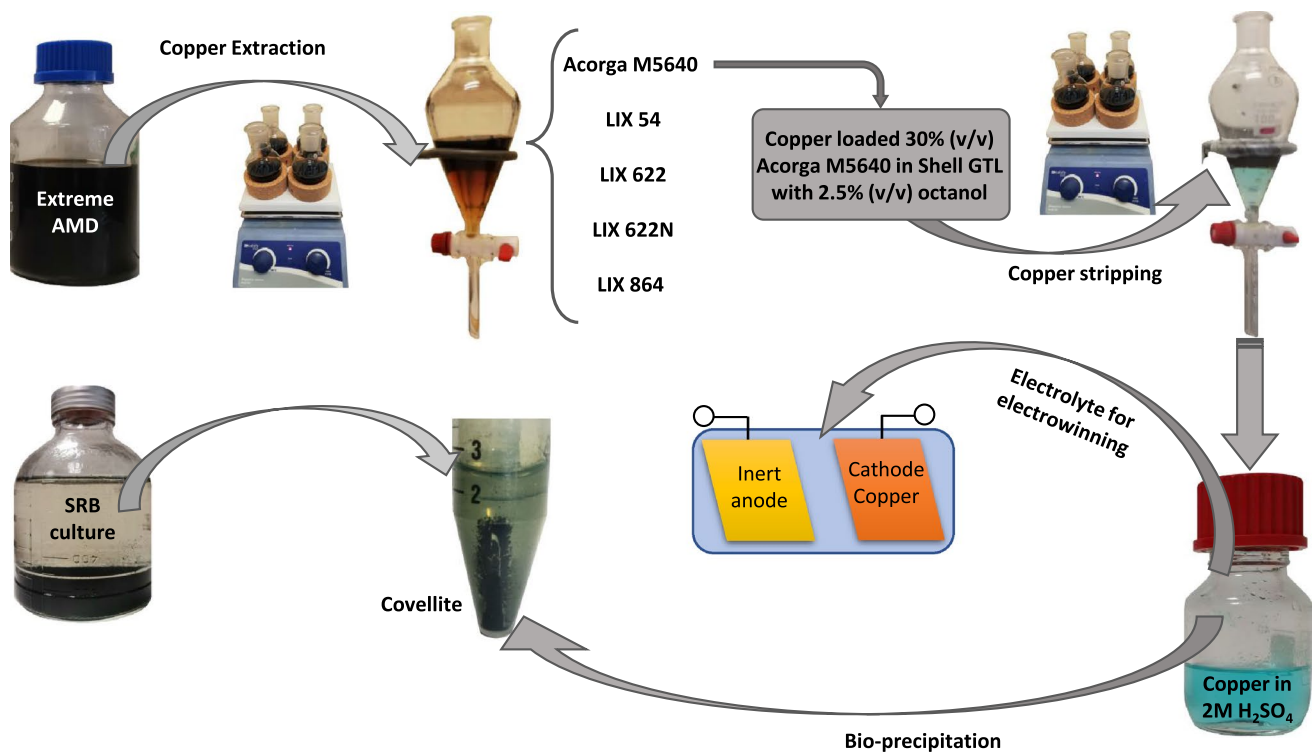
✉ Jorge Dias Carlier  
jcarlier@ualg.pt

<sup>1</sup> Centre of Marine Sciences (CCMAR), University of the Algarve, Gambelas Campus, 8005-139 Faro, Portugal

<sup>2</sup> Faculty of Sciences and Technology, University of the Algarve, Gambelas Campus, 8005-139 Faro, Portugal

<sup>3</sup> Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av Rovisco Pais, 1049-001 Lisbon, Portugal

## Graphical Abstract



**Keywords** Copper recovery · AMD remediation · Liquid–liquid extraction · Metal bio-recovery

## Introduction

Acid mine drainage (AMD) is formed by the oxidation of sulfide-rich ores exposed to the atmosphere by mining (Kefeni et al. 2017). Conventional pH control with cost-effective neutralizing reagents has been the most widely used approach for AMD treatment (Kalin et al. 2006; Taylor et al. 2005), but lime neutralization produces large amounts of precipitated metals and sludge that require further management and appropriate disposal. AMD is being increasingly considered a secondary source of metals with the goal of establishing effective methods to recover metals from AMD, increasing the circular economy, and contributing to environmental protection and resource conservation (e.g. Macías et al. 2017; Wang and Ren 2014)).

Portugal has more than 100 inactive mine sites (Morais et al. 2008), and São Domingos is one of the most representative mining districts in the Portuguese sector of the Iberian Pyrite Belt. The intensive mining activity has caused environmental deterioration of the area (Álvarez-Valero et al. 2008; Batista 2000; Matos et al. 2006). The massive ore body of the São Domingos Mine consists of 45–48% total sulfur, primarily in the form of pyrite (FeS<sub>2</sub>), chalcopyrite (CuFeS<sub>2</sub>), sphalerite (ZnS), galena (PbS), and blended [(Zn,

Fe)S] minerals that are usually found in association with pyrite (Oliveira and Oliveira 1996). Currently, no measures are in place to remediate the local environment affected by the inactive mine, and local watercourses and surrounding soils are heavily contaminated with various metals. Considering the size of the São Domingos area ( $\approx 50 \text{ km}^2$ ) affected by historical mining and the volume and type of wastewaters, an environmentally friendly and economically viable AMD treatment and recovery method is needed to reduce the associated environmental problems, recover metals, and increase the availability of water for irrigation.

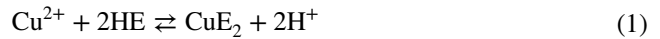
Most metal supplied to the global economy is obtained through mining of finite sources that are rapidly decreasing due to economic expansion, higher living standards, and modern industrialisation (Arndt et al. 2017; Segura-Salazar and Tavares 2018). Copper (Cu) is one of the important metals present in high concentrations in the São Domingos AMD, and its recovery could generate additional economic activity and value due to its high demand. Since 2011, the recycling rate of Cu has been continuously decreasing (from 36% in 2011 to 29% in 2016), while refined secondary production is relatively stable over the same period (ICSG 2018). According to available data, 20,474,372 metric tons of Cu are produced per year (based on 2018 data) (Reichl

and Schatz 2020), and, according to the International Copper Study Group (2019), global Cu consumption will continuously increase due to population growth, product innovation, and economic development. In a recent study using different scenarios with regression and stock dynamics methods, Schipper et al. (2018) estimated the Cu demand for the year 2100 to be in the range of 3 to 21 times the current Cu demand. Indeed, estimates of the short-term supply risk criticality indicate that in the next 2–3 decades, different industrial sectors will struggle to maintain their demand for several metals (Elshkaki et al. 2016; European Commission 2014; Frenzel et al. 2015). As a result, to meet future Cu demand, a combination of primary raw materials coming from mines plus recycled and recovered materials from secondary sources is required, preferably taking advantage of eco-friendly and sustainable technological improvements and more efficient process designs. Until now, metal recycling rates from secondary sources are still very low, and significant potential exists for improving metals recovery from such sources (Schäfer and Schmidt 2019).

In this context, solvent extraction (SX) is a powerful technique that allows the recovery of metal ions from both diluted and concentrated solutions (Andersson and Reinhardt 1983). SX is a well-demonstrated and widely used technique at the industrial scale for separation and recovery of metals from aqueous solutions in the hydrometallurgical treatment of ores and other secondary materials (Hedrich et al. 2018). In the hydrometallurgical industry, SX processes make use of organic phases consisting of extractants diluted in solvents to specifically target metal ions (e.g.  $\text{Cu}^{2+}$ ) from impure multi-metallic leaching solutions; the metals are then stripped from the organic phase into pure aqueous solutions from which the metals can be recovered (Davis-Belmar et al. 2012; Ruiz et al. 2019). Nevertheless, such processes are often challenged by the inability to separate valuable metals from low-concentration, metal-bearing solutions (Matinde 2018; Nordstrom et al. 2017). For example, Cu recovery by SX from waters with Cu concentrations below 1 g/L is not considered economically viable (Sole and Hardwick 2016).

The most widely used commercial Cu extractants, recognised for their selectivity, are hydroxy oxime-type organic acids, such as Acorga and LIX extractants (Ruiz et al. 2020; Vander Linden 1998). The equilibrium reaction of cupric ion ( $\text{Cu}^{2+}$ ) with these extractants has attracted interest, and several models have been proposed (e.g. Alguacil et al. 2004). In the case of Acorda M5640, Agarwal et al. (2010, 2012) reported that the extractant optimises the metallurgical performance relative to ketoxime-based extractants while protecting against nitration and oxidative degradation. These characteristics reduce the extractant consumption and improve operational reliability, as it ensures a final high-quality extractant that can be reused in the extraction circuit (Alguacil et al. 2004). In the extraction reaction,

$\text{Cu}^{2+}$  complexes with the extractant and releases a hydrogen ion, according to the reversible mechanism (Flett et al. 1973) presented in Eq. (1):



where E is the extractant and  $\text{CuE}_2$  is the Cu-chelate complex.

In this reaction, the acidity of the aqueous phases in the extraction and stripping stages controls the loading and stripping of Cu to and from the organic phase (Hoh and Wang 2007).

In recent years, technologies that recover value from metal-bearing wastewaters have gained attention as a way to reduce the negative impact of mine water treatment processes. Moreover, combining chemical and biological extraction technologies to remove and recover metals can improve the adaptability to changes in feed flow and the ease of operation, which are essential characteristics in the treatment process. The use of sulfate-reducing bacteria (SRB) is a good option for metal recovery from mine-impacted waters (Kaksonen and Puhakka 2007; Villa-Gomez et al. 2011). Biogenic sulfide is advantageous because it allows the formation of insoluble metal sulfides, even at low metal concentrations and low pH values (Lewis 2010).

The need to develop alternative processes for metal recovery from secondary sources stimulated the present research. The application of an SX process like those used in the hydrometallurgical industry for extraction of Cu from pregnant solutions was tested and optimised to separate this metal from extreme AMD waters, using a mine water sample collected at the São Domingos Mine as a model. In addition, a process was tested to recover Cu from the resulting purified solution using biogenically produced sulfide to precipitate covellite nanoparticles.

## Materials and Methods

### Extreme AMD

Mina de São Domingos, a village in southeastern Portugal, has a mine that was exploited during the Roman and Islamic occupations of the Iberian Peninsula that was the largest mine operating in Europe between 1857 and 1966. The primary ore body was a massive pyrite deposit, and Cu and sulfur (S) were the main elements extracted (Tavares et al. 2008).

Since mining activity ceased in the 1960s, the vast mining area, from the open-pit to the ruins of the Achada do Gamo factories where the ore was processed and the large waste piles were deposited, has produced a significant environmental footprint. Here the most prominent concern is AMD with

high concentrations of sulfate ( $\text{SO}_4^{2-}$ ) and metals, mainly aluminium (Al), iron (Fe), Cu, zinc (Zn), and manganese (Mn) (Álvarez-Valero et al. 2008; Pereira et al. 2004).

Most of the AMD flows through several reddish-yellow diversion channels and dams until merging in a unique stream that joins the Mosteirão stream, which enters the Reservoir of Chança River, a major tributary of the Guadiana River. However, some AMD generated in the Achada do Gamo zone remains in two impoundments: one of about 8700 m<sup>2</sup> (Fig. 1, area 2) and another of about 2400 m<sup>2</sup> (Fig. 1, area 3). These impoundments are in the area where low-grade Cu ores were roasted in piles and washed with acidic water to extract the Cu that was later precipitated onto iron sheets in a cementation tank. The impoundments are surrounded by slag remaining from the roasted pyrite ore piles (sulfur factory tailings), roasted iron oxide (hematite-rich) ore, and leached materials in seasonally flooded areas (Álvarez-Valero et al. 2008). The AMD in the larger impoundment has a very dark colour, is very dense and extremely contaminated, likely due to successive cycles of accumulation in winters and evaporation in summers, and was the source of the AMD sample used in our work (Fig. 1, area 2). The sample was collected on 25 October 2018 and immediately transported ( $\approx 90$  min transport time) to the laboratory for characterisation and Cu recovery tests.

## Solvent Extraction

The extraction procedures and the experiments performed to select the extractant and optimise and characterise the extraction conditions are described in Melka (2019). The initial metal concentrations (Fe, Al, Cu, Zn, and Mn) in the

raw AMD,  $[\text{M}_{\text{aq}}]_i$ , and their final concentrations in the aqueous phase after solvent extraction,  $[\text{M}_{\text{aq}}]_f$ , were measured. The metal concentrations in the final organic phase,  $[\text{M}_{\text{org}}]_f$ , were calculated by mass balance, and their removal efficiencies were determined by:  $\text{Removal \%} = 100 \times [\text{M}_{\text{org}}]_f / [\text{M}_{\text{aq}}]_i$ . The extraction distribution ratios (D) of the target metal ions were calculated as  $D = [\text{M}_{\text{org}}]_f / [\text{M}_{\text{aq}}]_f$ .

## Recovery Through Bioprecipitation

### Precipitation with Biogenic Sulfide

The addition of the sulfide-rich liquid phase from an SRB culture was tested as a method to precipitate Cu sulfide (covellite) from the loaded stripping solution (2 M  $\text{H}_2\text{SO}_4$ ) obtained after SX with the selected organic phase. Three stripping solutions from successive extractions and stripping steps were mixed to produce enough Cu solution for the tests.

The SRB consortium used in our work was enriched using Postgate B medium (Postgate 1984) inoculated with sludge from a wastewater treatment plant located in southern Portugal and incubated at room temperature ( $25 \pm 3$  °C) under anaerobic conditions (for SRB enrichment details see Carlier et al. 2019). The SRB consortium is maintained in the laboratory through successive cultures in Postgate B medium inoculated with 1 to 10% (v/v) of previous cultures. A fresh culture was prepared and used when all sulfate in the medium had been reduced to sulfide. Sulfate reduction was monitored by analysing the sulfate and sulfide concentrations in the culture medium every 3 days.

**Fig. 1** Aerial view of the São Domingos mining area and a closer view of the sampled zone obtained from Google Maps: coordinates: 37°40'06.7"N 7°29'28.5"W. **1** Open pit mine; **2** Sampled impoundment with extreme acid mine drainage (AMD); **3** Another AMD impoundment; **A** Roasted pyrite ore slag; **B** modern slag





To find the optimal sulfide to Cu ratio (S:Cu) that would maximize Cu precipitation, a fixed volume of stripping solution was mixed with different volumes of bacterial culture media to test different S:Cu ratios above the stoichiometric value of 1:1 for CuS (covellite). The mixtures were maintained in closed Falcon tubes for 24 h at room temperature ( $25 \pm 3$  °C), and the volumes were then adjusted to a constant volume with distilled water to facilitate centrifugation and calculations. Afterwards, the mixtures were centrifuged at  $2500 \times g$  for 20 min at room temperature, and the supernatants were collected and used for Cu determination and mass balance calculations of Cu precipitation efficiencies.

After removing the supernatant, the precipitates were covered with 45 ml of a 50% (v/v) ethanol in water solution and sonicated for 15 min. The samples were then centrifuged for 15 min at  $2500 \times g$  for 10 min at room temperature, and the supernatant was discarded. Afterwards, they were washed overnight with 96% ethanol in an orbital shaker and centrifuged at  $2500 \times g$  for 60 min at room temperature, and the supernatant was removed. Finally, the precipitates were dried under vacuum overnight.

## Analytical Methods

A pH/E meter GLP 21 (Crison) with a glass pH electrode (VWR, SJ 223) was used to measure pH. A Pt electrode coupled with a reference-saturated calomel electrode (CRISON, 52 61) was used to measure redox, which was converted to Eh using a conversion factor of 241 mV. A UV–visible spectrophotometer DR2800 (Hach-Lange) was used to measure sulfate and sulfide concentrations using the sulfaVer4 (Method 8051, Hach-Lange) and the methylene blue (Method 8131, Hach-Lange) methods, respectively. The samples collected for metals determination were acidified with concentrated nitric acid (5%). Flame atomic absorption spectroscopy (FAAS) with a novAA 350 system (Analytik Jena) was used to measure the concentrations of Fe, Zn, Cu, Mn, and chromium (Cr), and microwave plasma atomic emission spectrometry with a 4200 MP-AES (Agilent) was used to measure the concentrations of Al, arsenic (As), and cobalt (Co). In both methods, calibration curves were built using standards prepared from the following stock solutions in 0.5 M HNO<sub>3</sub>: Fe(NO<sub>3</sub>)<sub>3</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, and NaNO<sub>3</sub> (Merck Certipur, Germany); Mn(NO<sub>3</sub>)<sub>2</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, As(NO<sub>3</sub>)<sub>3</sub>, and Co(NO<sub>3</sub>)<sub>2</sub> (Panreac AA, Spain); and Cr(NO<sub>3</sub>)<sub>3</sub> (BDH Laboratory Supplies, England). The concentrations of lead (Pb), nickel (Ni), selenium (Se), cadmium (Cd), magnesium (Mg), sodium (Na), and calcium (Ca) were determined by inductively coupled plasma mass spectrometry (ICP-MS) at an external accredited laboratory (Hidrolab, Spain). Ferrous iron (Fe<sup>2+</sup>) concentrations were determined with a UV–visible spectrophotometer DR2800 (Hach-Lange) using the 1,10-phenanthroline (Method 8146,

Hach-Lange) procedure at 510 nm, and ferric iron (Fe<sup>3+</sup>) concentrations were calculated by difference with total iron determined by FAAS.

The precipitates collected and washed in the recovery experiments were analysed by x-ray diffraction (XRD), by a variable pressure scanning electron microscope coupled with energy dispersive x-ray spectrometry (VP-SEM–EDX), and by transmission electron microscopy (TEM). XRD analysis was performed using a PANalytical X'Pert Pro powder diffractometer, operating at 45 kV and 30 mA, with Cu K $\alpha$  radiation filtered by Ni. The XRD patterns were recorded using an X'Celerator detector, with a step size ( $2\theta$ ) of  $0.03^\circ$  and a time per step of 400 s. Peak analysis and crystalline phase identification were conducted using High-Score Plus software with the ICDD PDF-2 database. The crystal size of each sample was estimated using the Scherrer equation,  $CS = \frac{K \cdot \lambda}{\beta \cdot \cos \theta}$ , considering a form factor of 0,94. VP-SEM–EDX analysis was carried out using a Hitachi™ S3700N SEM coupled to a Bruker™ XFlash 5010 SDD EDS Detector®. The samples were analysed at low vacuum (40 Pa) with an accelerating 5- and 20-kV voltage.

For the TEM analysis, precipitates were resuspended in ethanol and sonicated for 30 min to pulverise the samples. Then, 5  $\mu$ l of each sample were applied to 400 mesh Cu grids with thin carbon support (01844-F, Carbon Film only on 400 mesh, Cu, Tedpella), and the grids were dried and stored in a desiccator until imaging. Samples in the grids were imaged with a JEOL JEM-2100 electron microscope, operating a LaB6 electron gun at 200 kV, and images were acquired with a “OneView” 4 k  $\times$  4 k CCD camera.

To analyze the purity of covellite, 64.47 mg of precipitates (weighted using a Sartorius MSA36S-000-DH Micro Balance) were dissolved in 2.5 mL of aqua regia using a temperature ramp from 50 to 107 °C for 6 h, followed by a period of 16 h at 107 °C. At the end, 4 mL of concentrated nitric acid was added, and the final volume (6.2 mL) was noted for calculations. Finally, a 1:3 dilution in dionized water (Milli-Q® purification system) was used for elemental analysis.

## Results and Discussion

### Extreme AMD

The AMD sample collected at the São Domingos inactive mine from the impoundment near the old sulfur factories of Achada do Gamo was analyzed at CCMAR's laboratories for pH, sulfate, Fe, Al, Cu, Zn, Mn, As, and Co). In addition, several other metals (Cr, Pb, Ni, Se, Cd, Mg, Na, Ca) were determined by an external accredited laboratory. The AMD composition is presented in Table 1.

**Table 1** Initial characterization of the extreme AMD sample from Mina de São Domingos (impoundment next to the sulphur factory ruins at Achada do Gamo) collected on 25 October 2018 [mg/L, and standard units for pH]

Parameter	Value	Standard deviation
pH	1.19	–
SO <sub>4</sub> <sup>2–a</sup>	142,000	15,100
Fe <sup>a</sup>	63,200	6074
Fe <sup>3+</sup>	55,500	6630
Fe <sup>2+</sup>	7770	551
Al <sup>a</sup>	6470	148
Cu <sup>a</sup>	5250	313
Zn <sup>a</sup>	1960	449
Mn <sup>a</sup>	131	2
As <sup>a</sup>	21.40	0.09
Co <sup>a</sup>	6.46	0.03
Pb <sup>b</sup>	5.280	–
Ni <sup>b</sup>	3.040	–
Se <sup>b</sup>	1.990	–
Cd <sup>b</sup>	1.890	–
Cr <sup>a</sup>	1.16	0.07
Mg <sup>b</sup>	0.260	–
Na <sup>b</sup>	0.251	–
Ca <sup>b</sup>	0.138	–

<sup>a</sup>Averages and standard deviations of five determinations using independent dilutions at CCMAR

<sup>b</sup>Analysis at the accredited laboratory Hidrolab (see analytical methods)

The acidity and the pollutant concentrations in the AMD sample used in our work were much higher than those in samples collected from the flowing AMD streams, which usually have pH values between 2 to 3 and have the following approximate pollutant concentration ranges: sulfate (1000–5000 mg/L), Al (100–500 mg/L), Fe (50–500 mg/L), Zn (20–150 mg/L), Cu (20–100 mg/L), and Mn (5–20 mg/L) (e.g. Costa and Duarte 2005; Costa et al. 2008). The AMD sampled can be classified as *High-acid* and *Extreme-Metal* using the Ficklin diagram, where the sum of the concentrations of Zn, Cu, Pb, Cd, Co, and Ni (rather than more common metals such as Fe, Al, and Mn) is plotted against pH (Ficklin et al. 1992; GARD Guide, Chapter 2, 2022).

## Solvent Extraction

### Extractant Selection

Among the five tested extractants, Acorga M5640 and LIX 622 more specifically extracted Cu, while LIX 864, LIX 54, and LIX 622 N co-extracted iron and zinc, iron, and aluminium, and iron, respectively (supplemental Fig. S1). The extraction distribution ratios are presented in Table 2.

**Table 2** Extraction distribution ratios (D) of primary metals in the extreme AMD sample, with 15% (v/v) of each extractant diluted in Shell GTL + 2.5% (v/v) octanol, using an A/O = 1/1 and a contact time of 30 min at room temperature (25 ± 3 °C)

Extractants	Metal	Distribution ratio (D) <sup>a</sup>
ACORGA M5640	Fe	–
	Al	–
	Cu	5.16
	Zn	–
	Mn	–
Lix622	Fe	–
	Al	–
	Cu	0.59
	Zn	–
	Mn	–
Lix864	Fe	0.26
	Al	–
	Cu	4.38
	Zn	0.005
	Mn	–
Lix54	Fe	0.24
	Al	0.01
	Cu	0.02
	Zn	–
	Mn	–
Lix622N	Fe	0.11
	Al	–
	Cu	5.77
	Zn	–
	Mn	–

– metal not detected in extractant, A/O aqueous/organic volume ratio

$$^aD = [M_{org}]_f / [M_{aq}]_f$$

Of the 5,250 ± 313 mg/L initial Cu concentration, 85 ± 4% was extracted from the aqueous phase to the organic phase containing Acorga M5640, and 37 ± 1% was extracted to the organic phase with LIX 622. LIX 54 preferentially extracted Fe over Cu from this AMD sample: just 2 ± 1% of Cu was extracted, but 20 ± 1% of Fe was co-extracted.

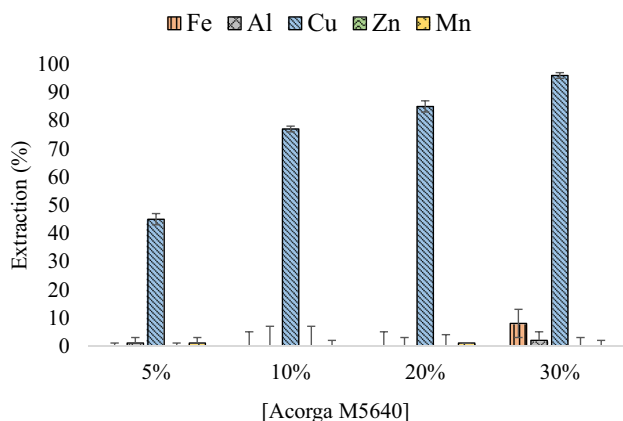
The higher efficiency of Acorga M5640 to specifically extract Cu from such extreme AMD confirms previous results obtained using model and leaching multi-metallic solutions. For example, Ochromowicz and Chmielewski (2013) showed that Acorga M5640 is a superior extractant for Cu compared to LIX 984 N and LIX 612 N-LV for multi-metallic sulfuric acid leachates. Wang et al. (2019) successfully extracted over 90% of Cu from multi-metallic sulfuric acid leachates of printed circuit boards (from electrical and electronic equipment) using Acorga M5640, and Tanaydin and Demirkiran (2020) found that Cu can be

extracted from perchloric acid leachates of malachite ore using Acorga M5640.

### Extraction Optimisation and Characterisation

Based on the results obtained in the extractants' screening, Acorga M5640 was selected for the subsequent experiments to optimise and characterise the extraction of Cu from the extreme AMD sample collected at the São Domingos Mine.

For the optimisation, different concentrations of Acorga M5640 in the organic phase were tested to find the best ratio of the extractant active compound to Cu ions. The Cu extraction percentage increased as the Acorga M5640 concentration increased in the organic phase, and the maximum efficiency of  $96.0 \pm 3\%$  (which corresponds to  $5,040 \pm 158$  mg/L Cu extracted) was achieved with 30% (v/v) Acorga M5640 (Fig. 2). This corresponds to 0.57 mol/L of the extractant's active compound (5-nonyl-2-hydroxy-benzaldoxime) to 0.0694 mol/L of Cu extracted, making an  $\approx 8:1$  ratio of active compound to Cu ions. Considering the complexity of the chemical matrix in the AMD sample, this can be considered a good ratio. It is just four times higher than the theoretical ratio of 2:1 in the equation expressing the extraction reaction of Cu with Acorga M5640 in sulfuric systems (see Eq. 1). On the other hand, the 8:1 ratio estimated in our work is three times lower than the 24:1 ratio reported by Agarwal et al. (2010) when using 20% (v/v) Acorga M5640 (0.38 M active compound) diluted in ShellSol D70 (also a kerosene-like diluent); the 24:1 ratio result held for both the initial aqueous solutions these authors tested (1 g/L  $\text{Cu}^{2+}$  and a more complex solution of 1 g/L  $\text{Cu}^{2+}$ , 40 g/L Zn(II), and 15 g/L Fe(III) at pH 1.4).



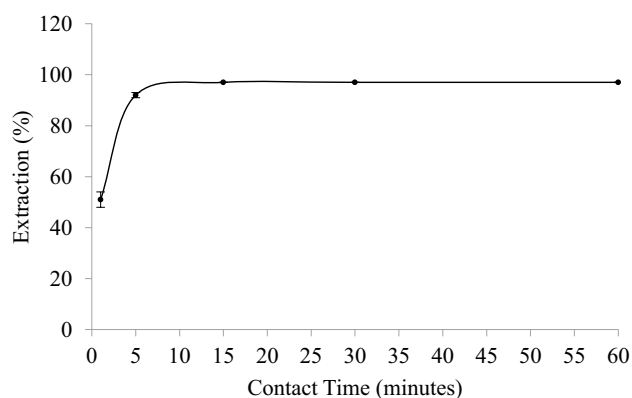
**Fig. 2** Extraction efficiencies from the extreme AMD with Acorga M5640 at concentrations of 5, 10, 20 and 30% (v/v) diluted in Shell GTL+2.5% (v/v) octanol, using an A/O=1/1 and a 60 min contact time at room temperature ( $25 \pm 3$  °C). Results are averages of triplicates, and the error bars are standard deviations

In the test with 30% Acorga M5640, the extraction of iron reached  $8 \pm 5\%$ , which reveals a high co-extraction of iron since its concentration in the initial extreme AMD sample is about 12 times higher than the concentration of Cu. This corresponds to a final concentration in the organic phase of  $5,060 \pm 3,160$  mg/L iron, similar to the Cu concentration achieved. Nevertheless, it is possible to separate these two metals in the stripping process (see below). The iron extraction (albeit in a small percentage) raised the question of some loss of specificity for Cu under these extraction conditions, leading to additional analysis of another concentrated contaminant: arsenic. The results ( $0 \pm 1\%$  arsenic removal) indicate that this metalloid is not efficiently extracted. Thus, 30% Acorga M5640 was chosen as the optimal percentage, and additional parameters were studied using this extractant concentration, including contact time (kinetics), Cu loading capacity in the organic phase, efficiency of stripping agents, and organic phase recyclability.

Finally, the raffinate water resulting from the extraction of Cu under these conditions has the potential to undergo further recovery because it still contains high concentrations of sulfate (133 g/L), metals, and metalloids (primarily Fe: 58,200 mg/L, Al: 6,340 mg/L, Zn: 1,960 mg/L, Mn: 131 mg/L and As: 21 mg/L). Indeed, zinc is another important metal with growing demand, for which the recovery from secondary sources will need to have a major role in the next 50 years (Sverdrup et al. 2019). Thus, the recovery of zinc from industrial wastes has been a focus of research for decades (e.g. Jha et al. 2001). Moreover, sulfuric acid could potentially be recovered and contribute to the economic feasibility of an integrated recovery process from extreme AMD samples. For example, Nleya et al. (2016) have reviewed techniques used to recover sulfuric acid from various wastewater solutions and studied the sustainability assessment of the recovery and utilisation of acid from AMD. In any case, the raffinate from the Cu extraction process under study in our work cannot be released to the environment without prior treatment.

### Contact Time (Kinetics)

The extraction of Cu from the extreme AMD using 30% (v/v) Acorga M5640 with an aqueous:organic (A/O) volume ratio of 1:1 required 5 min to transfer 92% of the Cu to the organic phase; after 15 min, the maximum Cu transfer ( $\approx 97\%$ ) was achieved (Fig. 3). Wang et al. (2019) found that only 1 min was needed with  $\text{CuSO}_4$  and chloride leaching solutions (with  $\approx 6$  g/L Cu at pH 1.1) to achieve over 90% Cu extraction with 16% (v/v) Acorga M5640 in kerosene. One significant difference that could have accounted for the longer time to achieve the extraction equilibrium in our work is the extremely high concentrations of other metals in our AMD sample. Nevertheless, our results are fairly consistent



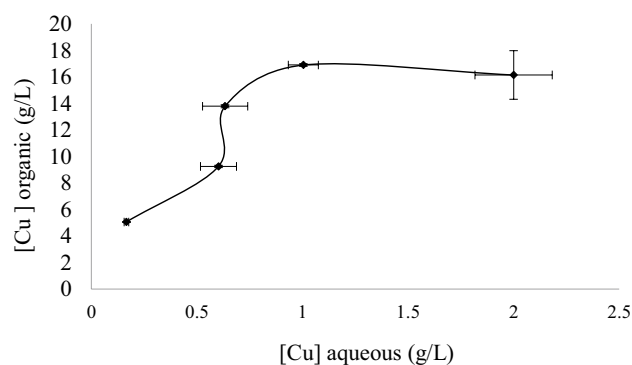
**Fig. 3** Copper extraction efficiency from the extreme AMD with 30% v/v ACORGA M5640 in Shell GTL+2.5% (v/v) octanol, using an A/O=1/1 and different contact times (1, 5, 15, 30 and 60 min) at room temperature ( $25 \pm 3$  °C). Results are averages of duplicates and the error bars are mean deviations

with the 85% Cu recovery from sulfuric acid feed solutions of 10 g/L Cu at pH 0.75 reported by Ochromowicz and Chmielewski (2013), who used 30% (v/v) Acorga 5640 diluted in a kerosene-type diluent Escaid® 100, with a contact time of 5 min at 25 °C and an A/O ratio of 0.75:1. In addition, Wang et al. (2019) did not add alcohol to the diluent, and in our work, 2.5% (v/v) octanol was added. Adding alcohol to the solvent used to dilute Acorga M5640 may affect the extraction of Cu. Agarwal et al. (2010) reported that adding 5% isotridecanol to the organic phase with 10% Acorga M5640 slightly impeded the rate of recovery by changing the equilibrium to 96% extraction in 1 min instead of the 99% achieved without the addition of alcohol or with the addition of 2.5% isotridecanol.

### Loading Capacity of Cu in the Organic Phase

The loading capacity of Cu extracted from the extreme AMD to 30% (v/v) Acorga M5640 in Shell GTL with 2.5% (v/v) octanol was determined by raising the aqueous/organic (A/O) volume ratio (Fig. 4). The results revealed good extraction performance, with a maximum loading capacity of 16.2 g/L of Cu in the organic phase. Afterwards, three consecutive cycles of extraction without the stripping step were carried out, always using the same organic phase but new extreme AMD in each cycle, to evaluate the potential to build up the Cu concentration in the organic phase through successive extractions and the capacity of accumulating concentrations of Cu up to  $\approx 16$  g/L (Table S1).

Agarwal et al. (2012) studied the extraction equilibrium of Cu from sulfate media with Acorga M5640 in ShellSol D70 (kerosene-like solvent). They proposed a model considering the non-ideality of the extractant (due to the dimerisation of the active compound) to predict the distribution ratio



**Fig. 4** Equilibrium isotherm for the extraction of copper from the extreme AMD, using different A/O volume ratios (1/1, 2/1, 3/1, 4/1, and 5/1, graph points from left to right) using 30% (v/v) Acorga M5640 in Shell GTL+2.5% (v/v) octanol and a contact time of 60 min at room temperature ( $25 \pm 3$  °C). Results are averages of duplicates and the error bars are mean deviations

and the Cu loading isotherms. In that work, they reported maximum loading capacities of 11 g/L Cu in 20% (v/v) Acorga M5640 in ShellSol D70, using extraction isotherms built either with simulated values or experimental results. Subsequently, Vasilyev et al. (2017) studied the extraction equilibrium of Cu in the organic phase over a wide range of Acorga M5640 extractant (5–25 vol%) in kerosene and using various Cu concentrations (1–45 g/L) in the aqueous phase, and confirmed that the extraction is highly correlated with the total concentration of the extractant in the organic phase. Moreover, the phase equilibrium model they developed and validated also accounts for the non-ideality of the organic phase: the extraction of Cu from the aqueous phase increased nonlinearly with an increase of extractant concentration in the organic phase for values above  $\approx 14$ % (v/v) Acorga M5640, with a less pronounced increase in Cu extraction at higher values. In addition to the limitations due to the high viscosity and high operational costs of concentrated Acorga M5640, these authors also pointed to chemical limitations. However, according to Vasilyev et al. (2017) neither the dimerisation of the unreacted extractant molecules nor the solvation of the Cu-extractant complexes was sufficient to explain the organic phase non-ideality.

In our work, Acorga M5640 was also diluted in a kerosene-like solvent (Shell GTL), but 2.5% (v/v) octanol was added for two reasons: (1) according to Agarwal et al. (2010), although the presence of 2.5% (v/v) isotridecanol in the solvent does not increase the Cu transference, it favours the rejection of iron; (2) according to Ferreira et al. (2010), adding 2.5% (v/v) isotridecanol to the solvent improved the stripping efficiency. Ferreira et al. (2010) reported a loading capacity of 5.2 g/L Cu in 10% (v/v) Acorga M5640 in ShellSol D70 with 2.5% isotridecanol when using leaching solutions with pH values of  $\approx 1$  as aqueous phases. Agarwal



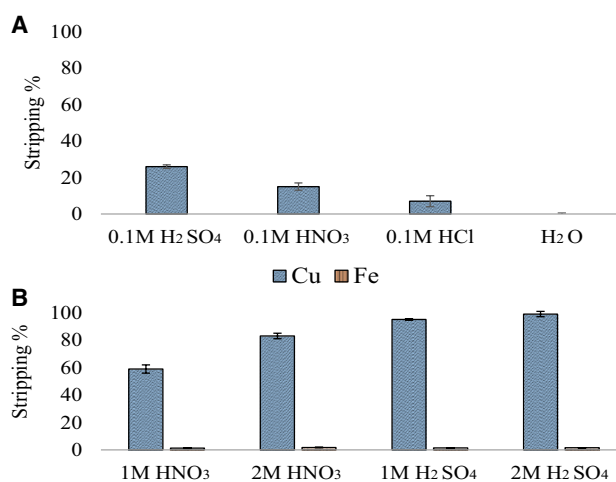
et al. (2010) have determined maximum loading capacities of 4.8, 5.2, and 5.5 g/L Cu for organic phases with 10% (v/v) Acorga M5640 in kerosene-like solvent (ShellSol D70) with 5% isotridecanol, with 2.5% isotridecanol, and without any alcohol, respectively. These authors also reported 10 and 11 g/L Cu loading capacities for systems with 20% (v/v) Acorga M5640 in solvents with 5% isotridecanol and without added alcohol, respectively. This allows us to roughly estimate a loading capacity of 10.5 g/L Cu for an organic phase with 20% (v/v) Acorga M5640 in a solvent with 2.5% alcohol.

By plotting these reported loading capacities for systems with Acorga M5640 in solvents with 2.5% alcohol and the loading capacity of Cu achieved in our work against the respective percentages of extractant, a linear correlation was obtained ( $y = 0.55x - 0.3667$ ) with high confidence ( $R^2 = 0.9996$ ). This suggests a linear phase equilibrium model for systems using 10% to 30% (v/v) Acorga M5640 in kerosene-like solvents with 2.5% (v/v) alcohol. Our results also suggest the ideality of such type of organic phase, contrasting with the non-linear models reported by Agarwal et al. (2012) and Vasilyev et al. (2017) for this extractant when diluted in such solvents without any alcohol. Nevertheless, the objective of our work was not to develop and validate a phase equilibrium model but rather to evaluate the feasibility of Cu recovery from complex wastewaters such as the extreme AMD.

### Stripping Agents

Different stripping agents were tested for the re-extraction of Cu from the loaded organic phases, which consisted of 30% (v/v) Acorga M5640 in Shell GTL with 2.5% (v/v) octanol. First, tests using three different acidic solutions at 0.1 M revealed stripping efficiencies in the following order: sulfuric acid > nitric acid > hydrochloric acid, although all had efficiencies below 30% (Fig. 5a). Then, a further experiment with the two best acidic solutions at higher molarities achieved the highest Cu stripping efficiency of sulfuric acid (Fig. 5b). In that experiment, sulfuric acid concentrations of 1 M and 2 M produced Cu stripping percentages of 95% and 99%, yielding Cu concentrations in the stripping solutions of 4,790 and 4,990 mg/L, respectively. Moreover, the stripping percentages of iron were low (1.3% to 1.8%) in the four tests, which in this case is particularly important due to the above-mentioned high co-extraction of this metal. The sulfuric acid concentrations of 1 M and 2 M stripped 1.5% and 1.6% of the iron in the organic phase, generating concentrations of this metal in the stripping solutions of 76 and 81 mg/L, respectively.

Other works have shown that sulfuric acid is highly efficient for stripping Cu from organic phases with Acorga M5640 (e.g. Ferreira et al. 2010; Vasilyev et al. 2017; Wang



**Fig. 5** Copper and iron stripping from loaded 30% (v/v) Acorga M5640 in Shell GTL + 2.5% (v/v) octanol, with an A/O = 1/1 and contact time of 60 min at  $25 \pm 3$  °C, **a** with sulfuric acid, nitric acid, and hydrochloric acid at 0.1 M and with a control of distilled water, **b** with nitric acid and sulfuric acid at 1 M and 2 M. Results are averages of duplicates, and the error bars are mean deviations

et al. 2019). Moreover, according to experimental data reported by Alguacil et al. (2004), in addition to a higher stripping efficiency, sulfuric acid has a less degradative effect on Acorga M5640 than nitric acid. Therefore, 2 M sulfuric acid was selected as the optimal stripping solution for the process, and was used in the subsequently reported experiments.

### Organic Phase Recyclability

In practical applications, the stability and recyclability of extractants are required factors for the economic and environmental sustainability of the extraction process. Supplemental Fig. S2 shows the effect of reusing the organic phase (30% (v/v) Acorga M5640 in Shell GTL with 2.5% (v/v) octanol) in successive cycles of extraction and stripping. After five extraction cycles, the Cu extraction efficiency remained unchanged. In the first cycle, the Cu extraction efficiency was  $96 \pm 1\%$ , and in the fifth cycle, it was  $96.0 \pm 0.5\%$ .

Deep et al. (2010) reported insignificant changes ( $< 0.5\%$ ) in five successive cycles of extraction and stripping to recover Cu from a sulfuric acid leaching liquor of a mined zinc concentrate (from the Neves-Corvo Mine, Portugal), using 25% (v/v) Acorga M5640 in ESCAID 110 plus 12.5% (v/v) isodecanol as the organic phase, and using a synthetic spent cell electrolyte (25 g/L Cu in 180 g L/H<sub>2</sub>SO<sub>4</sub>) as the stripping solution. However, after the stripping step, the authors washed the organic phase with water before its reuse in subsequent extraction cycles; in our experiments, the organic phase was directly reused without a washing

step. Wang et al. (2019) also reused the organic phase (16% (v/v) Acorga M5640 in kerosene) directly, without washing after stripping, in successive cycles of extraction and stripping (with 2.5 M sulfuric acid) when testing the recovery of Cu from a sulfuric acid leaching liquor of printed circuit boards from electronic equipment waste. They reported a 5% decrease over the first five cycles, followed by stabilising extraction efficacy in seven subsequent additional cycles.

In our work, despite the co-extraction of iron and its accumulation in the organic phase (since it is barely stripped with 2 M sulfuric acid), the stable Cu extraction efficiency in the successive extraction cycles (Fig. S2) indicates that iron is not effectively competing with Cu for the extractant's active compound. While Cu ions form complexes with the active compound (5-nonyl-2-hydroxy-benzaldoxime) of Acorga M5640, steric hindrance prevents the formation of iron complexes (Deep et al. 2010). Thus, the slight decrease in the extraction efficiency observed by Wang et al. (2019) in five successive cycles may have been caused by the relatively low Cu stripping efficiency (90%) reported by those authors, compared with that achieved in our work (99%).

Another important characteristic for the successive utilisation of the organic phase is the immiscibility of both organic and aqueous phases. In the system under study, the phases separated clearly and quickly once the stirring stopped. Moreover, an experiment consisting of two extractions performed in 100 mL cylinders (with strong magnetic stirring for 60 min to achieve adequate contact between phases) revealed that the volumes (50 mL each) did not change (for an error of 0.5% due to the visual analysis of volumes using cylinder markings). Therefore, major losses of extractant and organic solvent in large-scale operations are not expected.

### Complete Cu Extraction

Another important aspect is extracting all Cu from the extreme AMD to avoid putative Cu contamination in subsequent processes that aim to recover other metals. The experiments of consecutive extraction cycles using new organic phases and the same aqueous phase revealed that three cycles are required to extract Cu from the extreme AMD to a concentration below the FAAS detection limit in the aqueous phase (supplemental Fig. S3).

### Electrolyte Production for Cu Electrowinning

The hydrometallurgical processes for Cu recovery generally involve three steps: leaching, solvent extraction, and electrowinning. In Cu electrowinning, the  $\text{Cu}^{2+}$  dissolved in the  $\text{H}_2\text{SO}_4$  (electrolyte solution) is reduced on cathode surfaces to pure metallic Cu when direct current is applied between anodes and cathodes. The spent electrolyte solution,

which will still have a relatively high concentration of Cu ( $\approx 25$  to  $\approx 35$  g/L Cu), is returned to the solvent extraction step as a stripping solution to recover  $\text{Cu}^{2+}$  from the loaded organic phase (Aksamitowski et al. 2018; Alguacil and Regel-Rosocka 2018; Schlesinger et al. 2011). Thus, when developing a hydrometallurgical process involving solvent extraction and electrowinning, it is essential that Cu concentrations in the initial stripping solution exceed those found in the spent electrolyte solutions. With that aim, four consecutive cycles of extraction and stripping were carried out, always using the same stripping solution (2 M  $\text{H}_2\text{SO}_4$ ) but with new organic phases loaded with Cu (Table 3). The results show that it is possible to achieve  $\approx 35$  g/L Cu in the stripping solution, maintaining stripping efficiencies above 95%, and that it is feasible to reach  $\approx 46$  g/L Cu even if the stripping efficiency drops to  $\approx 77\%$ . This means that with this process, it is viable to extract Cu from this extreme mine water and transfer it to electrolyte-like solutions with Cu concentrations suitable for the electrowinning process.

### Cu Recovery with Biogenic Sulfide

The recovery of Cu from a loaded stripping solution (2 M  $\text{H}_2\text{SO}_4$  with  $8,360 \pm 124$  mg/L Cu) obtained in the SX process under study was attempted using sulfide generated by SRB. The SRB culture inoculated for that purpose evolved as expected (Supplemental Fig. S4) and was used 28 days after inoculation, when most of the sulfate ( $> 90\%$ ) had been reduced to sulfide (the concentration of sulfide was  $377 \pm 9$  mg/L). The results achieved by mixing a fixed volume of stripping solution with different volumes of the supernatant from a bacterial culture indicate that an S:Cu ratio of 1.75 is needed to ensure complete Cu precipitation ( $> 95\%$ ), and higher ratios are unnecessary (Fig. S5).

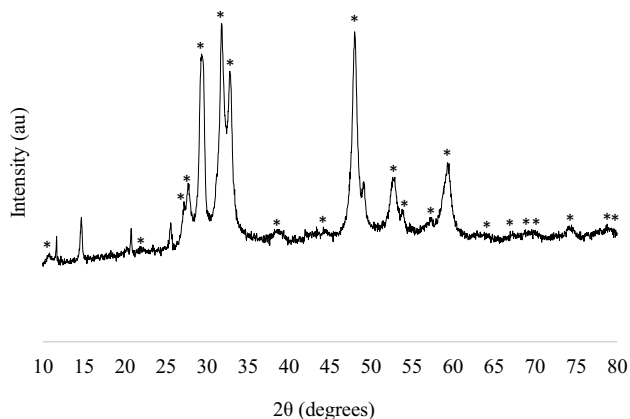
The XRD pattern generated with the precipitates produced (after washing) revealed prominent peaks corresponding to covellite ( $\text{CuS}$ ), along with a few small peaks that

**Table 3** Copper concentrations in the initial organic phase (30% Acorga M5640 in Shell GTL + 2.5% (v/v) octanol) and final stripping solution (2 M  $\text{H}_2\text{SO}_4$ ) in four consecutive cycles of extraction and stripping

Cycle	[Copper] in initial organic phase (g/L)	[Copper] in final stripping solution (g/L)	Copper stripping efficiency (%)
1	$5.56 \pm 0.07$	$5.3 \pm 0.5$	95.3
2	$16.11 \pm 0.03$	$21 \pm 3$	97.5
3	$13.8 \pm 0.1$	$34.5 \pm 0.9$	97.8
4	$15 \pm 2$	$46 \pm 3$	76.7

The same stripping solution was used with new organic phases loaded with copper. Conditions were an A/O ratio of 1/1 and a contact time of 60 min at room temperature ( $25 \pm 3$  °C). Results are averages of 3 replicates  $\pm$  standard deviations

did not match any crystalline phase pattern in the database (Fig. 6). The estimated crystal size of the covellite phase was 15 nm. Mapping of the precipitates using SEM–EDX revealed the presence of Cu and sulfur in the particles, as expected for covellite (CuS), and traces of carbon around them indicating low contamination of precipitates with



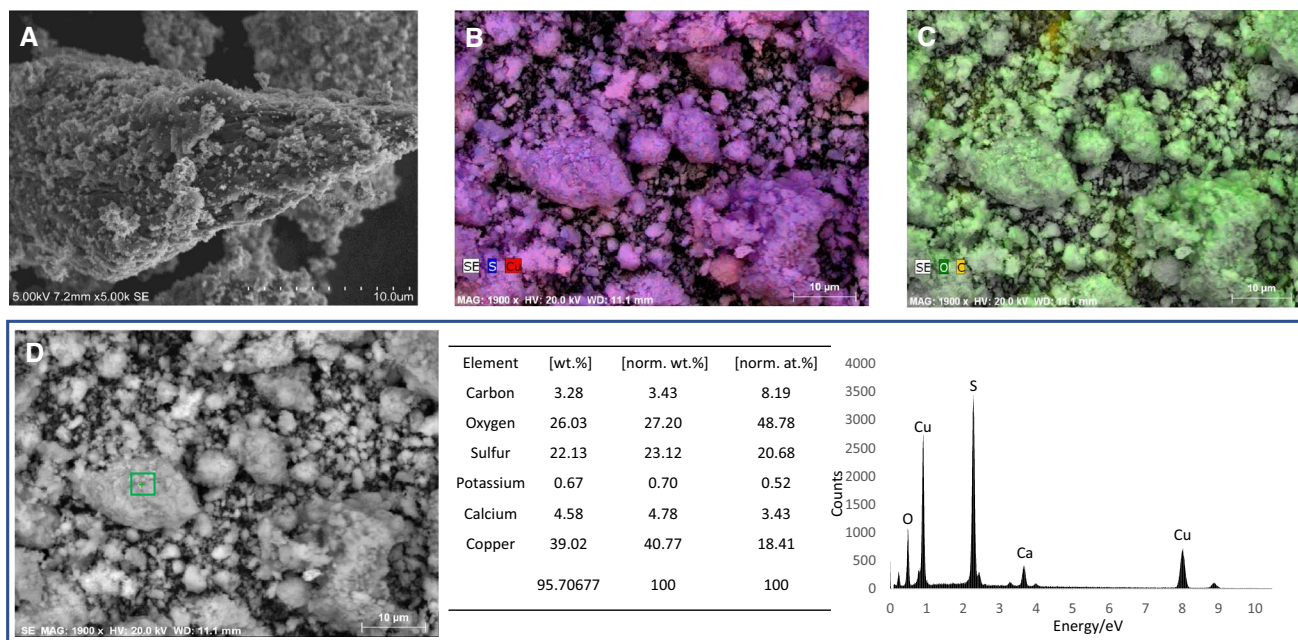
**Fig. 6** XRD pattern of precipitates obtained by adding the supernatant from a biogenic sulfide-rich ( $377 \pm 9 \text{ mg/L S}^{2-}$ ) SRB culture medium to a 2 M  $\text{H}_2\text{SO}_4$  stripping solution loaded with copper ( $8356 \pm 124 \text{ mg/L}$  copper) from the solvent extraction process to recover copper from the extreme AMD. The “\*” symbol refers to the peaks for covellite (ICDD PDF2 database, reference code 01–078–0877)

organic compounds. Moreover, point analysis of one of the particles showed an approximate Cu:S ratio of approximately 18:21, which is close to the expected 1:1 molar ratio for covellite (Fig. 7).

The samples prepared for TEM analysis showed a priori evidence of incomplete dispersion of crystalline particles (aggregates were visible by eye). Still, the samples were suitable for TEM imaging and the results allowed us to identify two types of particles:

- Nanoparticles with a wide range of sizes and shapes, caused by the agglomeration of different numbers of smaller unique nanoparticles, for which it is possible (in some cases) to recognise hexagonal shapes and internal crystalline structures (Fig. 8). Automatic measurements of 4,820 particles in the 12 TEM images, using the ParticleSizer v1.0.9 plugin (Wagner and Eglinger 2021) on the Fiji–ImageJ software (Schindelin et al. 2012), revealed a particle Feret size range from 3 to 87 nm with a mean of  $12 \pm 9 \text{ nm}$  and sizes fitting a normal distribution (for a 1% probability ( $\alpha=0.01$ ) in a Kolmogorov–Smirnov test).
- Micro-sized structures of needle-like and radiating forms containing multiple small nanoparticles (Fig. 9). Manual measurements of 10 particles, using the Fiji – ImageJ software (Schindelin et al. 2012), revealed a particle Feret size range from 2 to  $5.5 \mu\text{m}$  with a mean of  $4 \pm 1 \mu\text{m}$  (the size distribution of these large agglomerates was not studied).

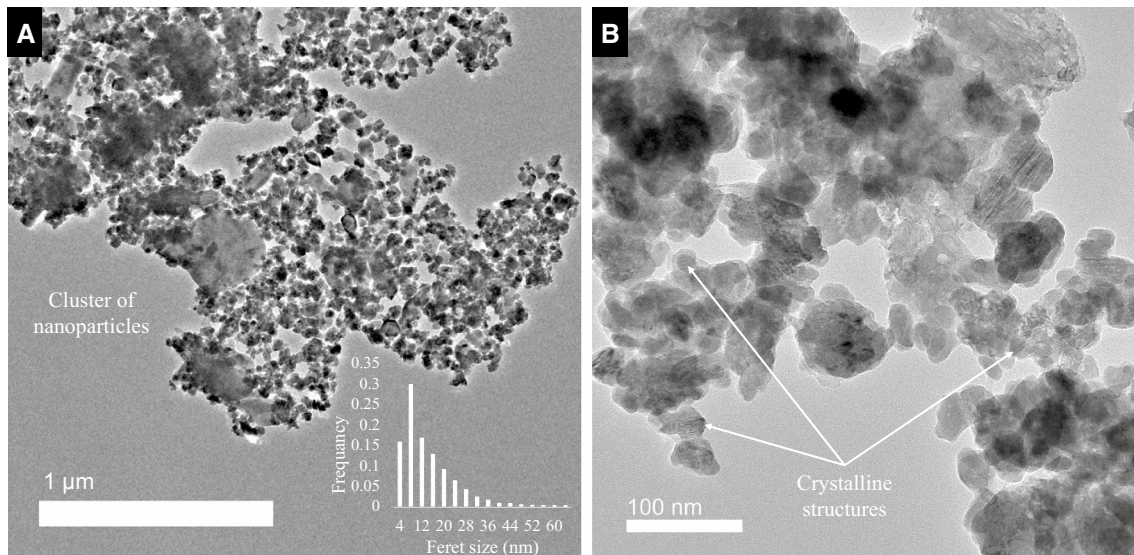
These results reveal that adding biogenic sulfide to the Cu stripping solution can produce covellite nanoparticles



**Fig. 7** SEM–EDX mapping of precipitates obtained by adding the supernatant from a biogenic sulfide-rich ( $377 \pm 9 \text{ mg/L S}^{2-}$ ) SRB culture medium to a 2 M  $\text{H}_2\text{SO}_4$  stripping solution loaded with cop-

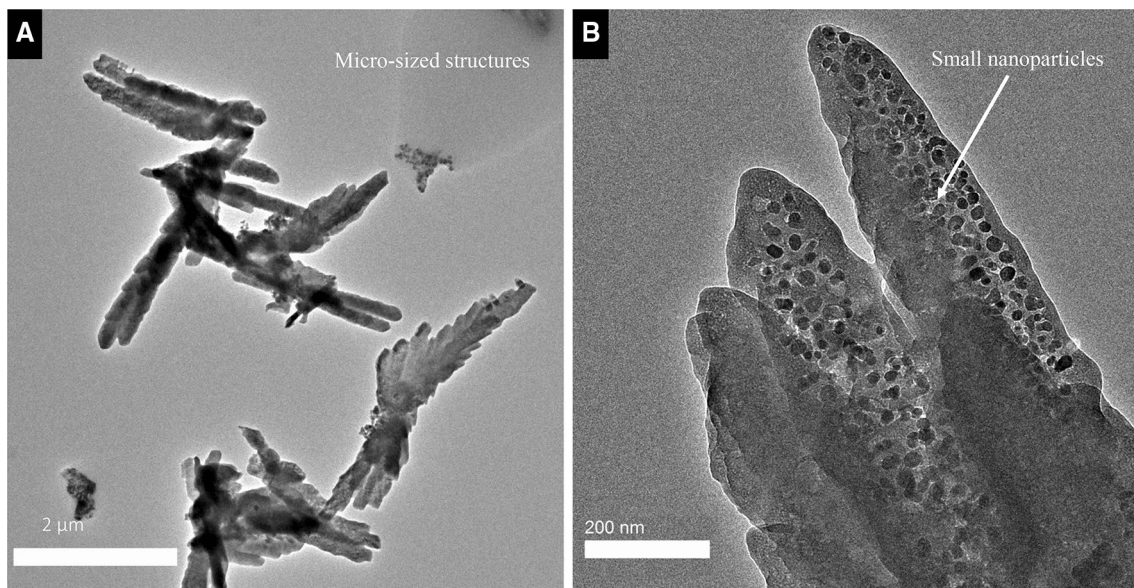
per ( $8,360 \pm 124 \text{ mg/L}$  copper). **A** SEM image of the particles. SEM–EDX mapping of **B** sulfur and copper, **C** carbon and oxygen. **D** point analysis of covellite





**Fig. 8** TEM images of precipitates obtained by adding the supernatant from a biogenic sulfide-rich ( $377 \pm 9$  mg/L  $S^{2-}$ ) SRB culture medium to a 2 M  $H_2SO_4$  stripping solution loaded with copper ( $8,360 \pm 124$  mg/L copper), showing **a** a cluster of nanoparticles of

multiple sizes together with the distribution of sizes for 4820 particles measured in 12 TEM images and **b** nanoparticles with visible hexagonal-like shapes and internal crystalline structures



**Fig. 9** TEM images of precipitates obtained by adding the supernatant from a biogenic sulfide-rich ( $377 \pm 9$  mg/L  $S^{2-}$ ) SRB culture medium to a 2 M  $H_2SO_4$  stripping solution loaded with copper

( $8,360 \pm 124$  mg/L copper), showing **a** a group of micro-sized particles of needle-like and radiating forms and **b** a detail of one structures with visible nanoparticles

aggregated in larger structures that may be larger than 10  $\mu m$ . Larger aggregates can be an advantage in a production process because it is easier to collect larger aggregates than nanoparticles. Sonication can be used to pulverise large aggregates into nanoparticles.

In a previous work in which a SRB growth medium containing biogenic sulfide was directly added to a much less

concentrated (100 mg/L Cu) artificial Cu sulfate solution, precipitation of Cu (>95%) as covellite particles was also achieved using an S:Cu ratio of 2:1 (Costa et al. 2013). These results, in combination with our own, suggest that it is possible to produce covellite (nano)particles from sulfuric acid stripping solutions containing a wide range of Cu concentrations. Therefore, the solvent extraction process



described herein can be applied to AMD waters of different Cu concentration levels and can be followed by a covellite precipitation process by adding biogenic sulfide-rich media to the loaded stripping solution.

It is known that  $\text{Cu}^{2+}$  ions can react with sulfide and form covellite ( $\text{CuS}$ ) precipitates at low pH values (e.g. Sampaio et al. 2009), and the production of covellite with biogenic sulfide directly added to AMD samples has been reported previously (e.g. Silva et al. 2019). However, to our knowledge, this is the first report about the addition of biogenic sulfide to a purified Cu solution obtained by SX from an AMD sample, which has the great advantage of reducing the risk of co-precipitation of other metal sulfide particles.

Due to their unique optical, electrical, and catalytic properties (Yadav et al. 2019), chalcogenide semiconductor covellite nanoparticles are promising new materials for a wide range of applications, including optoelectronic devices (Coughlan et al. 2017), solar cells (van der Stam et al. 2016), lithium-ion batteries (Jiang et al. 2019), nanoscale switches (Sakamoto et al. 2003), sensors (Coughlan et al. 2017), photodegradation of pollutants (Wang et al. 2009), photocatalysis (van der Stam et al. 2016), and biomedicine (Goel et al. 2014; Yadav et al. 2019). However, the purity of covellite must be considered for each specific application. In our work, analysis of the covellite revealed 97.3% purity for a covellite weight calculated based on the Cu concentration in the dissolved precipitates, and the sum of constituents other than Cu (supplemental Table S2). Moreover, the relatively high unidentified “other” constituents (1.5%) may be related to anions that could have binded to the metal cations (mainly calcium and iron) and formed precipitates. Therefore, further purification steps may be performed depending on the desired application.

## Conclusions

This work attempts to contribute in two ways to raising the interest in implementing metal recovery from AMD-affected areas. Such an approach will treat highly contaminated mine waters, decreasing the environmental impact of AMD, and simultaneously increase the circular economy of metals.

The reported results confirm the potential utility of using a SX process with 30% (v/v) Acorga M5640 in kerosene-like solvents with 2.5% octanol to extract over 95% of the Cu present in highly acidic, metal-rich AMD, generating 2 M sulfuric acid solutions with Cu concentrations greater than 45 g/L that are suitable as electrolytes for the well-established Cu electrowinning process that often accompanies the acid-leaching of oxide Cu ores.

Our work also demonstrates the feasibility of combining SX systems with biological processes that add biogenic sulfide at S:Cu ratios of  $\approx 2:1$  to recover the extracted Cu

as covellite nanoparticles. The covellite produced can be used in a variety of renewable energy, biomedical, and other applications.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s10230-022-00858-7>.

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