

# Solvent Extraction to Recover Copper from Extreme Acid Mine Drainage

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## Abstract

This study evaluated the application of a solvent extraction process from an extreme Acid Mine Drainage (AMD) (with  $5.3 \pm 0.3$  g/L Cu). The extractant Acorga M5640 showed high copper selectivity and 30% (v/v) of this extractant, extracted  $\approx 96\%$  of this metal with a maximum loading capacity of  $\approx 16$  g/L in the organic phase. Then, 2M sulfuric acid solution stripped  $\approx 99\%$  of copper and through successive stripping steps the concentration of copper was raised up to  $\approx 46$  g/L, which is suitable for the electrowinning process. Recyclability of the organic phase was also confirmed in five successive extraction and stripping cycles.

**Keywords:** Acid Mine Drainage, Solvent Extraction, Copper, Metal Recovery

## Introduction

Most strategic metal are obtained through mining from primary sources that are finite and rapidly decreasing as a result of population explosion and modern industrialization (Arndt *et al.*, 2017; Segura-Salazar & Tavares, 2018). Some estimates indicate that in the next 2–3 decades different industrial sectors will struggle to maintain their demand for several metals (Elshkaki *et al.* 2016; Frenzel *et al.* 2015; European Commission 2014). Based on world annual data of mining (for year 2018), 20 474 372 metric tons of copper are obtained per year (Reichl & Schatz, 2020) and according to the International Copper Study Group (2019), global consumption of this metal will continuously increase due to population growth, product innovation and economic development. In a recent study, Schipper *et al.* (2018) estimated the copper demand for the year 2100 to be in a range of 3 to 21 times the current demand. Thus, a combined production from mining of primary raw materials and from recycling and recovering from secondary sources is required.

In general, metals' recycling rates from secondary sources are still low and there is significant potential to increase the recovery

from such sources (Schäfer & Schmidt, 2019). In the case of copper, the recycling rates continuously decreased from 2011 to 2016 (from 36% to 29%) while the secondary refined production was quite stable over the same period (ICSG, 2018).

Solvent extraction (SX) is a method of separation used in the hydrometallurgical industry to separate and recover metals from aqueous leachates obtained from ores and secondary materials such as slags or tailings (Hedrich *et al.*, 2018). In these processes, organic phases of extractants diluted in solvents are used to separate target metal ions (e.g.  $\text{Cu}^{2+}$ ) from multimetallic leaching solutions, which are then stripped from the organic phase to aqueous pure solutions (Davis-Belmar *et al.* 2012; Ruiz *et al.* 2019).

Copper is present in high concentrations in the Acid Mine Drainage (AMD) generated at many mining sites such as São Domingos mining area in Portugal (Álvarez-Valero *et al.*, 2008). In this study a solvent extraction process using Acorga M5640 as extractant, like processes in place in the hydrometallurgical industry to separate copper from leaching solutions, was investigated for the separation of this metal but from an extreme AMD collected at Mina de São Domingos.

## Materials and methods

### *Extreme AMD*

The extreme AMD sample used in this work was collected at the São Domingos mine, Portugal, from a pond near the sulphur factory ruins, and was transported in the same day to the laboratory for characterization and copper SX tests. The pond is surrounded by roasted pyrite ores (sulphur factories ashes), iron oxides (hematite roasted pyrite) and leached materials in seasonal flooded areas (Álvarez-Valero *et al.*, 2008).

### *SX experiments*

SX was carried out by mixing the extreme AMD (aqueous phase (A)) with 30% (v/v) Acorga M5640 diluted in a kerosene-like solvent called Shell GTL with 2.5% (v/v) octanol (organic phase (O)) in 100 mL round bottom flasks, using a A:O ratio of 1:1 and contact with magnetic stirring during 30 minutes at room temperature ( $25 \pm 3$  °C). Initial ( $[M_{aq}]_i$ ) and final ( $[M_{aq}]_f$ ) concentrations of metals in the aqueous phase, measured before and after SX, were used to calculate concentrations in the final organic phase ( $[M_{org}]_f$ ); then, metals' extraction efficiencies were determined through: (%) Extraction percentages =  $100 \times [M_{org}]_f / [M_{aq}]_i$  and (D) Distribution ratios =  $[M_{org}]_f / [M_{aq}]_f$ . Loading capacity of copper in the organic phase was determined by performing a cumulative copper extraction in consecutive SX cycles directly using the same organic phase, but new extreme AMD in each cycle.

Stripping of copper from the loaded organic phase was done by mixing it with 2M  $H_2SO_4$  in 100 mL round bottom flasks, using a A:O ratio of 1:1 and contact with magnetic stirring during 60 minutes at room temperature ( $25 \pm 3$  °C). Cumulative copper stripping cycles were carried out using the same 2M  $H_2SO_4$  solution but different loaded organic phases, to verify the feasibility of raising copper concentration to values suitable for the electrowinning process.

### *Analytical methods*

The pH was measured using a pH/E Meter GLP 21 (Crison) with a glass pH electrode

(VWR, SJ 223). The sulphate concentration was determined with a UV-visible spectrometer DR2800 (Hach-Lange) using the sulfaVer4 (Method 8051, Hach-Lange) procedure at 450 nm. The concentrations of iron, zinc, copper and manganese were determined through flame atomic absorption spectroscopy with a novAA 350 system (Analytik Jena), and the concentration of aluminium was measured by microwave plasma atomic emission spectrometry with a 4200 MP-AES (Agilent). Calibration curves were built using standards prepared from metals stock solutions of 1000 mg/L metal in 0.5 M nitric acid: iron, zinc and copper (Merck Certipur, Germany), manganese and aluminium (Panreac AA, Spain). Several samples' dilutions were prepared in 1% nitric acid (0.224 M), and the lowest dilutions fitting in the linear calibration curves were chosen.

## Results and Discussion

### *Extreme AMD*

The acidity and concentrations of main pollutants in the AMD sample collected from the pond near the sulphur factory ruins at São Domingos mine (Table 1) are much higher than in the flowing water streams affected by AMD at mining site: pH  $\approx$  2 to 3, sulphate  $\approx$  1000 to 5000 mg/L, aluminium  $\approx$  100 to 500 mg/L, iron  $\approx$  50 to 500 mg/L, zinc  $\approx$  20 to 150 mg/L, copper  $\approx$  20 to 100 mg/L and manganese  $\approx$  5 to 20 mg/L (e.g. Costa and Duarte 2005; Costa *et al.* 2008).

### *SX experiments*

The extraction from extreme AMD using 30% (v/v) Acorga M5640 in Shell GTL with 2.5% (v/v) octanol was highly selective for copper (with a D value for this metal of  $23 \pm 2$  and D values below 0.1 for the other metals) and allowed to extract of  $96 \pm 1\%$  of this metal (Table 2). This makes approximately a ratio of Acorga M5640's active compounds (5-nonyl-2-hydroxy-benzaldoxime) to copper ions ( $Cu^{2+}$ ) of 8, which can be considered a good result. It is only four times higher than the theoretical ratio of 2 for this extractant, and for example the results reported by Agarwal, *et al.* (2010) when using 20% (v/v) Acorga M5640 correspond approximately to a ratio of 24.

**Table 1** Brief characterization of extreme AMD sample collected for this work at the São Domingos mine.

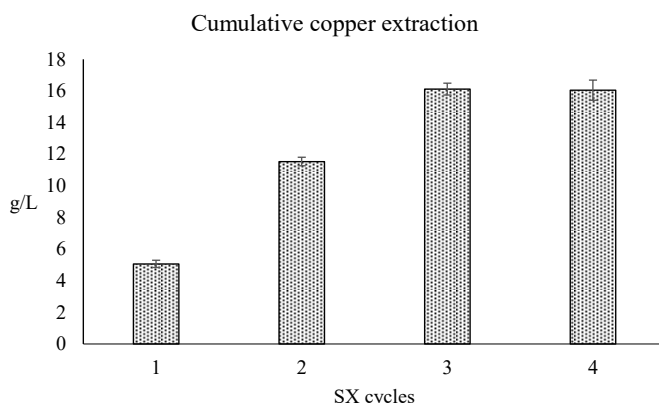
		Standard unit (s.u.)
pH	1.19	
[SO <sub>4</sub> <sup>2-</sup> ]*	142 ± 15	
[Fe]*	63 ± 6	
[Al]*	6.4 ± 0.2	
[Cu]*	5.3 ± 0.3	g/L
[Zn]*	1.9 ± 0.5	
[Mn]*	0.131 ± 0.002	

\*Averages and standard deviations of five analysis using independent dilutions.

**Table 2** Extraction efficiencies\* in percentages and distribution ratios (D) of metals analysed in the SX studies (with 30% (v/v) Acorga M5640 in Shell GTL with 2.5% octanol).

Metals	%	D
Fe	8 ± 5	0.08 ± 0.06
Al	2 ± 3	0.02 ± 0.03
Cu	96 ± 1	23 ± 2
Zn	0 ± 3	0.04 ± 0.03
Mn	0 ± 2	0.01 ± 0.02

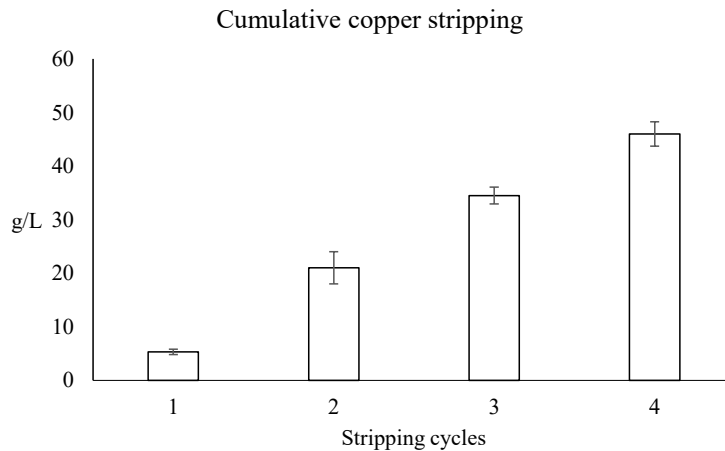
\*Averages and standard deviations of three SX replicates.



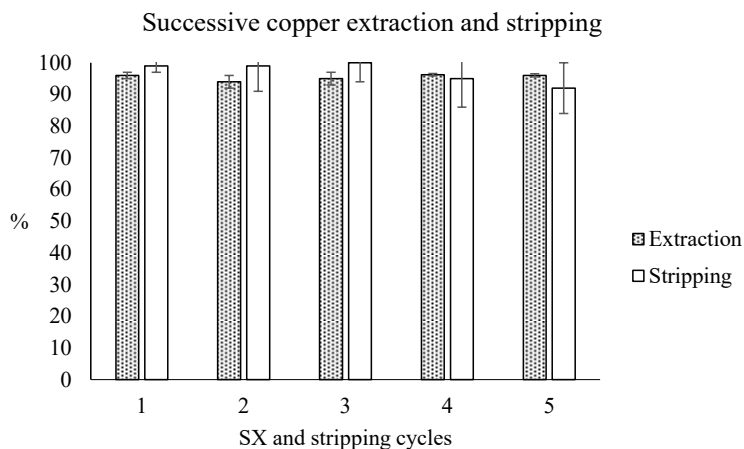
**Figure 1** Copper concentrations in the organic phase after consecutive cycles of extraction using directly the same organic phase (30% (v/v) Acorga M5640 in Shell GTL with 2.5% octanol) and new extreme AMD in each cycle. Results are averages of triplicates ± standard deviations.

The cumulative copper extraction cycles revealed that after the third cycle, when the tested organic phase was loaded with 16.1 ± 0.4 g/L of copper, it was no longer able to extract this metal from the extreme ADM in the fourth cycle, indicating this is the maximum loading capacity of the tested SX process (Figure 1).

This value goes in line with results obtained for the same type of organic phase, but with lower concentrations of extractant: 4.8 g/L and 10g/L, respectively for 10% and 20% Acorga M5640 in ShellSol D70 + 5% isotridecanol (Agrawal & Sahu, 2010).



**Figure 2** Copper concentrations in the stripping solution after consecutive cycles of stripping directly using the same stripping solution (2M  $H_2SO_4$ ) and new organic phases loaded with copper in each cycle (5.56, 16.11, 13.8 and 15 g/L of copper, respectively for cycles 1, 2, 3 and 4). Results are averages of triplicates  $\pm$  standard deviations.



**Figure 3** Copper extraction and stripping efficiencies in five consecutive cycles from extreme AMD using the same organic phase (30% (v/v) Acorga M5640 in Shell GTL with 2.5% octanol) and stripping solution (2M  $H_2SO_4$ ). Results are averages of triplicates  $\pm$  standard deviations.

The fourth cumulative copper stripping cycles revealed that it is possible to achieve at least  $46 \pm 2$  g/L Cu in the tested stripping solution (Figure 2). This value is in the range of concentrations ( $\approx 30$  to 50 g/L of copper) of typical aqueous stripping solutions exiting the SX operation and entering the electrowinning operation in the hydrometallurgical extraction of copper from slags or tailings (Aksamitowski *et al.*, 2018; Jose Alguacil & Regel-Rosocka, 2018; Schlesinger *et al.*, 2011).

During the five successive cycles of extraction and stripping with the organic phase and the stripping solution under study, the efficiency remained very high in both processes:  $95.4 \pm 0.9\%$  for copper extraction and  $97 \pm 3\%$  for copper stripping (Figure 3). These results are promising regarding the development of copper recovery processes from extreme AMDs, since the reusability of the organic phase is crucial for an environmentally and economically viable operation.

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