AliCy as Extractant to Remove Iron from Copper-Free Extreme AMD for Further Extraction of Zinc

NOBAHAR A.[1], MELKA A.B.[1,2], das NEVES L.L.[1,2] , CARLIER J.D. [1] and COSTA M.C.[1,2,*]

[1]Centre of Marine Sciences (CCMAR), University of the Algarve, Gambelas Campus, 8005-139 Faro, Portugal
[2]Faculty of Sciences and Technologies, Gambelas Campus, University of the Algarve, 8005-139 Faro, Portugal

*corresponding author:
e-mail: mcorada@ualg.pt

Abstract
A previous work showed that copper can be specifically extracted from acid mine drainage (AMD) classified as high-acid and extreme-metals (pH 1.19, ~63 g/L Fe, ~6.5 g/L Al, ~5.3 g/L Cu, ~1.9 g/L Zn and ~0.1 g/L Mn), using 30% (v/v) Acorga M5640 in Shell GTL (a kerosene like solvent) as extractant. Yet, to further extract zinc, another strategic metal in this water, using 0.9M D2EHPA or a mixture of 0.72 M D2EHPA plus 0.18M Cyanex 272 in kerosene as extractants, difficulties were observed due to iron co-extraction. Thus, an alternative solvent extraction strategy based on the use of the self-prepared ionic liquid AliCy 0.3M in kerosene was tested. The results revealed potential selectivity since 35% of iron was removed, while the removal of other metals was < 5%. Afterwards, higher concentrations of AliCy (0.6, and 1.2M) at different aqueous to organic ratios (A:O = 1:1, 1:2, 1:3 and 1:4) were tested on copper-free extreme AMD (after copper recovery with Acorga M5640), and the best compromise between iron extraction efficiency and selectivity was observed for 0.6M at A:O = 1:4 and also for 1.2M at A:O = 1:2 (75 to 80% removal or iron and 5 to 10% of zinc in both cases).
Keywords: Acid mine drainage, metals recovery, solvent extraction, extractants, ionic liquids.

1. Introduction

Acid mine drainage (AMD) is a common environmental issue, marked by severe acidity, high sulfate and metal (e.g. Fe, Zn, and Cu) concentrations (Naidu et al. 2019). Zinc is among the most important metals for industrial activities that is listed as an endangered metal (Tolchin 2014). Recent estimations suggest that demand for this metal is expected to rise steadily by the end of this century (Watari et al. 2021). Emerging environmental problems caused by AMD and necessity of metals' circular economy and water reuse has directed increasingly the attentions on metal recovery from these secondary resources.

Among different extraction methods, solvent extraction (SX) is known as a mastered technique of metal recovery from different metal bearing solutions due to its significant potential on metal ion extraction and selectivity (Hedrich et al. 2018). Different types of organophosphorus extractants are reported to be efficient in zinc extraction including Di-(2-ethylhexyl) phosphoric acid (D2EHPA), TBP, Bis-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) etc. (Deep and de Carvalho 2008).

However, iron which is often present in AMD in high concentrations (Sinha et al. 2014), is highly co-extracted by various types of organophosphorus extractants like D2EHPA (Principe and Demopoulos 2004; Azizi et al. 2015). There are various techniques to overcome the iron content of the solutions such as chemical precipitation methods (e.g. jarosite and goethite processes etc.) (Pappu et al. 2006; Pradel et al. 1993) that frequently have economical disadvantageous. It is known that Fe^{3+} can be extracted from different solutions by SX using different extractants (Biswas et al. 2007; Stefánsson 2007; Principe and Demopoulos 2004). Not only iron separation from extremely concentrated AMD will prevent its co-extraction in the recovery of zinc, but also its extraction in a pure state will allow to produce iron in a markable form and contribute to the economic viability of metals recovery from AMD (Agrawal and Sahu 2010; Mishra et al. 2010).

2. Materials and methods

2.1. Copper-free AMD

In a previous work, copper was totally extracted through solvent extraction (SX) from an extremely concentrated AMD collected in the São Domingos Mine, Portugal (Nobahar et al. submitted). The end aqueous phase resulting from that SX process is the copper-free AMD used in this work and has the following characteristics: pH 1.45, ~63 g/L Fe, ~6.5 g/L Al, ~1.9 g/L Zn and ~0.1 g/L Mn.

2.2 Solvent Extraction (SX) experiments

SX was carried out by mixing the copper-free AMD (aqueous phase (A)) and extractants diluted in kerosene (organic phase (O)) in round bottom flasks, using a A:O ratio of 1:1 and contact with magnetic stirring during 30

minutes at room temperature (25 ± 3 ºC). Then, separation funnels were used to separate phases and the concentrations of metals in the aqueous phase measured before and after SX, were used to calculate metals' extractions percentages.

First, SX experiments were carried out to test the extraction of zinc from the copper-free AMD using 0.9M D2EHPA, a mixture of 0.72M D2EHPA and 0.18M Cyanex 272, and 0.3M of the self-prepared ionic liquid AliCY (prepared as described by Fortuny et al. (2012), diluted in kerosene.

Afterwards, trying to optimize previous iron removal before zinc extraction, tests were carried out with two different AliCy concentrations (0.6M and 1.2M) and using four different aqueous to organic phases (A:O) ratios: 1:1, 1:2, 1:3, 1:4.

3. Results and Discussion

3.1. Zinc extraction from copper free AMD

The current study was conducted to investigate the efficiency of zinc recovery from Cu-free AMD by SX using different extractants. As shown in figure 1, D2EHPA could successfully extract 45 ± 6% of Zn. However, 40 ± 1% of iron present in the AMD solution was co-extracted by this extractant along with zinc. Moreover, when a synergistic mixture of 80% D2EHPA plus 20% Cyanex 272 was applied, 57 ± 7% of zinc and 33 ± 11% of iron were extracted. There are reports in the literature regarding the excellent selectivity of D2EHPA and CYANEX 272 over different metals except iron, which normally depends on the physiochemical characteristics and metal composition of the solutions (Cole and Sole, 2003). Literature also reports that synergistic mixture of D2EHPA and Cyanex 272 has higher efficiency on Zn recovery than using sole D2EHPA in sulphate liquors (Asadi, et al. 2017; Azizitorghabeh et al. 2016). However, in this work co-extraction of iron was observed in both cases, and therefore an iron elimination step seems necessary to avoid its co-extraction with zinc. Moreover, an additional experiment was performed using the ionic liquid AliCy as extractant. Through these tests, it was observed that AliCy is more selective to extract iron (52 ± 4% Fe extraction) than other metals including zinc (11 ± 6% Zn extraction) (Figure 1). Therefore, although zinc extraction from such type of copper-free AMD cannot be successful using AliCy, this ionic liquid revealed potential for a previous step of iron SX, aiming to prevent further co-extraction of this metal with zinc.

3.2. Iron separation to optimize the zinc SX process

In metals SX, extraction and separation of the metals from complex metal bearing solutions is highly depended on the nature of metals and the physiochemical features of the solution (Shah et al., 2017). In order to explore the iron extraction selectivity by AliCy from copper-free AMD, following investigations were designed to improve the iron extraction efficiency, aiming to obtain an iron free solution suitable for zinc SX. In this regard, investigations were conducted using 0.6 M and 1.2 M of AliCy with different A:O ratios (Figures 2 and 3).

As depicted in figure 2, extraction efficiency of iron using 0.6 M AliCy with A:O = 1:1 and A:O = 1:2 is around 50% with minor fractions (< 5%) of other metals co-extracted. Moreover, higher iron extractions by 0.6 M AliCy were observed for A:O = 1:3 and 1:4 (~77% and ~80% Fe removal, respectively). However, in these conditions ~10 to 14% of zinc was co-extracted, which is a drawback for the zinc recovery process.

In what concerns the tests using 1.2 M AliCy, at A:O = 1:1 and A:O = 1:2, iron was extracted from the copper-free AMD solution with high selectivity, and while at A:O = 1:1 iron extraction was just ~50%, with a A:O ratio of 1:2 ~80% of iron was extracted. Moreover, only ~1% and ~5% of zinc was co-extracted. With the same AliCy concentration (1.2M) but for lower A:O ratios (1:3 and 1:4), iron extraction was not improved (still ~80%) and the selectivity decayed (~23% and 79% zinc co-extracted, respectively).

This work reveals a good iron extraction efficiency and selectivity by AliCy for 0.6M at A:O = 1:4 and also for 1.2M at A:O = 1:2, accounting 75% to 80% removal of iron (~47 to ~50 g/L Fe removed) and 5% to 10% of zinc (~95 to 190 mg/L Zn removed) respectively. Despite this, it is also evident that it will be necessary to combine the iron SX with Alicy with other physical-chemical and/or biological processes to achieve the objective of a subsequent recovery of zinc from this type of AMD without iron contamination.

This problem of iron contamination in zinc SX and the need to look for new strategies is present even when it does not seem. For example, in a similar work, Sarangi et al. (2007) used different concentrations of TBP (tri-n-butyl phosphate) (0.5 to 2.5 M) diluted in kerosene from a sulphate solution containing various metals, including 11.8 g/l iron and 230 mg/l zinc. Through their iron separation optimization, they report a successful extraction of 98% of iron using 1M of TBP along with 10% co-extraction of zinc (Sarangi et al. 2007), which corresponds to a final aqueous phase with similar concentrations of iron and zinc (~236 mg/L Fe and ~207 mg/L Zn).

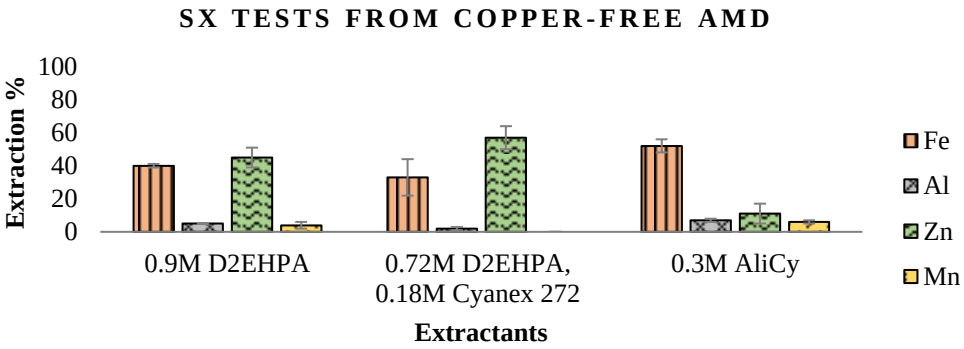

Figure 1. Extraction percentages of metals analyzed in the SX studies from copper-free AMD using D2EHPA, a mixture of D2EHPA and Cyanex 272, or the ionic liquid AliCy, diluted in kerosene as extractants, with an A:O ratio of 1:1 and contact during 30 minutes with magnetic stirring at room temperature (25 ± 3 ºC). Results are averages and absolute mean deviations of two SX replicates.

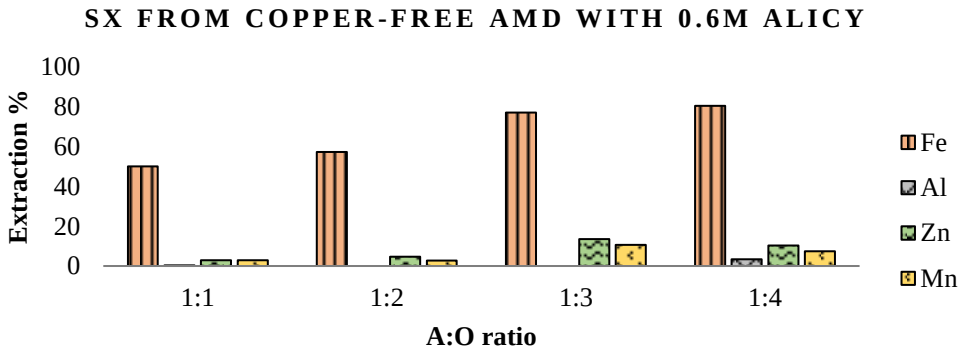

Figure 2. Extraction percentages of metals analyzed in the SX studies from copper-free AMD using 0.6M AliCy in kerosene as extractant, with different A:O ratios and contact during 30 minutes with magnetic stirring at room temperature (25 ± 3 ºC).

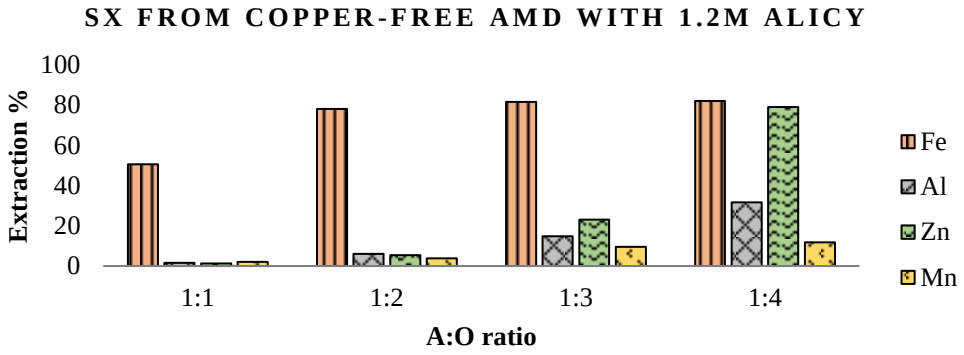

Figure 3. Extraction percentages of metals analyzed in the SX studies from copper-free AMD using 1.2M AliCy in kerosene as extractant, with different A:O ratios and contact during 30 minutes with magnetic stirring at room temperature (25 ± 3 ºC).

Acknowledgments

This work was supported by (1) the Portuguese Foundation for Science and Technology (FCT) through the projects UIDB/04326/2020 and UIDB/00100/2020; and (2) national funds from FCT co-financed by the Algarve´s Regional Operational Program (CRESC Algarve 2020) through Portugal 2020 and European Regional Development Fund (FEDER), under the project METALCHEMBIO (no. 29251).

References

Agrawal A, Sahu KK (2010) Treatment of Chloride Waste Pickle Liquor by Solvent Extraction for the Recovery of Iron. Mineral Processing and Extractive Metallurgy Review 31(3):121–134. https://doi.org/10.1080/08827501003727006

Asadi T, Azizi A, Lee J and Jahani M (2017) Solvent extraction of zinc from sulphate leaching solution of a sulphide-oxide sample using D2EHPA and Cyanex 272. Journal of Dispersion Science and Technology, 39(9), pp.1328-1334.

Azizi A, Rashchi F, Babakhani A, Noori M (2015) Synergistic extraction and separation of Fe (III) and Zn (II) using TBP and D2EHPA. Proceedings of Pb-Zn

Azizitorghabeh A, Rashchi F, Babakhani A and Noori M, (2016) Synergistic extraction and separation of Fe(III) and Zn(II) using TBP and D2EHPA. Separation Science and Technology, 52(3), pp.476-486.

Biswas RK, Habib MA, Karmakar AK (2007) Kinetics of Solvent Extraction of Iron(III) from Sulfate Medium by Purified Cyanex 272 using a Lewis Cell. Solvent Extraction and Ion Exchange 25(1):79–98. https://doi.org/10.1080/07366290601067838

Cole P and Sole K (2003) Zinc solvent extraction in the process industries. Mineral Processing and Extractive Metallurgy Review, 24(2), pp.91-137.

Deep A, de Carvalho JMR (2008) Review on the Recent Developments in the Solvent Extraction of Zinc. Solvent Extraction and Ion Exchange 26(4):375–404. https://doi.org/10.1080/07366290802179267

Fortuny A, Coll MT, Sastre AM (2012) Use of methyltrioctyl/decylammonium bis 2,4,4 (trimethylpentyl)phosphinate ionic liquid (ALiCY IL) on the boron extraction in chloride. Separation and Purification Technology 97, 137–141.

Hedrich S, Kermer R, Aubel T, Martin M, Schippers A, Johnson DB, Janneck E (2018) Implementation of biological and chemical techniques to recover metals from copper-rich leach solutions. Hydrometallurgy 179:274–281. https://doi.org/10.1016/j.hydromet.2018.06.012

Mishra RK, Rout PC, Sarangi K, Nathsarma KC (2010) A comparative study on extraction of Fe(III) from chloride leach liquor using TBP, Cyanex 921 and Cyanex 923. Hydrometallurgy 104(2):298–303. https://doi.org/10.1016/j.hydromet.2010.07.003

Naidu G, Ryu S, Thiruvenkatachari R, Choi Y, Jeong S, Vigneswaran S (2019) A critical review on remediation, reuse, and resource recovery from acid mine drainage. Environmental Pollution 247:1110–1124. https://doi.org/10.1016/j.envpol.2019.01.085

Pappu A, Saxena M, Asolekar SR (2006) Jarosite characteristics and its utilisation potentials. Science of The Total Environment 359(1–3):232–243. https://doi.org/10.1016/j.scitotenv.2005.04.024

Passos H, Cruz B, Schaeffer N, Patinha C, da Silva E and Coutinho J (2021) Selective Sequential Recovery of Zinc and Copper from Acid Mine Drainage. ACS Sustainable Chemistry & Engineering, 9(10), pp.3647-3657.

Pradel J, Castillo S, Traverse JP, Grezes-Besset R, Darcy M (1993) Ferric hydroxide oxide from the goethite process: characterization and potential use. Ind Eng Chem Res 32(9):1801–1804. https://doi.org/10.1021/ie00021a001

Principe F, Demopoulos GP (2004) Comparative study of iron(III) separation from zinc sulphate–sulphuric acid solutions using the organophosphorus extractants, OPAP and D2EHPA. Hydrometallurgy 74(1–2):93–102. https://doi.org/10.1016/j.hydromet.2004.01.004

Sarangi K, Parhi P, Padhan E, Palai A, Nathsarma K and Park K (2007) Separation of iron(III), copper(II) and zinc(II) from a mixed sulphate/chloride solution using TBP, LIX 84I and Cyanex 923. Separation and Purification Technology, 55(1), pp.44-49. https://doi.org/10.1016/j.seppur.2006.10.021

Shah K, Gupta K and Sengupta B (2017) Selective separation of copper and zinc from spent chloride brass pickle liquors using solvent extraction and metal recovery by precipitation-stripping. Journal of Environmental Chemical Engineering, 5(5), pp.5260-5269.

Sinha MK, Sahu SK, Meshram P, Pandey BD (2014) Solvent extraction and separation of zinc and iron from spent pickle liquor. Hydrometallurgy 147–148:103–111. https://doi.org/10.1016/j.hydromet.2014.05.006

Stefánsson A (2007) Iron(III) Hydrolysis and Solubility at 25 °C. Environ Sci Technol 41(17):6117–6123. https://doi.org/10.1021/es070174h

Tolchin AC (2014) 2012 Minerals Yearbook-Zinc.

Watari T, Nansai K, Nakajima K (2021) Major metals demand, supply, and environmental impacts to 2100: A critical review. Resources, Conservation and Recycling 164:105107. https://doi.org/10.1016/j.resconrec.2020.105107