Selective sequential recovery of zinc and copper from acid mine drainage

Helena Passos,† Brayan Cruz,† Nicolas Schaeffer,† Carla Patinha,‡ Eduardo Ferreira da Silva‡ and João A. P. Coutinho*†

†CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
‡GeoBioTec, Department of Geoscience, University of Aveiro, 3810-193 Aveiro, Portugal.

*Corresponding author: E-mail: jcoutinho@ua.pt. Fax: +351 234370084. Phone: +351 234401507.
**Abstract**

The observed imbalance between the unsustainable consumption of available natural metal resources and finite deposits makes the recovery and recycling of metals from metal-containing wastes an imperative. Here, ionic-liquid-based aqueous biphasic systems (IL-based ABS) are proposed as an efficient alternative for selective metal recovery from real copper acid mine drainage (AMD) effluents. ABS composed of different IL and Na$_2$SO$_4$ were evaluated for Zn, Al, Cu, Co and Ni extraction from both model solutions and AMD samples. It is shown that IL composed of thiocyanate anion ([SCN]$^-$) presented a remarkable ability to extract metals from AMD through the formation of stable metal-complexes. The addition of NaSCN to ABS composed of tetrabutylammonium chloride ([N$_4$$+$]$^4$Cl) allowed to mimic the use of [SCN]-based IL with additional advantages: tunable metal selectivity by the concentration of [SCN]$^-$ added to the ABS, and reduction of system cost and environmental impact. Furthermore, at the [SCN]$^-$ concentration range studied here, it is observed the formation of a hydrophobic salt composed of IL cations and metal complex anions, which allows the selective extraction and recovery of transition metals in a single-step. The IL-rich phase recyclability in three extraction cycles is demonstrated, showing the possibility to recover two times more Zn than with a single extraction cycle while using the same amount of IL and thiocyanate. Salt-rich phases were also recycled in a new IL-based ABS for the subsequent Cu extraction and recovery. These results allow the development of a sustainable process for the selective sequential recovery of transition metals from AMD.

**Keywords:** waste valorization, recovery, liquid-liquid extraction, ionic liquids, process design.
Introduction

The growth of the world’s population is creating a huge pressure on natural resources. The increased global demand for these raw materials is leading to metals scarcity and creating an unsustainable imbalance between supply and demand.\textsuperscript{1,2} The reduced availability of minable deposits and their concentration in a limited number of countries will cause an increase of metals price and potential political instability.

Metal-containing wastes appear as an important secondary source of these raw materials and several efforts have been done to find novel and more efficient strategies for metals recovery and recycling. Mining industry residues are considered potential sources of valuable metals. This type of residues is produced in large amounts – about 20 to 25 billion tons/year worldwide – and present high environmental impact if not correctly treated.\textsuperscript{3} Acid mine drainage (AMD) are produced by mining activity, during and even after the end of mining exploitation. These are highly acidic waters that result from the oxidation of exposed sulfide-rich minerals, such as pyrite, pyrrhotite and arsenopyrite, by air and water.\textsuperscript{4} Besides their high acidity and sulfate content, AMD also contain an important amount of dissolved elements and toxic metals, such as Fe, Al, Mn, Cu, Ni, Co, Pb, and As, whose composition is dependent on the ore body being explored. Due to the long-term environmental impact caused by these waters, the treatment and management of AMD is nowadays one of the biggest economic and environmental challenges faced by the mining industry.\textsuperscript{5,6}

Metal recovery allows to add value to waste treatment processes; still only few works discuss the use of AMD as a potential secondary source of strategic metals.\textsuperscript{4,7-13} Different technologies were developed, namely the application of fractional precipitation,\textsuperscript{8-10} magnetic nanoparticles,\textsuperscript{11} extraction resins\textsuperscript{12} and remediation systems,\textsuperscript{13} to recover transition metals and rare earth elements (REE). Amongst these, fractional precipitation is the technology that attracted most attention. This process is commonly used to treat AMD, is cost effective and can be easily applied at large scale. Furthermore, it was demonstrated by Yan et al.\textsuperscript{9} through a simplified economic analysis, that when fractional precipitation is used to recover Fe, Cu, Zn and Mn present in AMD, the benefit obtained from the recycled metals is able to cover at least the costs of the chemical reagents used. However, this process results in the production of large amounts of sludges and metals recovery is hard to achieve. Similarly, the remaining proposed technologies also present some drawbacks, namely related with recovery efficiencies, associated costs, or low potential for scale-up.
Liquid-liquid extraction processes are commonly used at industrial level in the selective extraction and recovery of metals. Liquid-liquid systems are usually prepared by using volatile organic compounds, which are well known for their toxicity. Hydrophobic ionic liquids (IL) were proposed as an alternative due to their negligible vapor pressure and higher extraction efficiencies. However, IL composition based on fluorinated anions and/or long alkyl chains, which result in high viscosity, cost and environmental impact, limit their applicability. Aqueous biphasic systems (ABS) composed of hydrophilic IL are more benign alternatives. ABS are formed by the mixture of two water soluble solutes, namely salts and/or polymers, which above a certain concentration induces the formation of two immiscible aqueous phases. IL-based ABS present a number of advantages derived from IL properties and their successful application to extract and separate metals was previously demonstrated. However, the application of these systems to selectively recover metals from AMD as well as the stability of most IL-based ABS under acidic conditions was never evaluated. A novel strategy for the sequential selective recovery of strategic metals from AMD water, collected from the Portuguese mine of São Domingos, using IL-based ABS is developed and presented in this work. São Domingos mine is in the Iberian Pyrite belt and was exploited during 100 years for pyrite, copper and sulfur production. During this time and even after its exhaustion, the exposure of the open pit mine to the atmospheric conditions resulted in the formation of AMD creating several environmental issues in this region.
**Methodology**

A detailed description of the materials and methods used in this work is described in the Supplementary Information (SI). AMD sample was collected in the open pit impoundment of the mine of São Domingos, Portugal. Sodium sulphate, Na$_2$SO$_4$, supplied by Merck with a purity of > 99 wt % was used in ABS formation mixed with ILs reported in Table 1. IL chemical structures are presented in Figure S1 of the SI.

**Table 1.** Name, acronym, purity (wt %) and supplier of the IL studied.

<table>
<thead>
<tr>
<th>IL</th>
<th>Acronym</th>
<th>Purity (wt %)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) 1-butyl-3-methylimidazolium thiocyanate</td>
<td>[C$_4$C$_1$im][SCN]</td>
<td>&gt; 98</td>
<td>Iolitec</td>
</tr>
<tr>
<td>(ii) 1-butyl-3-methylimidazolium dicyanamide</td>
<td>[C$_4$C$_1$im][N(CN)$_2$]</td>
<td>98</td>
<td>Iolitec</td>
</tr>
<tr>
<td>(iii) 1-butyl-3-methylimidazolium octylsulfate</td>
<td>[C$_4$C$_1$im][C$_8$SO$_4$]</td>
<td>99</td>
<td>TermoFisher</td>
</tr>
<tr>
<td>(iv) 1-butyl-3-methylimidazolium triflate</td>
<td>[C$_4$C$_1$im][CF$_3$SO$_3$]</td>
<td>99</td>
<td>Iolitec</td>
</tr>
<tr>
<td>(v) 1-butyl-3-methylimidazolium ethylsulfate</td>
<td>[C$_4$C$_1$im][C$_2$SO$_4$]</td>
<td>98</td>
<td>Iolitec</td>
</tr>
<tr>
<td>(vi) 1-butyl-3-methylimidazolium tosylate</td>
<td>[C$_4$C$_1$im][TOS]</td>
<td>&gt; 98</td>
<td>Iolitec</td>
</tr>
<tr>
<td>(vii) 1-butyl-3-methylimidazolium bromide</td>
<td>[C$_4$C$_1$im]Br</td>
<td>&gt; 98</td>
<td>Iolitec</td>
</tr>
<tr>
<td>(viii) 1-heptyl-3-methylimidazolium chloride</td>
<td>[C$_7$C$_1$im]Cl</td>
<td>&gt; 98</td>
<td>Iolitec</td>
</tr>
<tr>
<td>(ix) 1-dodecyl-3-methylimidazolium chloride</td>
<td>[C$_{12}$C$_1$im]Cl</td>
<td>&gt; 98</td>
<td>Iolitec</td>
</tr>
<tr>
<td>(x) tributylethylphosphonium diethylphosphate</td>
<td>[P$_{4442}$][DEP]</td>
<td>99</td>
<td>Cytec Ind.</td>
</tr>
<tr>
<td>(xi) tributylmethylphosphonium methylsulfate</td>
<td>[P$_{4441}$][C$_1$SO$_4$]</td>
<td>pure</td>
<td>Cytec Ind.</td>
</tr>
<tr>
<td>(xii) tributyltetradecylphosphonium hydrogensulfate</td>
<td>[P$_{4444}$][HSO$_4$]</td>
<td>&gt; 95</td>
<td>Iolitec</td>
</tr>
<tr>
<td>(xiii) triisobutyl(methyl)phosphonium tosylate</td>
<td>[P$_{i(444)1}$][TOS]</td>
<td>pure</td>
<td>Cytec Ind.</td>
</tr>
<tr>
<td>(xiv) bis(2-hydroxyethyl)dimethylammonium chloride</td>
<td>[N$_{11201120n}$]Cl</td>
<td>99</td>
<td>Acros Organics</td>
</tr>
<tr>
<td>(xv) benzyltributylammonium chloride</td>
<td>[N$_{4444b}$]Cl</td>
<td>&gt; 97</td>
<td>Acros Organics</td>
</tr>
<tr>
<td>(xvi) tetrabutylammonium chloride</td>
<td>[N$_{4444}$]Cl</td>
<td>&gt; 97</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>

**Characterization of AMD from São Domingos**

The nature and concentration of metals present in the AMD water sample from the mine of São Domingos were determined by inductively coupled plasma mass spectrometry (ICP-MS) using an Agilent Technologies 7700 Series spectrometer. The concentration of sulfates (SO$_4$) was determined by ion chromatography using a Dionex 2000i equipment, while water pH and conductivity were measured at (25 ± 1) °C using a Mettler Toledo SevenMulti pH meter within ± 0.02. Details on AMD pre-treatment carried-out before metal extraction are presented in SI.

**Metal extraction in IL-based ABS**

Metals extraction was carried-out in ternary systems composed of 25 wt % of IL + 10 wt % of Na$_2$SO$_4$ + 65 wt % of H$_2$O (metal standard aqueous solution or AMD sample).
Ternary mixtures composition was defined by comparing the binodal curves of previously reported phase diagrams for IL + Na₂SO₄ ABS and choosing a mixture point common to all the biphasic regions (cf. Table S1).²²

A first screening on IL-based ABS ability to extract metals was carried out by using individual aqueous metal solutions of Cu, Ni and Co at 0.01 M. The ternary mixtures were vigorously stirred and, to guarantee the complete separation of the ABS coexisting phases and metals partition, the systems were centrifuged at (298 ± 1) K, for 30 min at 3500 rpm. After this, the top and bottom phases were carefully separated, and their weight (within ± 10⁻⁴ g) and volume (± 0.01 mL) were measured. The quantification of the metals in salt-rich phase was carried out through UV-spectroscopy, using a SynergyHT Microplate Reader, from Biotek, at 803 nm for Cu, 394 nm for Ni and 512 nm for Co, using calibration curves previously established. The concentration of metals in IL-rich phase was determined by mass balance. To avoid possible interferences from ABS phase forming components, blank controls of each ternary system, without metals, were always prepared and used. The influence of Na₂SO₄ concentration in metals molar extinction coefficient was also evaluated and confirmed to be negligible. Three samples of each phase were analyzed, in at least three individual systems, in order to determine the partition coefficients ($K_M$) and the respective standard deviations, according to the following equation,

$$
K_M = \frac{[M]_{IL}}{[M]_{salt}}
$$

where $[M]_{IL}$ and $[M]_{salt}$ are the concentrations of each metal in the IL- and salt-rich phases, respectively.

Metal extraction from acid mine drainage by IL-based ABS

The extraction of metals from AMD was tested in the ABS composed of 25 wt % of IL + 10 wt % of Na₂SO₄ + 65 wt % of treated AMD with the IL [N₄₄₄₄]Cl, [C₄C₁im][N(CN)₂] and [C₄C₁im][SCN], and by using the same experimental procedure described above. Systems composed of [N₄₄₄₄]Cl were prepared by adding NaSCN salt, as adjuvant in the following molar ratios with total molar amount of Zn present in the treated mine water ($8.2 \times 10^{-3}$ mol·L⁻¹): 1:0, 1:1, 1:2, 1:5, 1:10, 1:25, 1:50 and 1:68 (Zn:SCN). In these systems the following mixture point was used: 25 wt % IL + 10 wt % Na₂SO₄ + 58 wt % treated AMD + 7 wt % aqueous solution containing variable content of NaSCN. Metal
quantification in IL- and salt-rich liquid phases and solid phase was carried-out by total X-ray fluorescence (TXRF) using a benchtop Picofox S2 (Bruker Nano) spectrometer with a molybdenum X-ray source. Quartz glass sample carriers were used in TXRF analysis and pre-treated with 10 μL of a solution of silicon in isopropanol and dried in a heat plate at 80 ºC for 10 min. IL-rich, salt-rich and solid phase samples were prepared by mixing 20 μL of each phase (solid phase was previously dissolved in 1 mL of pure ethanol) with 5 μL of Y standard solution and 495, 970 and 70 μL, respectively, of 1 wt % polyvinyl alcohol solution. 6.0 μL of each mixture was added to treated sample carriers which were dried in a heat plate at 80 ºC for 20 min and analyzed in the TXRF spectrometer for 300 s. A solid phase sample was also analyzed by Fourier transform infrared (FTIR).

The partition coefficients of Al, Cu, Co, Ni and Zn were calculated by using Eq. (1). Metal precipitation percentage (P%) in solid phase was calculate through the following equation:

$$P\% = \frac{[M]_S \times w_{OH}}{[M]_{AMD} \times w_{AMD}} \times 100$$  

where $[M]_S$ and $[M]_{AMD}$ represent, respectively, metal concentration in solid phase and treated AMD, while $w_{OH}$ and $w_{AMD}$ are the weight of pure ethanol used to dissolve solid phase (0.769 g) and treated AMD added in ABS preparation.

The concentration of $[\text{N}_{4444}]\text{Cl}$ in the salt-rich phase of each system was determined by $^1$H nuclear magnetic resonance (NMR) analysis using a Bruker Advance 300 NMR at 300 MHz, with deuterated dimethyl sulfoxide as the solvent and tetramethylsilane as the internal reference.

IL-rich phase recycling was also studied, and more details are given in the SI. Zn and Cu purity percentages were determined by considering the total amount of metals present in solid phases, while recovery percentages were calculated taking into account the total amount of metals present in each system or treated AMD (designated as total recovery).

**Results and Discussion**

**AMD composition**

AMD sample collected from São Domingos was chemically characterized and the results obtained are presented in Table 2. It presents an acidic pH (1.7) and a high concentration on sulfates and metals such as Fe, Al, Zn and Cu. Co, Ni, As and Pb were also identified
at low concentrations (< 6 ppm) which is in agreement with previous data reported in the literature concerning São Domingos mine waste.\textsuperscript{21,23,24}

**Table 2.** Characterization of São Domingos AMD original sample and after pretreatment.

<table>
<thead>
<tr>
<th></th>
<th>AMD</th>
<th>AMD after pretreatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1.7</td>
<td>4.0</td>
</tr>
<tr>
<td>Conductivity (μS·cm(^{-1}))</td>
<td>7.9</td>
<td>---</td>
</tr>
<tr>
<td>Sulfates (g·L(^{-1}))</td>
<td>11.1</td>
<td>---</td>
</tr>
<tr>
<td>Metals (mg·L(^{-1}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>546.7</td>
<td>778.0</td>
</tr>
<tr>
<td>Fe</td>
<td>715</td>
<td>2.4</td>
</tr>
<tr>
<td>Co</td>
<td>3.2</td>
<td>8.0</td>
</tr>
<tr>
<td>Ni</td>
<td>1.0</td>
<td>2.7</td>
</tr>
<tr>
<td>Cu</td>
<td>82.5</td>
<td>217.8</td>
</tr>
<tr>
<td>Zn</td>
<td>210.1</td>
<td>538.4</td>
</tr>
<tr>
<td>As</td>
<td>5.8</td>
<td>0.04</td>
</tr>
<tr>
<td>Pb</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Before metal extraction, the AMD was pre-treated. Water evaporation was carried out aiming to reduce the total volume of AMD sample and increase the concentration of Al, Zn, Co, Ni and Cu. This type of procedure is already implemented at industrial level for lithium extraction from brines to increase the metal concentration before the recovery step.\textsuperscript{25} Here, a total reduction of 67 % of the initial volume was carried leading to an increase on metals concentration of 3 times, which guarantees that the minimum concentration required for an adequate detection of metals after extraction (namely those at very low concentrations).

Iron is the most concentrated metal in the AMD sample collected in the mine of São Domingos. This metal presents high complexation constants when compared with the remaining transition metals and Al present in AMD, blocking their preferential extraction by a coordinating agent.\textsuperscript{26} Therefore, iron removal from AMD sample before strategic metals extraction becomes imperative for the development of an efficient process. It is well known that iron starts to precipitate at lower pH values than other transition metals in aqueous sulfate-rich solutions. Thus, the selective precipitation of iron by pH adjustment was evaluated in an AMD concentrated sample with the results shown in Figure S2 and Table S2. As can be seen in Figure S2, metals precipitation efficiency is highly sensitive to the solution pH. Iron and arsenic present a similar profile and are the
metals that reach the highest precipitation efficiency at lower pH value, attaining an
almost complete precipitation (99.91 and 99.82 %, respectively) at pH 4.0. At this pH,
more than 60 % of Al is precipitated, followed by the remaining metals (< 25 % of
precipitation). At a pH around 2.7, it is possible to avoid significant losses of Al, Cu, Co,
Ni and Zn; yet, at these conditions and even with a precipitation efficiency of 78 %, the
iron concentration in AMD would still be high, when compared with the metals of interest
– for example, 2 and 60 times higher than Cu and Co, respectively (cf. Table S2). Thus,
a compromise was needed and pH 4.0 was selected as the optimum pH to treat the AMD
before the metal extraction step.

Metal precipitation from AMD concentrated sample (or any other wastewater sample) is
not only ruled by the solubility of metal hydroxides in water. Since AMD is a sample of
high complexity, with a high amount of solubilized organic matter, this may influence the
metals precipitation. In fact, along with the increase of the pH it was possible to observe
the flocculation of dissolved organic and inorganic matter in the AMD (cf. Figure S2A).
The complete or partial removal of this organic matter from AMD sample is also
important to guarantee the development of an efficient process. Only close to pH 4.0 it
was possible to obtain a clear water sample (cf. Figure S2B). The solid formed during
this procedure was collected, treated and analyzed by XRD – Figure S3.

Selection of IL + Na\textsubscript{2}SO\textsubscript{4} + H\textsubscript{2}O ABS for metal extraction

The ability of IL-based ABS to extract Cu, Ni and Co and the influence of IL anion and
cation nature in metal partition, were evaluated. Single metal solutions were used in the
screening, allowing to infer the IL impact on metals partition in the absence of metal
competitive effects. Furthermore, Cu, Ni and Co were selected as representative metals
of AMD composition since their quantification can be easily carried out by UV-Vis
spectroscopy.

Ternary mixtures at the composition of 25 wt % of IL + 10 wt % of Na\textsubscript{2}SO\textsubscript{4} + 65 wt %
of metal aqueous solution were used. This ternary mixture composition was defined by
taking into account the previously reported binodal curves for IL + Na\textsubscript{2}SO\textsubscript{4} ABS,\textsuperscript{22} and
choosing a mixture point common to all the biphasic regions. Sodium sulphate was
selected as the salting-out agent since AMD naturally presents a high concentration on
sulfates in its composition (cf. Table 2). Concerning the 16 IL tested, only the following
were able to induce the formation of ABS when mixed with Na\textsubscript{2}SO\textsubscript{4} in the selected
mixture point: [C\textsubscript{4}C\textsubscript{1}im][SCN], [C\textsubscript{4}C\textsubscript{1}im][N(CN)\textsubscript{2}], [C\textsubscript{4}C\textsubscript{1}im][TOS], [C\textsubscript{4}C\textsubscript{1}im][CF\textsubscript{3}SO\textsubscript{3}],
[C4C1im][C8SO4], [P4441][TOS], [P4441][C1SO4], [P44414][HSO4], [N444Bz]Cl and [N4444]Cl (cf. Table S1). Nevertheless, these allowed to evaluate the impact of the IL cation (imidazolium, quaternary ammonium and phosphonium) and anion (namely, [SCN]-, [N(CN)2]-, [TOS]-, Cl-) on metal partition.

The obtained results for Co, Ni and Cu partition in IL-based ABS are presented in Figure 1. Data presented show that only the system composed of the IL [C4C1im][SCN] was able to partition all the three metals preferentially to the IL-rich phase (ln(KM) > 0). The ABS composed of [C4C1im][N(CN)2] was able to extract only Cu and Ni, while [C4C1im][CF3SO3]-based ABS presented an equal distribution of metals between the system phases (ln(KM) ~ 0). All the remaining biphasic systems showed no metal extraction for IL-rich phase (ln(KM) < 0). Importantly, no metal precipitation in any of the systems studied was observed.
Figure 1. IL effect in the partition coefficient ($K_M$) of Cu, Co and Ni in ABS composed of 25 wt % of IL + 10 wt % of Na$_2$SO$_4$ + 65 wt % of metal aqueous solution at (25 ± 1) °C and atmospheric pressure.

Metal extraction in ABS systems may occur through the formation of negatively charged metal complexes with inorganic anions in the absence of an extractant. Among them, halides and [SCN]$^-$ are commonly used as extracting agents. Thiocyanate is an ambidentate ligand, i.e., it coordinates with metals through either the nitrogen and/or sulfur atom, and its ability to coordinate with metals such as Co, Ni and Cu is well established in literature and explains the results obtained for metals extraction by using [C$_4$C$_1$im][SCN]-based ABS (cf. Figure 1). Considering the first complexation constants of these metals with SCN$^-$ the following trend was expected to be observed: Cu$^{2+}$ (log$\beta_1$ = 1.7) > Ni$^{2+}$ (log$\beta_1$ = 1.14) > Co$^{2+}$ (log$\beta_1$ = 1.01). However, while Cu and Co are extracted in the form of tetrahedral metal-thiocyanate complexes – Cu(SCN)$_4^{2-}$ and Co(SCN)$_4^{2-}$ – which are rarely formed in aqueous solution, Ni is known to stay in the form of octahedral complex anion, which present a more hydrophilic character and, thus, a lower partition to the IL-rich phase. These results are also supported by the comparison of UV-Vis spectra of metals in IL-rich phase and aqueous solution presented in Figure S4. [N(CN)$_2$]-based ILs ability to extract metals in two liquid phases systems was also previously demonstrated. Similar to [SCN]$^-$ anion, [N(CN)$_2$]$^-$ also presents a high ability to interact with metallic cations through the formation of stable metal complexes. Furthermore, the trend observed on metal partitions in [C$_4$C$_1$im][N(CN)$_2$]-based ABS – $K_{Cu} > K_{Ni} >> K_{Co}$ – is in good agreement with data previously reported. Thus, it seems clear that IL-based ABS ability to extract metals such as Ni, Co and Cu, to IL-rich phase is mainly ruled by the IL anion nature, while the partition extension is related to the type and stability of metal complexes that are formed between metal cation and IL anion.

Among all the systems evaluated only those composed of [SCN]$^-$ and [N(CN)$_2$]$^-$ were able to extract metals to the IL-rich phase, being thus selected as the best candidates to the metals extraction from AMD.

Metal extraction from AMD real sample by IL-based ABS

ABS composed of Na$_2$SO$_4$ and the ILs [C$_4$C$_1$im][SCN], [C$_4$C$_1$im][N(CN)$_2$] and [N$_{4444}$]Cl were tested in metal extraction from treated AMD sample. [N$_{4444}$]Cl-based ABS showed no metal extraction when single metal aqueous solutions were used (cf. Figure 1).
Nevertheless, to guarantee that AMD composition is not affecting the trends previously observed, this IL was also considered in these experiments. It is also important to note that, when dealing with metal extraction from AMD, the sulfate present in the system needs to be taken into account; nevertheless, it represents only 7.3% of the total amount of Na₂SO₄ (0.72 wt % of mixture point composition) needed to induce the phases separation, being always necessary to add 9.3 wt % more sulfate salt to the mixture. The results obtained are presented in Figure 2.

Figure 2. Metal extraction from AMD treated sample by using IL + Na₂SO₄ + H₂O ABS at pH 4 and (298 ± 1) K: metal partition coefficients, ln($K_M$) (at the top) and macroscopic aspect of Co partition in the identified systems (at the bottom).

The extractions of Al, Co, Ni, Cu and Zn from pretreated AMD sample in IL-based ABS were experimentally assessed. The following trends were observed for the partition coefficients: Zn > Co > Cu >> Ni > Al in [C₄C₁im][SCN]-, Cu > Zn > Ni > Co > Al in [C₄C₁im][N(CN)₂]-, and no metal extraction was observed in the [N₄₄₄₄]Cl-based system. For Cu, Co and Ni, the results obtained are in good agreement with those obtained when
single-metal aqueous solutions were considered at the same conditions (cf. Figure 1). In what concerns Zn and Al, IL-based ABS composed of [C₄C₁im][SCN] and [C₄C₁im][N(CN)₂] were able to induce the preferential partition of Zn to the IL-rich phase, while there were no systems capable to extract Al. Al is not able to form anionic complexes in presence of any of these ions. In fact, only the hydrophilic complex [Al(SCN)(H₂O)₅]²⁺ was reported for temperature and ionic strength conditions similar to the tested system – which may justify its preferential partition to the salt-rich phase. Selective extraction of strategic metals from AMD

The relatively high costs associated to imidazolium-based ILs may create limitations to their use at industrial scale. Quaternary ammonium-based ILs are much less expensive than their imidazolium-based counterparts and, generally, present also a lower environmental impact. In Figure 2 are also presented the results obtained for metal extraction from treated AMD by using an ABS composed of Na₂SO₄, [N₄₄₄₄]Cl and 2.0 wt % of NaSCN. The observed results are quite interesting since metal partition coefficients similar to those obtained with the [C₄C₁im][SCN]-based system were obtained in a system that was previously shown to be unable to extract metals. It is expected that a similar result can be obtained if the IL [N₄₄₄₄][SCN] is directly used. However, the addition of thiocyanate anion to the system in the form of NaSCN presents some advantages: (i) it allows to reduce the costs of the system since it is less expensive to use NaSCN (~0.32 €/g at Sigma-Aldrich) and [N₄₄₄₄]Cl (~2.5 €/g at Sigma Aldrich) than [N₄₄₄₄][SCN] (~4.8 €/g at Sigma-Aldrich), (ii) it allows to reduce system environmental impact, being possible to control the amount of [SCN]⁻ added and reduce it up to the minimum necessary to achieve the desired metal extraction, and (iii) it allows tunable metal selectivity controlled by the concentration of [SCN]⁻ added to the ABS, as will be demonstrated further. As previously referred, metal extraction by coordinating ions such as [SCN]⁻ is ruled by the formation of stable complexes, better extracting those metals that present high complexation constants and result in complexes of more stable conformation. Thus, metal selectivity may be controlled by the amount of coordination anion added to the system. The effect of thiocyanate anion concentration on metals partition from AMD sample was evaluated and the results obtained are presented in Figure 3.
Figure 3. Thiocyanate molar ratio effect on metal extraction from AMD sample: [SCN]⁻ influence in metal partition between IL- and salt-rich liquid phases, ln($K_M$), (at the top) and in metals precipitation percentage (at the bottom).

The trend observed for metal partition coefficients between IL- and salt-rich liquid phases is maintained in the whole range of [SCN]⁻ concentrations studied. Zn is the most extracted metal followed by Cu and Co, while Ni is not extracted to the IL-rich phase independently of [SCN]⁻ concentration. Due to limitations on Al quantification by TXRF, the partition of this metal was not determined here; still, it was previously demonstrated that this system is not able to extract Al (cf. Figure 2). It is also clear that [SCN]⁻ concentration has a significant impact on metal separation efficiency, being possible to tune the system for the selective separation of different metal pairs. Unexpectedly, in the ABS composed of [SCN]⁻/Zn²⁺ molar factors between 1 and 25 the formation of a dark red colored precipitate was observed (cf. Figure S5 in the SI), with
the Zn, Cu and Co extracted metals partitioning between the IL-rich phase and precipitate as shown in Figure 3. The occurrence of this type of solid phases in liquid-liquid systems composed of ILs was previously reported and used for metals recovery, namely platinum, gold and palladium.\textsuperscript{36-38} Under certain conditions depending on the IL and ligand concentration, mixed metallic organic precipitate can occur with IL cations compensating for the charge of the anionic metal complex. In the studied system, precipitation occurs when both [N\textsubscript{4444}]Cl and NaSCN are mixed together with treated AMD sample independently of Na\textsubscript{2}SO\textsubscript{4} addition. The FTIR spectra of the resulted precipitate is presented in Figure S6 and clearly shows that the IL cation and thiocyanate anion are co-precipitating with the transition metals. These results suggest that the formation of [N\textsubscript{4444}]\textsubscript{2}[M(SCN)\textsubscript{4}] is occurring and precipitation can be thus represented according to Eq. (3):\textsuperscript{38}

\begin{equation}
2[N_{4444}]Cl + [M(SCN)\textsubscript{4}]^{2-} \leftrightarrow [N_{4444}]\textsubscript{2}[M(SCN)\textsubscript{4}](s) + 2Cl^-
\end{equation}

Despite 4 mols of [SCN]\textsuperscript{-} being necessary to form the IL metalate complex presented in Eq. (3), solid phase and red colored IL-rich liquid phase were observed at lower ratios (1:1). Thus, the possibility that Cl\textsuperscript{-} anions participate also in this reaction cannot be excluded and an organic metal complex of the type [N\textsubscript{4444}]\textsubscript{2}[M(SCN)\textsubscript{X}(Cl)\textsubscript{Y}] may be occurring, with \(X\) and \(Y\) ratio changing with the amount of [SCN]\textsuperscript{-} added to the ABS. More experimental work is needed to clarify the mechanism and the type of complex that is occurring at these conditions. At [SCN]\textsuperscript{-} higher concentrations the IL-metalate complex solubility in IL-rich phase increases and becomes completely soluble, with no precipitation occurring at [SCN]/Zn\textsuperscript{2+} \(\geq 50\) (cf. Figures 3 and S5).

Data presented in Figure 3 shows that when precipitation occurs it is possible to recover more than 80\% of the total Zn present in the AMD with high selectivity. The question therefore arises, is there any advantage to using an ABS over direct precipitation? To address this, metal precipitation percentage in homogeneous mixtures of AMD for the same [N\textsubscript{4444}]Cl and NaSCN ratio in the absence of Na\textsubscript{2}SO\textsubscript{4} was determined and compared to those using ABS, the obtained results are presented in the Figure 4. Remarkably, almost 100\% of Co, Cu and Zn precipitation is achieved when AMD is mixed only with IL and thiocyanate salt, allowing for higher metal recovery percentages when compared with those obtained in the ABS phase (cf. Figure 3). However, by considering Zn purity in the solid phase – Figure 4 – it is possible to conclude that the precipitation in homogenous solutions results in decreased Zn purity in the precipitate. When ABS are
induced by the addition of Na$_2$SO$_4$ to the homogenous mixtures, anionic metal complex solubility in IL-rich liquid phase increases due to the decrease of water concentration. This is visually evident by the increase of IL-rich phase red color (cf. Figure S5). At the same time, the selectivity is improved and the Zn purity percentages of 99.7% can be reached at low [SCN$^-$] concentrations. These results suggest that IL-based ABS can be used to develop a process for the sequential selective extraction and simultaneous recovery of transition metals from AMD.

**Figure 4.** Thiocyanate molar ratio effect on metal precipitation from AMD sample in homogenous mixtures composed AMD + IL + aqueous solution of NaSCN (at the top) and on Zn purity percentage in the solid phase obtained in homogenous mixtures (Solution) and ABS at the same conditions (at the bottom).

Considering that Zn is the most concentrated metal in AMD and the first to be extracted in ABS (higher complexation constant), searching for a balance between the percentage
of Zn that is extracted in solid-phase and its final purity, [SCN]−/Zn²⁺ molar factor of 5 seems to be the best option for Zn recovery, resulting in 81.6 % of Zn precipitation with 95.3 % of purity in a single extraction/recovery step (cf. Figures 3 and 4). Furthermore, at this ratio only Zn is partitioned to the IL-rich phase (ln(K_M)>0), while Ni and most part of Cu and Co (> 91 % of total metal amount) remain in salt-rich phase, allowing for the sequential extraction of the remaining metals. Nevertheless, aiming at the development of a sustainable process it is important to consider and study the reuse and recycling of the main chemicals/solvents used. Thus, the reuse of IL-rich phase for several extraction steps without the addition of extra amount of [SCN]− and the reuse of salt-rich phase for the sequential extraction of Cu was evaluated.

**IL- and salt-rich phases reuse in consecutive cycles of extraction**

To optimize the selective extraction and simultaneous recovery of Zn over the remaining metals present in the AMD sample, 3 consecutive cycles were carried out and the results obtained are presented in Figure 5.
Figure 5. Zn extraction and recovery from treated AMD by using the recycled IL-rich phase for 3 cycles (CYCLE 1, 2 and 3) and salt-rich phase to Cu extraction (CYCLE Cu): (A) metal partition coefficients in ABS liquid phases, ln($K_M$); (B) metal precipitation percentage; (C) Zn purity % in the solid phase (yellow) and Zn total recovery % (green).

The first extraction step was carried-out at the conditions previously considered as the best for the simultaneous extraction and recovery of Zn ([SCN]$^-$/Zn$^{2+} = 5$). The cycles 2 and 3 were induced by adding Na$_2$SO$_4$ (10 wt %, to induce phase separation) and fresh AMD treated sample (in the amount required to fulfill the system initial weight), to the IL-rich phase collected from the previous system. The results obtained for these 3 cycles demonstrate that, without the addition of NaSCN, the Zn preferential partition to the IL-
rich liquid phase decreases. Nevertheless, Zn precipitation percentage was always significantly higher than remaining metals and its purity in the solid phase increased along the cycles, reaching a maximum of 98.8 % in cycle 3 – cf. Figure 5. Furthermore, considering the total amount of AMD used in the 3 cycles of extraction/recovery, 73.1 % of total Zn was recovered in solid phase. This means that with the amount of IL added in the first extraction/recovery cycle it is possible to extract (at least) 2.1 times more Zn than if a single extraction step was used, reducing the process cost and environmental impact. This is also achieved with a very small amount of SCN-based salt, which was added to the system only in the first extraction step (cycle 1). This suggests that, after the first extraction there is still free [SCN]− anion in IL-rich liquid phase to form complexes with the novel metal loading introduced in the cycle 2 and 3. However, the decrease of [SCN]−/Zn molar ratio as a significant impact on the preferential partition of Zn to IL-rich liquid phase (cf. Figure 5A).

It is also important to note that IL losses during IL-rich phase recycling should be low – after the first cycle 2.1 % of the IL total amount is lost to salt-rich phase – due to the impact of thiocyanate addition to the system (more details are discussed in SI). Furthermore, considering that there is no co-precipitation of IL beyond the IL metalate complex in the solid phase, it is possible to estimate that the total amount of IL lost in the three extraction cycles in the form of insoluble organic metal is < 0.6 % of the initial amount of IL used to induce the first cycle.

After each extraction cycle there is a new salt-rich phase almost free of Zn and rich in the remaining metals, namely Cu. From the previous results, Cu is the metal, after Zn, with higher extraction, meaning that in the absence of Zn, Cu will be selectively extracted to the IL-rich if the correct ratio between Cu and [SCN]− anions is selected (cf. Figure 3). Thus, a last extraction cycle (designated as CYCLE Cu) was carried-out by collecting and mixing the three salt-rich phases that resulted from cycle 1 to 3 and by adding the same amount of IL (~25 wt %) added to induce the first extraction step (CYCLE 1) and excess NaSCN (2 wt %). Since most part of Cu (together with Co and Ni) loaded in each previous cycle was concentrated in the salt-rich phases, and almost no Zn was present, the increase of [SCN]− concentration was enough to result in the preferential and selective partition of Cu to the IL-rich phase, as presented in Figure 5. However, as previously observed, at this concentration of [SCN]− there is no formation of solid phase and Cu recovery requires an additional recovery step.
Discussion

The obtained results lead us to the conceptual development of a novel process which allows the sequential selective separation of strategic metals from AMD, as presented in **Figure 6**. This process is divided in three main steps: 

(i) the AMD treatment for metals concentration and Fe and organic matter precipitation by evaporation and pH adjustment,

(ii) the selective extraction and simultaneous recovery of Zn from AMD by IL-based ABS and 

(iii) the selective extraction and recovery of Cu from the salt-rich phase. All data presented in **Figure 6** was obtained from the study on IL- and salt-rich phases reuse discussed above (cf. **Figure 5**). Process steps concerning IL-rich phase recycling to initial extraction steps were not experimentally tested. Still, the results obtained in this work and previously reported data can support the feasibility of proposed process as it will be discussed further.
Figure 6. Process diagram of the sequential selective extraction and recovery of strategic metals from AMD real sample by using IL-based ABS. The IL recycling in new extraction cycles are theoretically described (process diagram described with dashed lines was not performed experimentally). TAMD: treated AMD.
The proposed process starts with AMD treatment by evaporation and pH adjustment. The evaporation in São Domingos, considering the favorable environmental conditions presented by the location, could be carried in open-air pounds. Treated AMD at pH 4.0 is obtained, as well as a waste stream that consists in Fe-rich sludge. Then, treated AMD proceeds to metal selective extraction step. Here three cycles of selective precipitation of Zn are sequentially applied, by reusing the IL-rich phase and introducing fresh treated AMD and Na$_2$SO$_4$ in each cycle (cf. Figure 5). Salt-rich phases obtained after each Zn extraction and recovery cycle are collected to a new extraction system, in which fresh IL and NaSCN are added to induce phase separation, allowing the selective extraction of Cu as previously demonstrated (cf. Figure 5). After extraction step, 95 % of Cu present in IL-rich phase (representing 46.3 % of the total Cu introduced in the full process) is recovered in the form of organic-metal complex by IL-rich phase dilution in water (at 1:5 mass ratio), with a purity of 87 %. Metals recovery allows to regenerate the IL-rich phases, allowing their reuse with minimal additional treatment to induce novel ABS and, consequently, reduce the amount of fresh IL added in the first cycle of Zn and Cu extraction ultimately leading to a more sustainable process.

Co and Ni concentrations are too low in the collected AMD (cf. Table 1) for their extraction be economically viable, despite their market price. Still, this process showed a high versatility and dynamism, induced by tunable character of IL-based ABS, and meaning that, in the presence of other AMD or similar wastewater richer in these valuable metals, the process can be optimized aiming their recovery.

Conclusion

The separation of Zn, Al, Cu, Co and Ni from real AMD water sample collected in São Domingos Portuguese mine was here studied. The selective sequential recovery of these strategic metals from AMD by using IL-based ABS was successfully demonstrated. It was shown that their ability to extract metals is mainly ruled by IL anion, while the partition coefficient is related with the formation of metal complexes of stable conformation. The [SCN]$^-$-based IL presented the best results for metal extraction. However, the system composed of [N$_{4444}$]Cl + Na$_2$SO$_4$ + H$_2$O with the addition of small and controlled amounts of NaSCN was shown to be the most promising, since it allowed to tune metal selective extraction and simultaneous recovery by adjusting the amount of [SCN]$^-$ added, and the development of a more cost-effective and sustainable process. The results obtained led to the conceptual development of a novel process for the selective
sequential extraction and recovery of Zn and Cu from AMD. In this process, 73.1 % of Zn present in treated AMD can be recovered with 98.8 % of purity, after three extraction cycles with IL-rich phase recycling and with no addition of extra amount of [SCN]− and no need of an extra recovery step. Cu is extracted in a last step from the salt-rich phases collected from Zn extraction systems and its recovery is carried out by precipitation of water insoluble IL metalate complex. The high tunable character of IL-based ABS confers to this process a high versatility, being possible to optimize it for the recovery of other strategic metals from different wastewaters. The proposed process appears as a promising strategy to the recovery of strategic metals from metal containing wastes, allowing to add value to treatment processes whilst simultaneously addressing an environmental problem if left untreated.

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Supporting Information

The Supporting Information is available free of charge and includes the detailed list of chemicals and instruments used, experimental details and analysis of AMD treatment and IL-rich phase recycling, XRD diffractograms of the obtained precipitate after AMD pH adjustment, UV-Vis spectra of metal at different experimental conditions, macroscopic aspect of ABS at different thiocyanate concentrations, FTIR and UV-Vis spectra of IL metalate complex, binodal curve of the ternary system [N4444]Cl + Na2SO4 + H2O with and without the addition of NaSCN, effect of thiocyanate anion on IL concentration in the salt-rich phase.

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Graphical Abstract

Acid Mine Drainage  Selective and tunable IL-based ABS

Metal-Rich Waste

Metal (M) extraction

$M(SCN)_2^{2-}$

Synopsis

Development of a tunable system for the sequential selective recovery of transition metals from acid mine drainage.