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.

12 **Abstract**

13 The observed imbalance between the unsustainable consumption of available natural

14 metal resources and finite deposits makes the recovery and recycling of metals from

15 metal-containing wastes an imperative. Here, ionic-liquid-based aqueous biphasic

16 systems (IL-based ABS) are proposed as an efficient alternative for selective metal

17 recovery from real copper acid mine drainage (AMD) effluents. ABS composed of

18 different IL and Na_2SO_4 were evaluated for Zn, Al, Cu, Co and Ni extraction from both

19 model solutions and AMD samples. It is shown that IL composed of thiocyanate anion

20 ($[SCN]^-$) presented a remarkable ability to extract metals from AMD through the

21 formation of stable metal-complexes. The addition of NaSCN to ABS composed of

22 tetrabutylammonium chloride ($[N_{4444}]Cl$) allowed to mimic the use of [SCN]-based IL

23 with additional advantages: tunable metal selectivity by the concentration of $[SCN]^-$

24 added to the ABS, and reduction of system cost and environmental impact. Furthermore,

25 at the $[SCN]^-$ concentration range studied here, it is observed the formation of a

26 hydrophobic salt composed of IL cations and metal complex anions, which allows the

27 selective extraction and recovery of transition metals in a single-step. The IL-rich phase

28 recyclability in three extraction cycles is demonstrated, showing the possibility to recover

29 two times more Zn than with a single extraction cycle while using the same amount of IL

30 and thiocyanate. Salt-rich phases were also recycled in a new IL-based ABS for the

31 subsequent Cu extraction and recovery. These results allow the development of a

32 sustainable process for the selective sequential recovery of transition metals from AMD.

33

34 **Keywords**: waste valorization, recovery, liquid-liquid extraction, ionic liquids, process

35 design.

36

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.[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.[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.[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.[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.[4,7-13] Different technologies were developed, namely the application of fractional precipitation,[8–10] magnetic nanoparticles,[11] extraction resins[12] and remediation systems,[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.[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.

71 Liquid-liquid extraction processes are commonly used at industrial level in the selective

72 extraction and recovery of metals. Liquid-liquid systems are usually prepared by using

73 volatile organic compounds, which are well known for their toxicity. Hydrophobic ionic

74 liquids (IL) were proposed as an alternative due to their negligible vapor pressure and

75 higher extraction efficiencies. However, IL composition based on fluorinated anions

76 and/or long alkyl chains, which result in high viscosity, cost and environmental impact,

77 limit their applicability.[14] Aqueous biphasic systems (ABS) composed of hydrophilic IL

78 are more benign alternatives.[15] ABS are formed by the mixture of two water soluble

79 solutes, namely salts and/or polymers, which above a certain concentration induces the

80 formation of two immiscible aqueous phases.[16,17] IL-based ABS present a number of

81 advantages derived from IL properties and their successful application to extract and

82 separate metals was previously demonstrated.[15,18–20] However, the application of these

83 systems to selectively recover metals from AMD as well as the stability of most IL-based

84 ABS under acidic conditions was never evaluated.

85 A novel strategy for the sequential selective recovery of strategic metals from AMD

86 water, collected from the Portuguese mine of São Domingos, using IL-based ABS is

87 developed and presented in this work. São Domingos mine is in the Iberian Pyrite belt

88 and was exploited during 100 years for pyrite, copper and sulfur production. During this

89 time and even after its exhaustion, the exposure of the open pit mine to the atmospheric

90 conditions resulted in the formation of AMD creating several environmental issues in this

91 region.[21]

92 **Methodology**

93 A detailed description of the materials and methods used in this work is described in the

94 **Supplementary Information (SI)**. AMD sample was collected in the open pit

95 impoundment of the mine of São Domingos, Portugal. Sodium sulphate, Na_2SO_4,

96 supplied by Merck with a purity of > 99 wt % was used in ABS formation mixed with

97 ILs reported in **Table 1**. IL chemical structures are presented in **Figure S1** of the **SI**.

98

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

	IL	Acronym	Purity (wt %)	Supplier
(i)	1-butyl-3-methylimidazolium thiocyanate	$[C_4C_1im][SCN]$	> 98	Iolitec
(ii)	1-butyl-3-methylimidazolium dicyanamide	$[C_4C_1im][N(CN)_2]$	98	Iolitec
(iii)	1-butyl-3-methylimidazolium octylsulfate	$[C_4C_1im][C_8SO_4]$	99	TermoFisher
(iv)	1-butyl-3-methylimidazolium triflate	$[C_4C_1im][CF_3SO_3]$	99	Iolitec
(v)	1-butyl-3-methylimidazolium ethylsulfate	$[C_4C_1im][C_2SO_4]$	98	Iolitec
(vi)	1-butyl-3-methylimidazolium tosylate	$[C_4C_1im][TOS]$	99	Iolitec
(vii)	1-butyl-3-methylimidazolium bromide	$[C_4C_1im]Br$	> 98	Iolitec
(viii)	1-heptyl-3-methylimidazolium chloride	$[C_7C_1im]Cl$	> 98	Iolitec
(ix)	1-dodecyl-3methylimidazolium chloride	$[C_{12}C_1im]Cl$	> 98	Iolitec
(x)	tributylethylphosphonium diethylphosphate	$[P_{4442}][DEP]$	99	Cytec Ind.
(xi)	tributylmethylphosphonium methylsulfate	$[P_{4441}][C_1SO_4]$	*pure*	Cytec Ind.
(xii)	tributyltetradecylphosphonium hydrogensulfate	$[P_{44414}][HSO_4]$	> 95	Iolitec
(xiii)	triisobutyl(methyl)phosphonium tosylate	$[P_{i(444)1}][TOS]$	*pure*	Cytec Ind.
(xiv)	bis(2-hydroxyethyl)dimethylammonium chloride	$[N_{11(2OH)(2OH)}]Cl$	99	Acros Organics
(xv)	benzyltributylammonium chloride	$[N_{444Bz}]Cl$	> 97	Acros Organics
(xvi)	tetrabutylammonium chloride	$[N_{4444}]Cl$	> 97	Sigma-Aldrich

100

101 *Characterization of AMD from São Domingos*

102 The nature and concentration of metals present in the AMD water sample from the mine

103 of São Domingos were determined by inductively coupled plasma mass spectrometry

104 (ICP-MS) using an Agilent Technologies 7700 Series spectrometer. The concentration of

105 sulfates (SO_4) was determined by ion chromatography using a Dionex 2000i equipment,

106 while water pH and conductivity were measured at (25 ± 1) ºC using a Mettler Toledo

107 SevenMulti pH meter within ± 0.02. Details on AMD pre-treatment carried-out before

108 metal extraction are presented in **SI**.

109

110 *Metal extraction in IL-based ABS*

111 Metals extraction was carried-out in ternary systems composed of 25 wt % of IL + 10

112 wt % of Na_2SO_4 + 65 wt % of H_2O (metal standard aqueous solution or AMD sample).

113 Ternary mixtures composition was defined by comparing the binodal curves of previously
114 reported phase diagrams for IL + Na_2SO_4 ABS and choosing a mixture point common to
115 all the biphasic regions (*cf.* **Table S1**).[22]
116 A first screening on IL-based ABS ability to extract metals was carried-out by using
117 individual aqueous metal solutions of Cu, Ni and Co at 0.01 M. The ternary mixtures
118 were vigorously stirred and, to guarantee the complete separation of the ABS coexisting
119 phases and metals partition, the systems were centrifuged at (298 ± 1) K, for 30 min at
120 3500 rpm. After this, the top and bottom phases were carefully separated, and their weight
121 (within $\pm 10^{-4}$ g) and volume (± 0.01 mL) were measured. The quantification of the metals
122 in salt-rich phase was carried out through UV-spectroscopy, using a SynergyHT
123 Microplate Reader, from Biotek, at 803 nm for Cu, 394 nm for Ni and 512 nm for Co,
124 using calibration curves previously established. The concentration of metals in IL-rich
125 phase was determined by mass balance. To avoid possible interferences from ABS phase
126 forming components, blank controls of each ternary system, without metals, were always
127 prepared and used. The influence of Na_2SO_4 concentration in metals molar extinction
128 coefficient was also evaluated and confirmed to be negligible. Three samples of each
129 phase were analyzed, in at least three individual systems, in order to determine the
130 partition coefficients (K_M) and the respective standard deviations, according to the
131 following equation,

132 $$K_M = \frac{[M]_{IL}}{[M]_{salt}}$$

133   **(1)**

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

136

137 *Metal extraction from acid mine drainage by IL-based ABS*
138 The extraction of metals from AMD was tested in the ABS composed of 25 wt % of IL +
139 10 wt % of Na_2SO_4 + 65 wt % of treated AMD with the IL $[N_{4444}]Cl$, $[C_4C_1im][N(CN)_2]$
140 and $[C_4C_1im][SCN]$, and by using the same experimental procedure described above.
141 Systems composed of $[N_{4444}]Cl$ were prepared by adding NaSCN salt, as adjuvant in the
142 following molar ratios with total molar amount of Zn present in the treated mine water
143 $(8.2 \times 10^{-3} \ mol \cdot L^{-1})$: 1:0, 1:1, 1:2, 1:5, 1:10, 1:25, 1:50 and 1:68 (Zn:SCN). In these
144 systems the following mixture point was used: 25 wt % IL + 10 wt % Na_2SO_4 + 58 wt %
145 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:

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

(2)

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 $[N_{4444}]Cl$ in the salt-rich phase of each system was determined by ^1H 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

179 at low concentrations (< 6 ppm) which is in agreement with previous data reported in the

180 literature concerning São Domingos mine waste.[21,23,24]

181

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

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

183

184 Before metal extraction, the AMD was pre-treated. Water evaporation was carried out

185 aiming to reduce the total volume of AMD sample and increase the concentration of Al,

186 Zn, Co, Ni and Cu. This type of procedure is already implemented at industrial level for

187 lithium extraction from brines to increase the metal concentration before the recovery

188 step.[25] Here, a total reduction of 67 % of the initial volume was carried leading to an

189 increase on metals concentration of 3 times, which guarantees that the minimum

190 concentration required for an adequate detection of metals after extraction (namely those

191 at very low concentrations).

192 Iron is the most concentrated metal in the AMD sample collected in the mine of São

193 Domingos. This metal presents high complexation constants when compared with the

194 remaining transition metals and Al present in AMD, blocking their preferential extraction

195 by a coordinating agent.[26] Therefore, iron removal from AMD sample before strategic

196 metals extraction becomes imperative for the development of an efficient process. It is

197 well known that iron starts to precipitate at lower pH values than other transition metals

198 in aqueous sulfate-rich solutions. Thus, the selective precipitation of iron by pH

199 adjustment was evaluated in an AMD concentrated sample with the results shown in

200 **Figure S2** and **Table S2**. As can be seen in **Figure S2**, metals precipitation efficiency is

201 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$_2$SO$_4$ + H$_2$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$_2$SO$_4$ + 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$_2$SO$_4$ ABS,[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$_2$SO$_4$ in the selected mixture point: [C$_4$C$_1$im][SCN], [C$_4$C$_1$im][N(CN)$_2$], [C$_4$C$_1$im][TOS], [C$_4$C$_1$im][CF$_3$SO$_3$],

236   [C$_4$C$_1$im][C$_8$SO$_4$], [P$_{i(444)1}$][TOS], [P$_{4441}$][C$_1$SO$_4$], [P$_{44414}$][HSO$_4$], [N$_{444Bz}$]Cl and

237   [N$_{4444}$]Cl (*cf.* **Table S1**). Nevertheless, these allowed to evaluate the impact of the IL

238   cation (imidazolium, quaternary ammonium and phosphonium) and anion (namely,

239   [SCN]$^-$, [N(CN)$_2$]$^-$, [TOS]$^-$, Cl$^-$) on metal partition.

240   The obtained results for Co, Ni and Cu partition in IL-based ABS are presented in **Figure**

241   **1**. Data presented show that only the system composed of the IL [C$_4$C$_1$im][SCN] was able

242   to partition all the three metals preferentially to the IL-rich phase (ln(K_M) > 0). The ABS

243   composed of [C$_4$C$_1$im][N(CN)$_2$] was able to extract only Cu and Ni, while

244   [C$_4$C$_1$im][CF$_3$SO$_3$]-based ABS presented an equal distribution of metals between the

245   system phases (ln(K_M) ~ 0). All the remaining biphasic systems showed no metal

246   extraction for IL-rich phase (ln(K_M) < 0). Importantly, no metal precipitation in any of

247   the systems studied was observed.
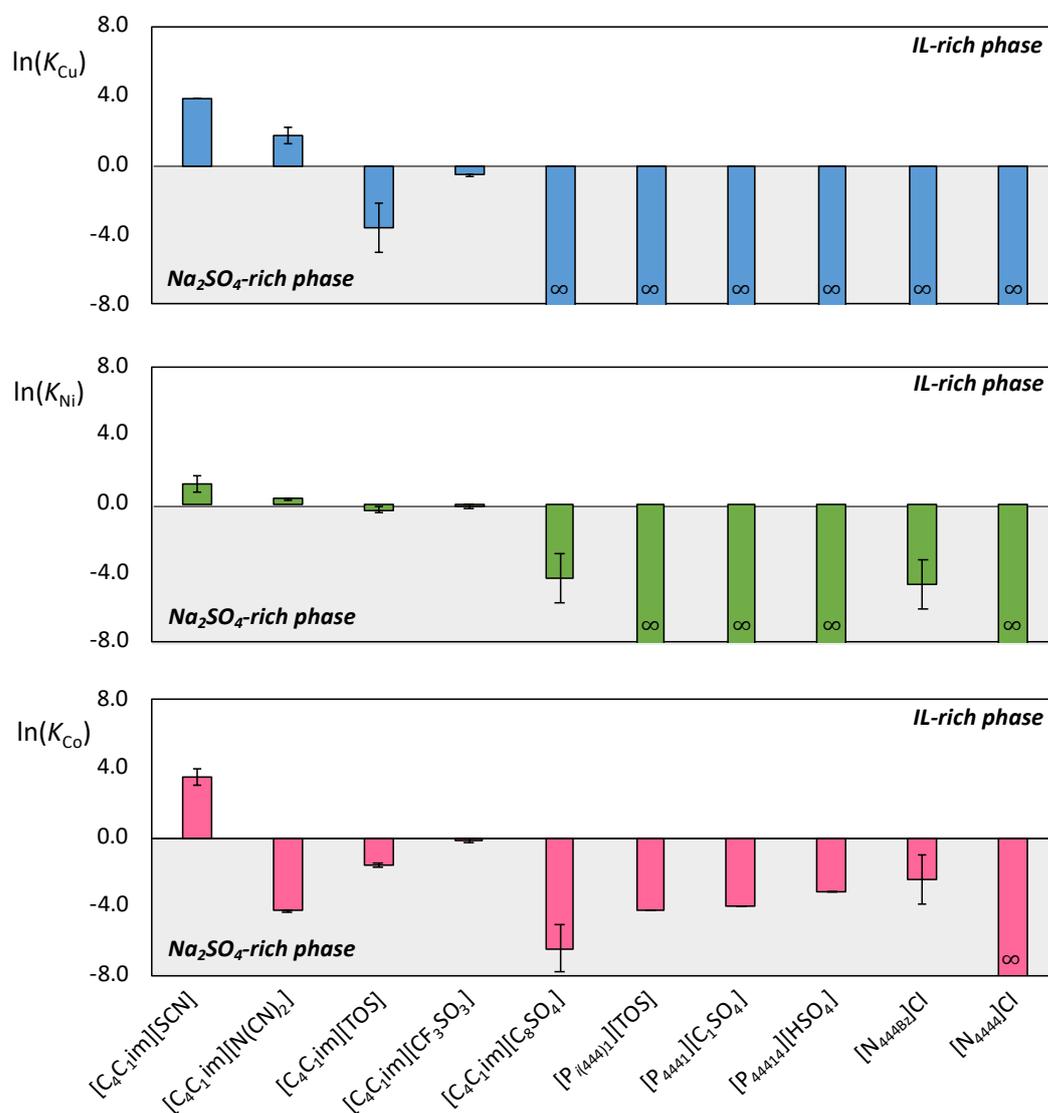
248

249   **Figure 1.** IL effect in the partition coefficient (K_M) of Cu, Co and Ni in ABS composed

250   of 25 wt % of IL + 10 wt % of Na_2SO_4 + 65 wt % of metal aqueous solution at (25 ± 1)

251   ºC and atmospheric pressure.

252

253   Metal extraction in ABS systems may occur through the formation of negatively charged

254   metal complexes with inorganic anions in the absence of an extractant.[27] Among them,

255   halides and [SCN]⁻ are commonly used as extracting agents. Thiocyanate is an

256   ambidentate ligand, *i.e.*, it coordinates with metals through either the nitrogen and/or

257   sulfur atom, and its ability to coordinate with metals such as Co, Ni and Cu is well

258   established in literature and explains the results obtained for metals extraction by using

259   [C_4C_1im][SCN]-based ABS (*cf.* **Figure 1**).[28–31] Considering the first complexation

260   constants of these metals with SCN⁻ the following trend was expected to be observed:

261   Cu^{2+} ($\log\beta_1$ =1.7) > Ni^{2+} ($\log\beta_1$ =1.14) > Co^{2+} ($\log\beta_1$ =1.01).[26] However, while Cu and

262   Co are extracted in the form of tetrahedral metal-thiocyanate complexes – $Cu(SCN)_4^{2-}$

263   and $Co(SCN)_4^{2-}$ – which are rarely formed in aqueous solution, Ni is known to stay in the

264   form of octahedral complex anion, which present a more hydrophilic character and, thus,

265   a lower partition to the IL-rich phase. These results are also supported by the comparison

266   of UV-Vis spectra of metals in IL-rich phase and aqueous solution presented in **Figure**

267   **S4**. [$N(CN)_2$]-based ILs ability to extract metals in two liquid phases systems was also

268   previously demonstrated.[32,33] Similar to [SCN]⁻ anion, [$N(CN)_2$]⁻ also presents a high

269   ability to interact with metallic cations through the formation of stable metal complexes.

270   Furthermore, the trend observed on metal partitions in [C_4C_1im][$N(CN)_2$]-based ABS –

271   $K_{Cu} > K_{Ni} \gg K_{Co}$ – is in good agreement with data previously reported.[33] Thus, it seems

272   clear that IL-based ABS ability to extract metals such as Ni, Co and Cu, to IL-rich phase

273   is mainly ruled by the IL anion nature, while the partition extension is related to the type

274   and stability of metal complexes that are formed between metal cation and IL anion.

275   Among all the systems evaluated only those composed of [SCN]⁻ and [$N(CN)_2$]⁻ were

276   able to extract metals to the IL-rich phase, being thus selected as the best candidates to

277   the metals extraction from AMD.

278

279   ***Metal extraction from AMD real sample by IL-based ABS***

280   ABS composed of Na_2SO_4 and the ILs [C_4C_1im][SCN], [C_4C_1im][$N(CN)_2$] and [N_{4444}]Cl

281   were tested in metal extraction from treated AMD sample. [N_{4444}]Cl-based ABS showed

282   no metal extraction when single metal aqueous solutions were used (*cf.* **Figure 1**).

283   Nevertheless, to guarantee that AMD composition is not affecting the trends previously

284   observed, this IL was also considered in these experiments. It is also important to note

285   that, when dealing with metal extraction from AMD, the sulfate present in the system

286   needs to be taken into account; nevertheless, it represents only 7.3 % of the total amount

287   of Na_2SO_4 (0.72 wt % of mixture point composition) needed to induce the phases

288   separation, being always necessary to add 9.3 wt % more sulfate salt to the mixture. The

289   results obtained are presented in **Figure 2**.
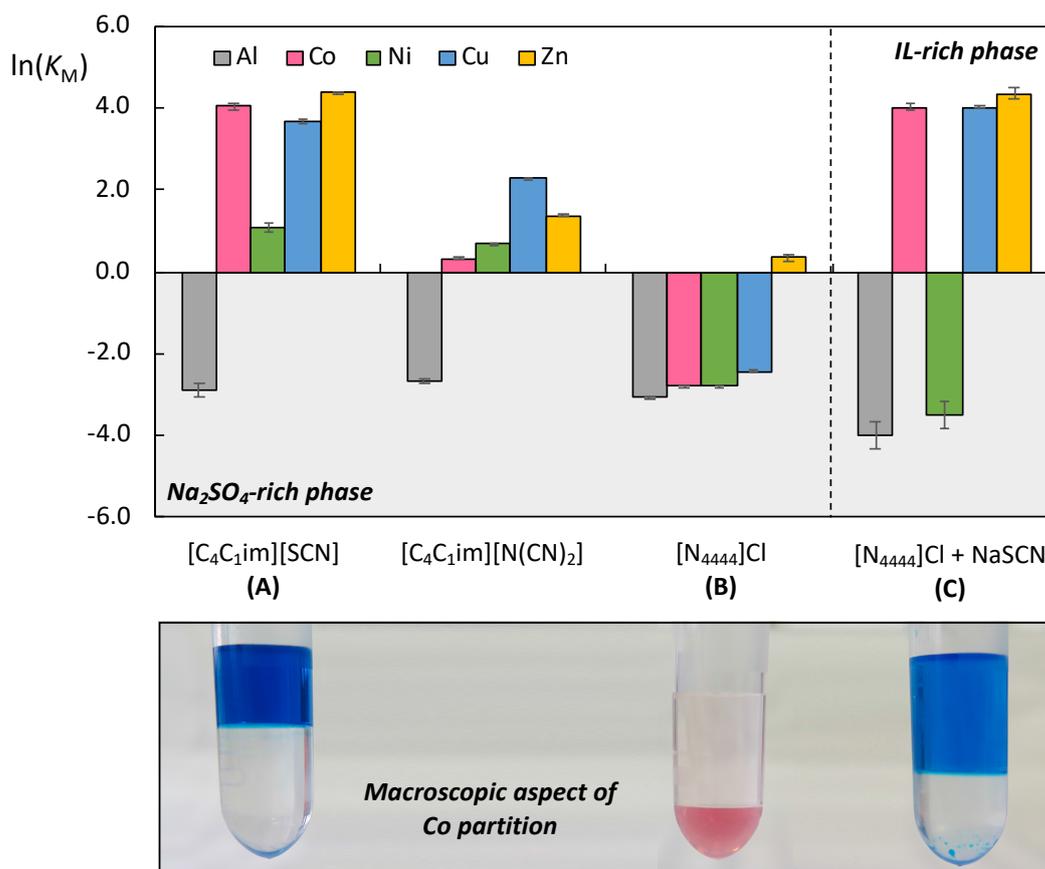
290

291

292   **Figure 2.** Metal extraction from AMD treated sample by using IL + Na_2SO_4 + H_2O ABS

293   at pH 4 and (298 ± 1) K: metal partition coefficients, $\ln(K_M)$ (at the top) and macroscopic

294   aspect of Co partition in the identified systems (at the bottom).

295

296   The extractions of Al, Co, Ni, Cu and Zn from pretreated AMD sample in IL-based ABS

297   were experimentally assessed. The following trends were observed for the partition

298   coefficients: Zn > Co > Cu >> Ni > Al in [C_4C_1im][SCN]-, Cu > Zn > Ni > Co > Al in

299   [C_4C_1im][N(CN)$_2$]-, and no metal extraction was observed in the [N_{4444}]Cl-based system.

300   For Cu, Co and Ni, the results obtained are in good agreement with those obtained when

12

301 single-metal aqueous solutions were considered at the same conditions (*cf.* **Figure 1**). In

302 what concerns Zn and Al, IL-based ABS composed of $[C_4C_1im][SCN]$ and

303 $[C_4C_1im][N(CN)_2]$ were able to induce the preferential partition of Zn to the IL-rich

304 phase, while there were no systems capable to extract Al. Al is not able to form anionic

305 complexes in presence of any of these ions. In fact, only the hydrophilic complex

306 $[Al(SCN)(H_2O)_5]^{2+}$ was reported for temperature and ionic strength conditions similar to

307 the tested system – which may justify its preferential partition to the salt-rich phase.[34]

308

309 *Selective extraction of strategic metals from AMD*

310 The relatively high costs associated to imidazolium-based ILs may create limitations to

311 their use at industrial scale. Quaternary ammonium-based ILs are much less expensive

312 than their imidazolium-based counterparts and, generally, present also a lower

313 environmental impact.[35] In **Figure 2** are also presented the results obtained for metal

314 extraction from treated AMD by using an ABS composed of Na_2SO_4, $[N_{4444}]Cl$ and 2.0

315 wt % of NaSCN. The observed results are quite interesting since metal partition

316 coefficients similar to those obtained with the $[C_4C_1im][SCN]$-based system were

317 obtained in a system that was previously shown to be unable to extract metals. It is

318 expected that a similar result can be obtained if the IL $[N_{4444}][SCN]$ is directly used.

319 However, the addition of thiocyanate anion to the system in the form of NaSCN presents

320 some advantages: (i) it allows to reduce the costs of the system since it is less expensive

321 to use NaSCN (~0.32 €/g at Sigma-Aldrich) and $[N_{4444}]Cl$ (~2.5 €/g at Sigma Aldrich)

322 than $[N_{4444}][SCN]$ (~4.8 €/g at Sigma-Aldrich), (ii) it allows to reduce system

323 environmental impact, being possible to control the amount of $[SCN]^-$ added and reduce

324 it up to the minimum necessary to achieve the desired metal extraction, and (iii) it allows

325 tunable metal selectivity controlled by the concentration of $[SCN]^-$ added to the ABS, as

326 will be demonstrated further.

327 As previously referred, metal extraction by coordinating ions such as $[SCN]^-$ is ruled by

328 the formation of stable complexes, better extracting those metals that present high

329 complexation constants and result in complexes of more stable conformation. Thus, metal

330 selectivity may be controlled by the amount of coordination anion added to the system.

331 The effect of thiocyanate anion concentration on metals partition from AMD sample was

332 evaluated and the results obtained are presented in **Figure 3**. The maximum amount of

333 Zn (the most concentrated metal in treated AMD sample) was considered as reference to

334 define the amount of $[SCN]^-$ to be added to the ABS.
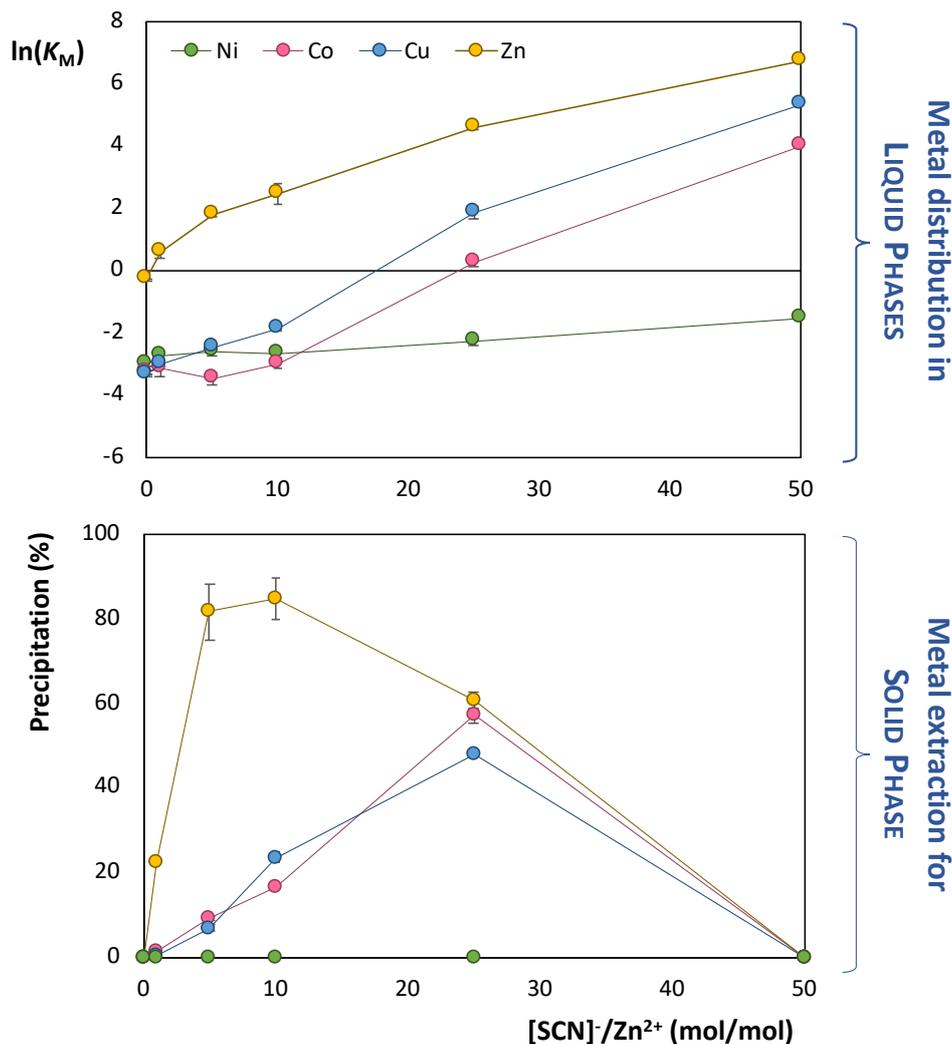
Figure 3. Thiocyanate molar ratio effect on metal extraction from AMD sample: [SCN]⁻ influence in metal partition between IL- and salt-rich liquid phases, $\ln(K_M)$, (at the top) and in metals precipitation percentage (at the bottom).

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]⁻/ Zn^{2+} molar factors between 1 and 25 the formation of a dark red colored precipitate was observed (*cf.* **Figure S5** in the **SI**), with

350   the Zn, Cu and Co extracted metals partitioning between the IL-rich phase and precipitate

351   as shown in **Figure 3**. The occurrence of this type of solid phases in liquid-liquid systems

352   composed of ILs was previously reported and used for metals recovery, namely platinum,

353   gold and palladium.[36-38] Under certain conditions depending on the IL and ligand

354   concentration, mixed metallic organic precipitate can occur with IL cations compensating

355   for the charge of the anionic metal complex. In the studied system, precipitation occurs

356   when both [N$_{4444}$]Cl and NaSCN are mixed together with treated AMD sample

357   independently of Na$_2$SO$_4$ addition. The FTIR spectra of the resulted precipitate is

358   presented in **Figure S6** and clearly shows that the IL cation and thiocyanate anion are co-

359   precipitating with the transition metals. These results suggest that the formation of

360   [N$_{4444}$]$_2$[M(SCN)$_4$] is occurring and precipitation can be thus represented according to

361   **Eq. (3)**:[38]

362    $2[N_{4444}]Cl + [M(SCN)_4]^{2-} \leftrightarrow [N_{4444}]_2[M(SCN)_4](s) + 2Cl^-$

363   **(3)**
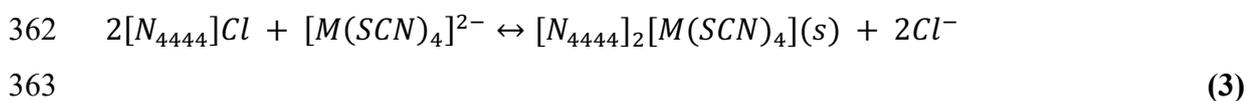
364   Despite 4 mols of [SCN]$^-$ being necessary to form the IL metalate complex presented in

365   **Eq. (3)**, solid phase and red colored IL-rich liquid phase were observed at lower ratios

366   (1:1). Thus, the possibility that Cl$^-$ anions participate also in this reaction cannot be

367   excluded and an organic metal complex of the type $[N_{4444}]_2[M(SCN)_X(Cl)_Y]$ may be

368   occurring, with X and Y ratio changing with the amount of [SCN]$^-$ added to the ABS.

369   More experimental work is needed to clarify the mechanism and the type of complex that

370   is occurring at these conditions. At [SCN]$^-$ higher concentrations the IL-metalate complex

371   solubility in IL-rich phase increases and becomes completely soluble, with no

372   precipitation occurring at [SCN]$^-$/Zn^{2+} ≥ 50 (*cf.* **Figures 3** and **S5**).

373   Data presented in **Figure 3** shows that when precipitation occurs it is possible to recover

374   more than 80 % of the total Zn present in the AMD with high selectivity. The question

375   therefore arises, is there any advantage to using an ABS over direct precipitation? To

376   address this, metal precipitation percentage in homogeneous mixtures of AMD for the

377   same [N$_{4444}$]Cl and NaSCN ratio in the absence of Na$_2$SO$_4$ was determined and compared

378   to those using ABS, the obtained results are presented in the **Figure 4**. Remarkably,

379   almost 100 % of Co, Cu and Zn precipitation is achieved when AMD is mixed only with

380   IL and thiocyanate salt, allowing for higher metal recovery percentages when compared

381   with those obtained in the ABS phase (*cf.* **Figure 3**). However, by considering Zn purity

382   in the solid phase – **Figure 4** – it is possible to conclude that the precipitation in

383   homogenous solutions results in decreased Zn purity in the precipitate. When ABS are

384   induced by the addition of Na_2SO_4 to the homogenous mixtures, anionic metal complex

385   solubility in IL-rich liquid phase increases due to the decrease of water concentration.

386   This is visually evident by the increase of IL-rich phase red color (*cf.* **Figure S5**). At the

387   same time, the selectivity is improved and the Zn purity percentages of 99.7 % can be

388   reached at low $[SCN]^-$ concentrations. These results suggest that IL-based ABS can be

389   used to develop a process for the sequential selective extraction and simultaneous

390   recovery of transition metals from AMD.
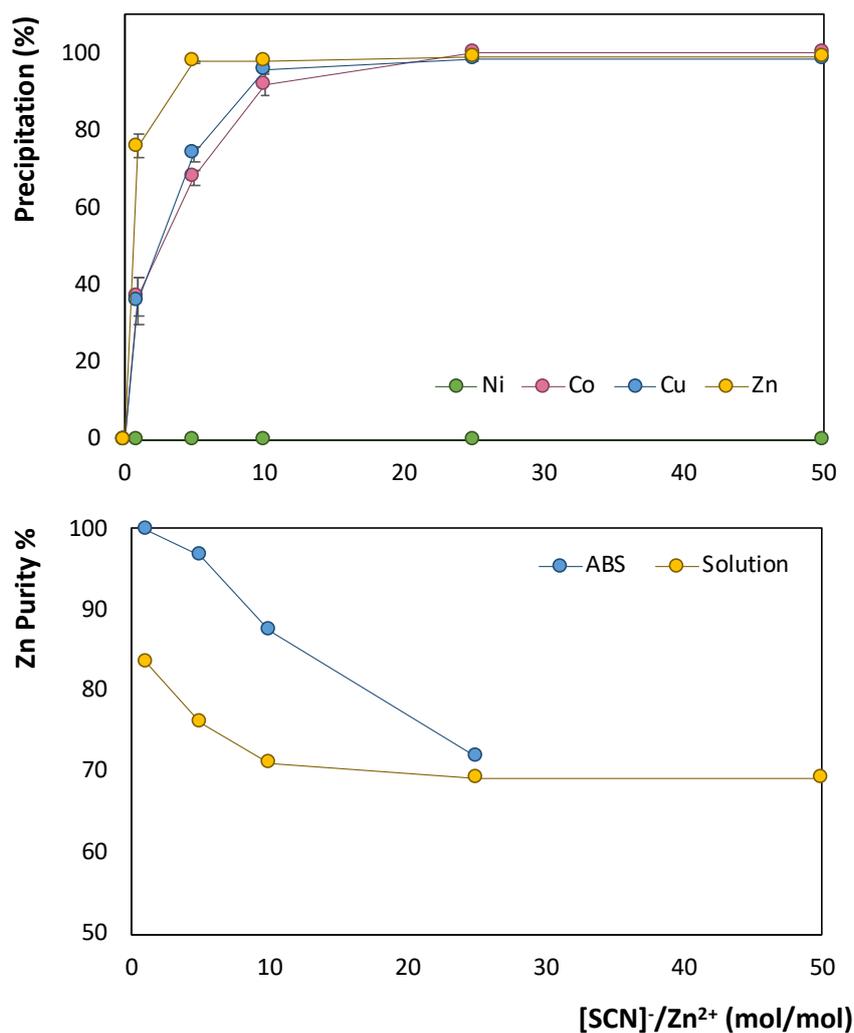
391

392   **Figure 4.** Thiocyanate molar ratio effect on metal precipitation from AMD sample in

393   homogenous mixtures composed AMD + IL + aqueous solution of NaSCN (at the top)

394   and on Zn purity percentage in the solid phase obtained in homogenous mixtures

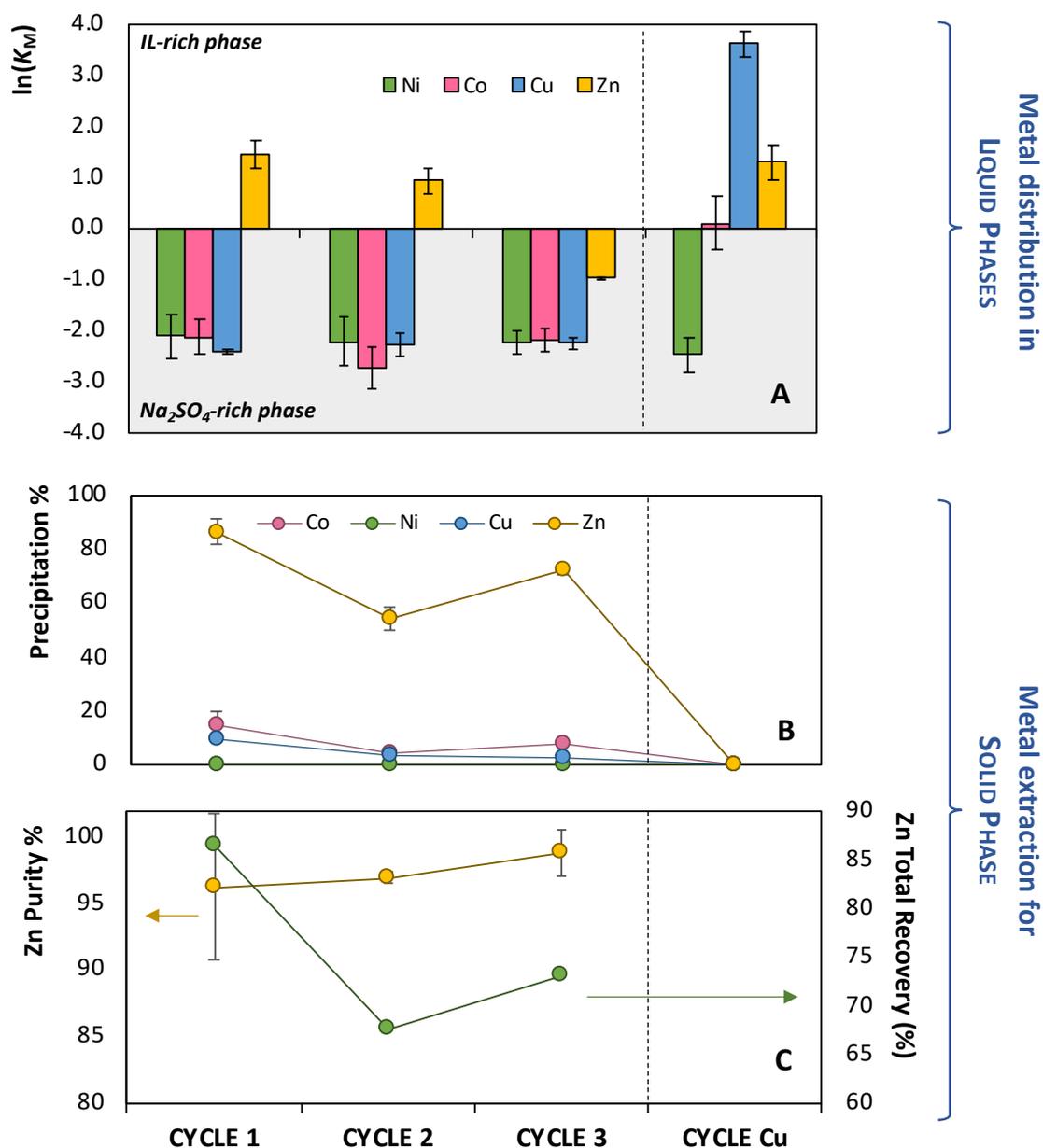395   (*Solution*) and ABS at the same conditions (at the bottom).

396

397   Considering that Zn is the most concentrated metal in AMD and the first to be extracted

398   in ABS (higher complexation constant), searching for a balance between the percentage

16

399   of Zn that is extracted in solid-phase and its final purity, $[SCN]^-/Zn^{2+}$ molar factor of 5

400   seems to be the best option for Zn recovery, resulting in 81.6 % of Zn precipitation with

401   95.3 % of purity in a single extraction/recovery step (*cf.* **Figures 3** and **4**). Furthermore,

402   at this ratio only Zn is partitioned to the IL-rich phase ($\ln(K_M)$>0), while Ni and most part

403   of Cu and Co (> 91 % of total metal amount) remain in salt-rich phase, allowing for the

404   sequential extraction of the remaining metals. Nevertheless, aiming at the development

405   of a sustainable process it is important to consider and study the reuse and recycling of

406   the main chemicals/solvents used. Thus, the reuse of IL-rich phase for several extraction

407   steps without the addition of extra amount of $[SCN]^-$ and the reuse of salt-rich phase for

408   the sequential extraction of Cu was evaluated.

409

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

411   To optimize the selective extraction and simultaneous recovery of Zn over the remaining

412   metals present in the AMD sample, 3 consecutive cycles were carried out and the results

413   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_2SO_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-

426 rich liquid phase decreases. Nevertheless, Zn precipitation percentage was always
427 significantly higher than remaining metals and its purity in the solid phase increased along
428 the cycles, reaching a maximum of 98.8 % in cycle 3 – *cf.* **Figure 5**. Furthermore,
429 considering the total amount of AMD used in the 3 cycles of extraction/recovery, 73.1 %
430 of total Zn was recovered in solid phase. This means that with the amount of IL added in
431 the first extraction/recovery cycle it is possible to extract (at least) 2.1 times more Zn than
432 if a single extraction step was used, reducing the process cost and environmental impact.
433 This is also achieved with a very small amount of SCN-based salt, which was added to
434 the system only in the first extraction step (cycle 1). This suggests that, after the first
435 extraction there is still free $[SCN]^-$ anion in IL-rich liquid phase to form complexes with
436 the novel metal loading introduced in the cycle 2 and 3. However, the decrease of $[SCN]^-$
437 /Zn molar ratio as a significant impact on the preferential partition of Zn to IL-rich liquid
438 phase (*cf.* **Figure 5A**).
439 It is also important to note that IL losses during IL-rich phase recycling should be low –
440 after the first cycle 2.1 % of the IL total amount is lost to salt-rich phase – due to the
441 impact of thiocyanate addition to the system (more details are discussed in **SI**).
442 Furthermore, considering that there is no co-precipitation of IL beyond the IL metalate
443 complex in the solid phase, it is possible to estimate that the total amount of IL lost in the
444 three extraction cycles in the form of insoluble organic metal is < 0.6 % of the initial
445 amount of IL used to induce the first cycle.
446 After each extraction cycle there is a new salt-rich phase almost free of Zn and rich in the
447 remaining metals, namely Cu. From the previous results, Cu is the metal, after Zn, with
448 higher extraction, meaning that in the absence of Zn, Cu will be selectively extracted to
449 the IL-rich if the correct ratio between Cu and $[SCN]^-$ anions is selected (*cf.* **Figure 3**).
450 Thus, a last extraction cycle (designated as CYCLE Cu) was carried-out by collecting and
451 mixing the three salt-rich phases that resulted from cycle 1 to 3 and by adding the same
452 amount of IL (~25 wt %) added to induce the first extraction step (CYCLE 1) and excess
453 NaSCN (2 wt %). Since most part of Cu (together with Co and Ni) loaded in each previous
454 cycle was concentrated in the salt-rich phases, and almost no Zn was present, the increase
455 of $[SCN]^-$ concentration was enough to result in the preferential and selective partition of
456 Cu to the IL-rich phase, as presented in **Figure 5**. However, as previously observed, at
457 this concentration of $[SCN]^-$ there is no formation of solid phase and Cu recovery requires
458 an additional recovery step.
459

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.
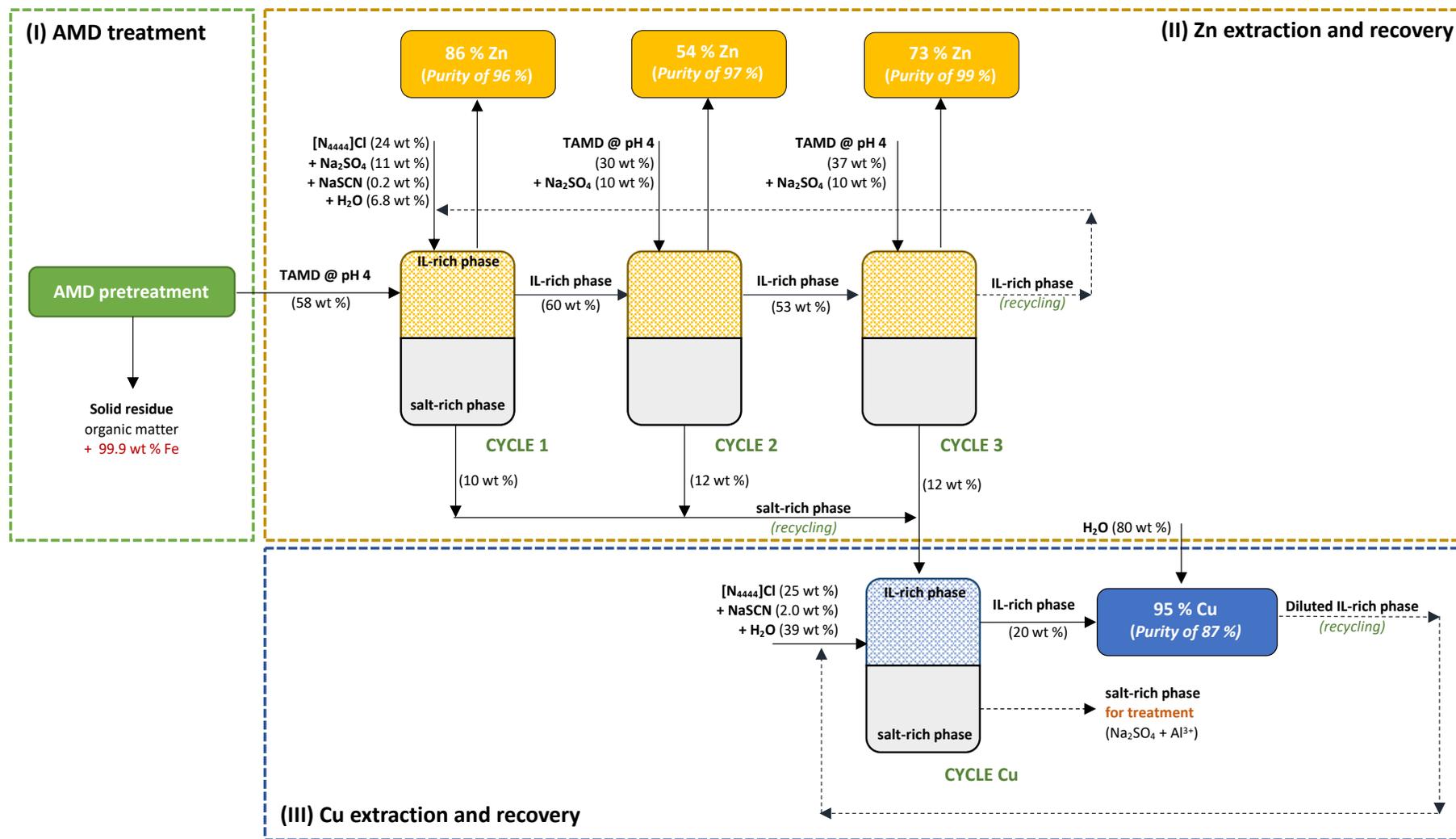
Figure 6. Process diagram of the sequential selective extraction and recovery of strategic metals from AMD real sample by using IL-based ABS. The IL recycling in new extraction cycles are theoretically described (process diagram described with dashed lines was not performed experimentally). *TAMD*: treated AMD.

476 The proposed process starts with AMD treatment by evaporation and pH adjustment. The
477 evaporation in São Domingos, considering the favorable environmental conditions
478 presented by the location, could be carried in open-air pounds. Treated AMD at pH 4.0 is
479 obtained, as well as a waste stream that consists in Fe-rich sludge. Then, treated AMD
480 proceeds to metal selective extraction step. Here three cycles of selective precipitation of
481 Zn are sequentially applied, by reusing the IL-rich phase and introducing fresh treated
482 AMD and Na_2SO_4 in each cycle (*cf.* **Figure 5**). Salt-rich phases obtained after each Zn
483 extraction and recovery cycle are collected to a new extraction system, in which fresh IL
484 and NaSCN are added to induce phase separation, allowing the selective extraction of Cu
485 as previously demonstrated (*cf.* **Figure 5**). After extraction step, 95 % of Cu present in
486 IL-rich phase (representing 46.3 % of the total Cu introduced in the full process) is
487 recovered in the form of organic-metal complex by IL-rich phase dilution in water (at 1:5
488 mass ratio), with a purity of 87 %. Metals recovery allows to regenerate the IL-rich
489 phases, allowing their reuse with minimal additional treatment to induce novel ABS and,
490 consequently, reduce the amount of fresh IL added in the first cycle of Zn and Cu
491 extraction ultimately leading to a more sustainable process.

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

497

498 **Conclusion**
499 The separation of Zn, Al, Cu, Co and Ni from real AMD water sample collected in São
500 Domingos Portuguese mine was here studied. The selective sequential recovery of these
501 strategic metals from AMD by using IL-based ABS was successfully demonstrated. It
502 was shown that their ability to extract metals is mainly ruled by IL anion, while the
503 partition coefficient is related with the formation of metal complexes of stable
504 conformation. The [SCN]-based IL presented the best results for metal extraction.
505 However, the system composed of $[N_{4444}]Cl + Na_2SO_4 + H_2O$ with the addition of small
506 and controlled amounts of NaSCN was shown to be the most promising, since it allowed
507 to tune metal selective extraction and simultaneous recovery by adjusting the amount of
508 [SCN]⁻ added, and the development of a more cost-effective and sustainable process. The
509 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.

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 $[N_{4444}]Cl + Na_2SO_4 + H_2O$ with and without the addition of NaSCN, effect of thiocyanate anion on IL concentration in the salt-rich phase.

References

(1)   European Commission, *Critical Raw Materials Resilience: Charting a Path towards Greater Security and Sustainability (COM/2020/474 Final)*; Brussels,

544   2020.

(2)   Graedel, T. E.; Harper, E. M.; Nassar, N. T.; Nuss, P.; Reck, B. K. Criticality of Metals and Metalloids. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 4257–4262. DOI: 10.1073/pnas.1500415112.

(3)   Park, I.; Tabelin, C. B.; Jeon, S.; Li, X.; Seno, K.; Ito, M.; Hiroyoshi, N. A Review of Recent Strategies for Acid Mine Drainage Prevention and Mine Tailings Recycling. *Chemosphere* **2019**, *219*, 588–606. DOI: 10.1016/j.chemosphere.2018.11.053.

(4)   Naidu, G.; Ryu, S.; Thiruvenkatachari, R.; Choi, Y.; Jeong, S.; Vigneswaran, S. A Critical Review on Remediation, Reuse, and Resource Recovery from Acid Mine Drainage. *Environ. Pollut.* **2019**, *247*, 1110–1124. DOI: 10.1016/j.envpol.2019.01.085.

(5)   Wei, X.; Zhang, S.; Shimko, J.; Dengler, R. W. Mine Drainage: Treatment Technologies and Rare Earth Elements. *Water Environ. Res.* **2019**, *91*, 1061–1068. DOI: 10.1002/wer.1178.

(6)   Rambabu, K.; Banat, F.; Pham, Q. M.; Ho, S.-H.; Ren, N.-Q.; Show, P. L. Biological Remediation of Acid Mine Drainage: Review of Past Trends and Current Outlook. *Environ. Sci. Ecotechnology* **2020**, *2*, 100024. DOI: 10.1016/j.ese.2020.100024.

(7)   Kefeni, K. K.; Msagati, T. A. M.; Mamba, B. B. Acid Mine Drainage: Prevention, Treatment Options, and Resource Recovery: A Review. *J. Clean. Prod.* **2017**, *151*, 475–493. DOI: 10.1016/j.jclepro.2017.03.082.

(8)   MacIngova, E.; Luptakova, A. Recovery of Metals from Acid Mine Drainage. *Chem. Eng. Trans.* **2012**, *28*, 109–114. DOI: 10.3303/CET1228019.

(9)   Yan, B.; Mai, G.; Chen, T.; Lei, C.; Xiao, X. Pilot Test of Pollution Control and Metal Resource Recovery for Acid Mine Drainage. *Water Sci. Technol.* **2015**, *72*, 2308–2317. DOI: 10.2166/wst.2015.429.

(10)   Chen, T.; Yan, B.; Lei, C.; Xiao, X. Pollution Control and Metal Resource Recovery for Acid Mine Drainage. *Hydrometallurgy* **2014**, *147–148*, 112–119. DOI: 10.1016/j.hydromet.2014.04.024.

(11)   Kefeni, K. K.; Msagati, T. M.; Mamba, B. B. Synthesis and Characterization of Magnetic Nanoparticles and Study Their Removal Capacity of Metals from Acid Mine Drainage. *Chem. Eng. J.* **2015**, *276*, 222–231. DOI: 10.1016/j.cej.2015.04.066.
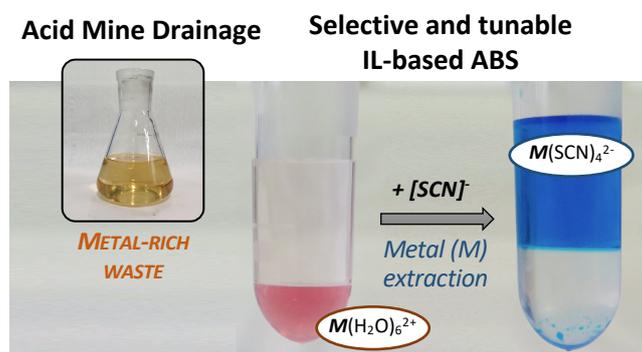
578   (12)   Larsson, M.; Nosrati, A.; Kaur, S.; Wagner, J.; Baus, U.; Nydén, M. Copper
579   Removal from Acid Mine Drainage-Polluted Water Using Glutaraldehyde-
580   Polyethyleneimine Modified Diatomaceous Earth Particles. *Heliyon* **2018**, *4*,
581   e00520. DOI: 10.1016/j.heliyon.2018.e00520.

582   (13)   Ayora, C.; Macías, F.; Torres, E.; Lozano, A.; Carrero, S.; Nieto, J. M.; Pérez-
583   López, R.; Fernández-Martínez, A.; Castillo-Michel, H. Recovery of Rare Earth
584   Elements and Yttrium from Passive-Remediation Systems of Acid Mine Drainage.
585   *Environ. Sci. Technol.* **2016**, *50*, 8255–8262. DOI: 10.1021/acs.est.6b02084.

586   (14)   Schaeffer, N.; Passos, H.; Billard, I.; Papaiconomou, N.; Coutinho, J. A. P.
587   Recovery of Metals from Waste Electrical and Electronic Equipment (WEEE)
588   Using Unconventional Solvents Based on Ionic Liquids. *Crit. Rev. Environ. Sci.
589   Technol.* **2018**, *4*, 859–922. DOI: 10.1080/10643389.2018.1477417.

590   (15)   Freire, M. G.; Cláudio, A. F. M.; Araújo, J. M. M.; Coutinho, J. A. P.; Marrucho,
591   I. M.; Lopes, J. N. C.; Rebelo, L. P. N. Aqueous Biphasic Systems: A Boost
592   Brought about by Using Ionic Liquids. *Chem. Soc. Rev.* **2012**, *41*, 4966–4995.
593   DOI: 10.1039/c2cs35151j.

594   (16)   *Partitioning in Aqueous Two-Phase System*; Walter, H., Brooks, D. E., Fisher, D.,
595   Eds.; Academic Press, 1985. DOI: 10.1016/B978-0-12-733860-6.50006-2.

596   (17)   Albertsson, P. Å. *Partition of Cell Particles and Macromolecules*, 2nd ed.; John
597   Wiley & Sons Inc.: New York, 1971.

598   (18)   Onghena, B.; Opsomer, T.; Binnemans, K. Separation of Cobalt and Nickel Using
599   a Thermomorphic Ionic-Liquid-Based Aqueous Biphasic System. *Chem.
600   Commun.* **2015**, *51*, 15932–15935. DOI: 10.1039/c5cc06595j.

601   (19)   Akama, Y.; Ito, M.; Tanaka, S. Selective Separation of Cadmium from Cobalt,
602   Copper, Iron (III) and Zinc by Water-Based Two-Phase System of
603   Tetrabutylammonium Bromide. *Talanta* **2000**, *53*, 645–650. DOI: 10.1016/S0039-
604   9140(00)00555-5.

605   (20)   Akama, Y.; Sali, A. Extraction Mechanism of Cr(VI) on the Aqueous Two-Phase
606   System of Tetrabutylammonium Bromide and $(NH_4)_2SO_4$ Mixture. *Talanta* **2002**,
607   *57*, 681–686. DOI: 10.1016/S0039-9140(02)00076-0.

608   (21)   Álvarez-Valero, A. M.; Pérez-López, R.; Matos, J.; Capitán, M. A.; Nieto, J. M.;
609   Sáez, R.; Delgado, J.; Caraballo, M. Potential Environmental Impact at São
610   Domingos Mining District (Iberian Pyrite Belt, SW Iberian Peninsula): Evidence
611   from a Chemical and Mineralogical Characterization. *Environ. Geol.* **2008**, *55*,

612   1797–1809. DOI: 10.1007/s00254-007-1131-x.

613   (22)   Cláudio, A. F. M.; Ferreira, A. M.; Shahriari, S.; Freire, M. G.; Coutinho, J. A. P.
614   Critical Assessment of the Formation of Ionic-Liquid-Based Aqueous Two-Phase
615   Systems in Acidic Media. *J. Phys. Chem. B* **2011**, *115*, 11145–11153. DOI:
616   10.1021/jp204865a.

617   (23)   Durães, N.; Bobos, I.; da Silva, E. F. Speciation and Precipitation of Heavy Metals
618   in High-Metal and High-Acid Mine Waters from the Iberian Pyrite Belt (Portugal).
619   *Environ. Sci. Pollut. Res.* **2017**, *24*, 4562–4576. DOI: 10.1007/s11356-016-8161-
620   4.

621   (24)   Costa, M. C.; Duarte, J. C. Bioremediation of Acid Mine Drainage Using Acidic
622   Soil and Organic Wastes for Promoting Sulphate-Reducing Bacteria Activity on a
623   Column Reactor. *Water. Air. Soil Pollut.* **2005**, *165*, 325–345. DOI:
624   10.1007/s11270-005-6914-7.

625   (25)   Flexer, V.; Baspineiro, C. F.; Galli, C. I. Lithium Recovery from Brines: A Vital
626   Raw Material for Green Energies with a Potential Environmental Impact in Its
627   Mining and Processing. *Sci. Total Environ.* **2018**, *639*, 1188–1204. DOI:
628   10.1016/j.scitotenv.2018.05.223.

629   (26)   Anraha Bahta; Parker, G. A.; Tuck, D. G. Critical Survey of Stability Constants of
630   Complexes of Thiocyanate Ion. *Pure Appl. Chem.* **1997**, *69*, 1489–1548. DOI:
631   10.1351/pac199769071489

632   (27)   Lommelen, R.; Vander Hoogerstraete, T.; Onghena, B.; Billard, I.; Binnemans, K.
633   Model for Metal Extraction from Chloride Media with Basic Extractants: A
634   Coordination Chemistry Approach. *Inorg. Chem.* **2019**, *58*, 12289–12301. DOI:
635   10.1021/acs.inorgchem.9b01782.

636   (28)   Shibukawa, M.; Nakayama, N.; Hayashi, T.; Shibuya, D.; Endo, Y.; Kawamura, S.
637   Extraction Behaviour of Metal Ions in Aqueous Polyethylene Glycol-Sodium
638   Sulphate Two-Phase Systems in the Presence of Iodide and Thiocyanate Ions.
639   *Anal. Chim. Acta* **2001**, *427*, 293–300. DOI: 10.1016/S0003-2670(00)01207-1.

640   (29)   Patrício, P. da R.; Mesquita, M. C.; da Silva, L. H. M.; Da Silva, M. C. H.
641   Application of Aqueous Two-Phase Systems for the Development of a New
642   Method of Cobalt(II), Iron(III) and Nickel(II) Extraction: A Green Chemistry
643   Approach. *J. Hazard. Mater.* **2011**, *193*, 311–318. DOI:
644   10.1016/j.jhazmat.2011.07.062.

645   (30)   Rodrigues, G. D.; da Silva, M. do C. H.; da Silva, L. H. M.; Paggioli, F. J.; Minim,

646   L. A.; Reis Coimbra, J. S. dos. Liquid-Liquid Extraction of Metal Ions without Use

647   of Organic Solvent. *Sep. Purif. Technol.* **2008**, *62*, 687–693. DOI:

648   10.1016/j.seppur.2008.03.032.

649 (31) Álvarez, M. S.; Gutiérrez, E.; Rodríguez, A.; Sanromán, M. Á.; Deive, F. J.

650   Environmentally Benign Sequential Extraction of Heavy Metals from Marine

651   Sediments. *Ind. Eng. Chem. Res.* **2014**, *53*, 8615–8620. DOI: 10.1021/ie500927q.

652 (32) Boudesocque, S.; Mohamadou, A.; Dupont, L.; Martinez, A.; Déchamps, I. Use of

653   Dicyanamide Ionic Liquids for Extraction of Metal Ions. *RSC Adv.* **2016**, *6*,

654   107894–107904. DOI: 10.1039/C6RA18991A.

655 (33) Diabate, P.; Dupont, L.; Boudesocque, S.; Mohamadou, A. Novel Task Specific

656   Ionic Liquids to Remove Heavy Metals from Aqueous Effluents. *Metals (Basel).*

657   **2018**, *8*, 412. DOI: 10.3390/met8060412.

658 (34) Sasic, S.; Zoric, D.; Jeremic, M.; Antic-Jovanovic, A. Study of Complex

659   Formation in Al(III)-Thiocyanate-Water System via Raman Spectra and Factor

660   Analysis. *Polyhedron* **2001**, *20*, 839–847. DOI: 10.1016/S0277-5387(01)00699-4.

661 (35) Ventura, S. P. M.; Marques, C. S.; Rosatella, A. A.; Afonso, C. A. M.; Gonçalves,

662   F.; Coutinho, J. A. P. Toxicity Assessment of Various Ionic Liquid Families

663   towards Vibrio Fischeri Marine Bacteria. *Ecotoxicol. Environ. Saf.* **2012**, *76*, 162–

664   168. DOI: 10.1016/j.ecoenv.2011.10.006.

665 (36) Papaiconomou, N.; Vite, G.; Goujon, N.; Lévêque, J. M.; Billard, I. Efficient

666   Removal of Gold Complexes from Water by Precipitation or Liquid-Liquid

667   Extraction Using Ionic Liquids. *Green Chem.* **2012**, *14*, 2050–2056. DOI:

668   10.1039/c2gc35222b.

669 (37) Gras, M.; Duclos, L.; Schaeffer, N.; Mogilireddy, V.; Svecova, L.; Eric Chaînet;

670   Billard, I.; Papaiconomou, N. A Comparison of Cobalt and Platinum Extraction in

671   Hydrophobic and Hydrophilic Ionic Liquids: Implication for Proton Exchange

672   Membrane Fuel Cell Recycling. *ACS Sustain. Chem. Eng.* **2020**, *8*, 15865–15874.

673   DOI: 10.1021/acssuschemeng.0c04263.

674 (38) Génand-Pinaz, S.; Papaiconomou, N.; Leveque, J. M. Removal of Platinum from

675   Water by Precipitation or Liquid-Liquid Extraction and Separation from Gold

676   Using Ionic Liquids. *Green Chem.* **2013**, *15*, 2493–2501. DOI:

677   10.1039/c3gc40557e.

678

679 **Graphical Abstract**

680

Acid Mine Drainage **Selective and tunable IL-based ABS**

METAL-RICH WASTE

+ [SCN]⁻

Metal (M) extraction

$M(SCN)_4^{2-}$

$M(H_2O)_6^{2+}$

681

682

683 **Synopsis**

684 Development of a tunable system for the sequential selective recovery of transition metals

685 from acid mine drainage.