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7 Synergistic aqueous biphasic systems: a new
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11 paradigm for the ‘one-pot’ hydrometallurgical
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ABSTRACT

Acidic aqueous biphasic system (AcABS), in which the inorganic salt component of traditional aqueous biphasic system (ABS) is replaced by the inorganic acid inherently present in typical hydrometallurgical leachate solution, is shown to selectively separate cobalt from nickel, a separation relevant to the recycling of NiMH batteries. To overcome the limitation of electrodeposition in the presence of high acid concentration, a mixed ABS-AcABS approach is developed in which HCl is partially substituted by addition of a predictable amount of NaCl. This synergistic ABS-AcABS system retains the metal extraction efficiency of AcABS whilst diminishing the acid concentration required to induce phase separation as well as its distribution to the ionic liquid-rich phase. Selective deposition of cobalt in the presence of co-extracted manganese impurities was achieved in AcABS, ABS and ABS-AcABS systems. The morphology and composition of the obtained deposits as well as the Faradic efficiency of the process can be altered by varying the NaCl to HCl ratio and water content, resulting in highly tailored cobalt deposits. These results highlight the potential of AcABS derived systems as a new extraction-separation platform for the integrated hydrometallurgical treatment of critical metals, from leaching to electrodeposition.

KEYWORDS: acidic aqueous biphasic systems, critical metals, ionic liquids, waste electrical and electronic equipment, electrodeposition

1 INTRODUCTION

2 The extraction, separation and purification of critical metals from complex matrices such as
3 minerals or electronic wastes is technologically challenging, often requiring a series of demanding
4 processing steps. A traditional flowsheet for the hydrometallurgical treatment of metal feedstocks
5 follows a series of concentration (leaching), purification (solvent extraction) and refining stages
6 (electrodeposition or precipitation).¹⁻⁵ Process intensification, i.e. the ability to conduct multiple
7 hydrometallurgical operations within a single processing unit, is of great interest industrially as
8 this can reduce the economic and environmental impact associated with metal consumption. In
9 this context, a sustainable, effective and affordable metal extraction process is an issue of critical
10 importance. To alleviate metal criticality and reduce the environmental impact of mining
11 operations, the development of a simple, robust and flexible platform is of particular relevance for
12 the recycling of metals from secondary ‘ores’.

13 We recently proposed a ‘one-pot’ solution for the simultaneous leaching and selective extraction
14 of various critical metals using an ionic liquid-based acidic aqueous biphasic system (AcABS).⁶
15 Ionic liquids (ILs) are salts composed of asymmetric ions with disperse charge that are liquid at
16 room temperature.⁷ In the newly reported AcABS composed of the IL tributyltetradecyl
17 phosphonium chloride ([P₄₄₄₁₄]Cl), the very acid present in the leaching solution was used to salt-
18 out the IL. This is markedly different from conventional aqueous biphasic systems (ABS), such as
19 the previously reported [P₄₄₄₁₄]Cl – NaCl – based ABS for metal extraction,⁸ in which the molar
20 entropy of hydration of an inorganic salt dictates the formation of a reversible biphasic system
21 composed of a salt-rich phase and organic-rich phase.⁹ Performing the extraction in aqueous media
22 reduces the overall environmental impact associated with IL application as (i) lower quantities are
23 required compared to solvent extraction, (ii) hydrophilic ILs are less toxic and more biodegradable

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3 24 than their hydrophobic counterparts and (iii) mass transfer properties are significantly improved
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5 25 due to the lower solution viscosity, resulting in faster extraction kinetics.¹⁰⁻¹⁴
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9 26 In this work, the scope AcABS processes is extended to investigate the extraction and separation
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11 27 of Co(II), a critical metal,¹⁵ from Ni(II) and Mn(II) – a separation relevant to the recycling of nickel
12
13 28 metal hydride and lithium-ion batteries.¹⁶ To this end, a mixed ABS-AcABS approach is proposed
14
15 29 in which the HCl content required to induce phase separation in AcABS is predictably substituted
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17 30 by small amounts of NaCl, further accentuating the versatility of the proposed approach.
18
19 31 Synergistic ABS-AcABS systems retains the advantages of AcABS whilst diminishing the acid
20
21 32 concentration required to induce phase separation as well as its distribution to the IL-rich phase.
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23 33 This enables the use of more environmentally friendly operating conditions and facilitates the
24
25 34 subsequent metal deposition from the IL-rich phase. Selective deposition of Co(II) is optimized as
26
27 35 a function of various parameters including water content, HCl concentration and NaCl
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29 36 concentration. The ability to directly deposit metals from the IL-rich phase opens the possibility
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31 37 for a fully integrated approach to the leaching, separation and deposition of critical metals from
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33 38 complex sources.
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43 40 **METHODOLOGY**

46 41 **Materials and Instrumentation**

49 42 A detailed description of the compounds used as well as the instrumentation employed is
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51 43 provided in the ‘Methodology’ section of the Supplementary information. The chemicals were
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53 44 used as received without further purification.
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45 Determination of mixed ABS-AcABS systems for metal extraction

46 It is important to emphasise that three different separation systems are employed in this work:
47 two ternary systems composed of $[P_{44414}]Cl-HCl-H_2O$ (AcABS) and $[P_{44414}]Cl-NaCl-H_2O$ (ABS)
48 respectively and a quaternary system $[P_{44414}]Cl-HCl-NaCl-H_2O$ referred to as ABS-AcABS. The
49 phase diagrams for the quaternary system ABS-AcABS containing a fixed NaCl concentration (1
50 wt.%, 2 wt.% and 4 wt.%) were determined through the cloud point titration method in a
51 temperature-controlled cell at 298 K under agitation and atmospheric pressure. The concentration
52 of NaCl was identical (1 wt.%, 2 wt.% and 4 wt.%) in all solutions used as to keep its concentration
53 constant throughout the cloud point titration procedure. The quaternary system compositions were
54 determined by the weight quantification of all components added within an uncertainty of $\pm 10^{-3}$ g.
55 The detailed experimental procedure adopted is described in a previous work.¹⁷ The extraction and
56 separation of Co(II) from Ni(II) and Mn(II) in different ABS-AcABS mixtures of total mass 5 g
57 containing 30 wt.% $[P_{44414}]Cl$ was studied as a function of the HCl to NaCl ratio. A mixed metal
58 ion solution containing $0.1 \text{ mol.L}^{-1} \text{ CoCl}_2 \cdot 6\text{H}_2\text{O}$, $0.1 \text{ mol.L}^{-1} \text{ NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.1 mol.L^{-1}
59 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was used for all experiments. Solutions were mechanically agitated for 5 min at 298
60 K until the complete dissolution of the IL. The resulting mixture was left to phase separate 60 min
61 in a thermostatic bath at 298 K. The volume of each phase of the ABS-AcABS was measured and
62 aliquots of the upper and lower phases were collected for metal concentration analysis by
63 inductively coupled plasma optical emission spectroscopy (ICP-OES) after appropriate dilution.
64 The chloride, acid and water content of the IL-rich phase (top phase) was also determined after
65 separation of the phases. The extraction efficiency (%EE) was calculated as follows:⁶

$$66 \quad \%EE = \frac{[M]_0 V_{initial}}{v_{low}} - [M]_{low} \times 100 \quad - (1)$$

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3 67 where $[M]_0$ is the initial metal concentration of the metal in solution before extraction (*i.e.* before
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5 68 addition of the IL). $V_{initial}$ is the volume in mL of the mixture before extraction whilst V_{low} is the
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7 69 volumes, expressed in mL, of the lower phase after extraction. $[M]_{low}$ is the concentration of the
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9 70 metal ion in the lower phase after extraction.
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13 71 **Electrodeposition of Co(II) from ABS-AcABS**

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16 72 Electrochemical investigations including chronoamperometry and cyclic voltammetry (CV)
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18 73 were carried out using a Metrohm Autolab potentiostat controlled with the GPES software. A
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20 74 three-electrode system was used consisting of a glassy carbon (GC) working electrode (3 mm
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22 75 diameter), an iridium counter electrode and a silver chloride (Ag/AgCl) reference electrode. The
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24 76 working electrode was polished with diamond paste, rinsed and dried prior to all measurements.
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26 77 All cyclic voltammograms of single 0.1 mol.L⁻¹ Co(II) aqueous solutions were obtained at 298 K
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28 78 and at a scanning rate of 0.01 V.s⁻¹ with varying [P₄₄₄₁₄]Cl (from 0 to 20 wt.%) and HCl
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30 79 concentrations (0 to 8 mol.L⁻¹).
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36 80 Chronometric deposition experiments were performed in the following three systems: ABS,
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38 81 AcABS and ABS-AcABS (with and without the addition of water). Compositions of all systems
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40 82 are presented in Table S1 in the ESI. After extraction from a single metal solution containing 0.1
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42 83 mol.L⁻¹ of CoCl₂.6H₂O or a mixed solution of 0.1 mol.L⁻¹ of CoCl₂.6H₂O, NiCl₂.6H₂O and
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44 84 MnCl₂.4H₂O, the IL-rich phase was isolated from the aqueous one. CV experiments were carried
45
46 85 out under agitation in a potential range of -2.50 to 2.00 V *vs.* Ag/AgCl at a scan rate of 0.01 V.s⁻¹.
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48 86 Electrodeposition of metals was undertaken by chronoamperometry agitation at a fixed potential
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50 87 of -2.00 V *vs.* Ag/AgCl during one hour. The three systems namely, AcABS, ABS and ABS-
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52 88 AcABS depicted in Table S1 were studied. A fourth system was considered to investigate the
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3 89 impact of the water content on the deposition. After separating and isolating the phases from the
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5 90 system ABS-AcABS, the IL-rich phase was diluted in a minimum of water (0.2 g of water per
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8 91 gram of isolated IL-rich phase) until the solution colour transitioned from deep blue to light red.
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10 92 This well-known colour change is due to the transition of blue chloride-complexes (CoCl_4^{2-} or
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12 93 CoCl_3^{2-}) to the formation of a red cobalt hexahydrate complex, $\text{Co}^{2+}(\text{H}_2\text{O})_6$.¹⁸ This system is
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14
15 94 referred to as “ABS-AcABs-diluted” in this work.

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18 95 Obtained deposits were analysed by SEM-Energy Dispersive Spectroscopy (SEM-EDS) for
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20 96 single metal extractions. Metallic deposits obtained after selective deposition of cobalt in
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22 97 multielemental solutions were analysed through X-ray Diffraction (XRD). In the latter case, the
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24 98 metal was fully leached in 5 mL of 4 mol.L⁻¹ nitric acid (HNO_3) in order to investigate (i) the
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26 99 purity of the metal and (ii) the Faradic efficiency of the electrodeposition (E_F). The Faradic yield
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29 100 corresponds to the ratio between the experimental and theoretical conversion of Co(II) to Co(0)
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32 101 during electrodeposition. E_F was calculated according to the following equation:

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$$E_F = \frac{C_{\text{Co}} \times V_{\text{HNO}_3}}{\frac{\int_0^t I(t) dt}{nF}} \times 100 \quad \text{-(2)}$$

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40 103 where C_{Co} represents the concentration of cobalt in mol.L⁻¹ in the aqueous phase containing nitric
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42 104 acid, used to leach the deposits. V_{HNO_3} is the volume of the nitric acid solution in L. I (A) represents
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44 105 the current produced during chronoamperometry measurements for a given time t in seconds. F
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46 106 and n stand for the Faraday constant and the number of moles of electrons exchanged during the
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49 107 reduction respectively.

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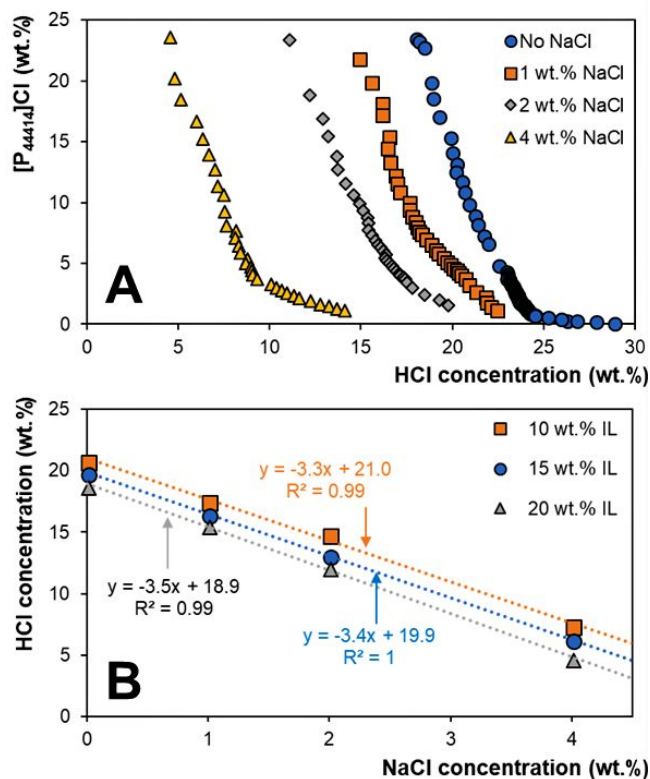
110 RESULTS AND DISCUSSION

111 Development of mixed ABS-AcABS systems for metal extraction

112 The innovation of AcABS lies in its ability to extract metals directly from leachates just by
113 adding a carefully selected IL. However, optimal extraction and separation of Co(II) in the
114 [P₄₄₄₁₄]Cl-HCl-H₂O AcABS was shown to occur for highly concentrated solutions of HCl above
115 8 mol.L⁻¹ or ~25 wt.%, considerably more concentrated than most common leaching solutions (*cf.*
116 Figure S1 of the ESI). A full description Co(II), Ni(II) and Mn(II) extraction in AcABS is provided
117 in the “Metal extraction in the [P₄₄₄₁₄]Cl-HCl-H₂O AcABS” section in the ESI. This includes the
118 effect of HCl concentration in AcABS on the partition of [H₃O]⁺, Cl⁻ and H₂O to the IL-rich phase
119 (Table S2, ESI), the IL-rich phase viscosity before and after metal extraction (Figure S2, ESI) and
120 the influence of Co(II) feed concentration on the extraction efficiency and system properties of
121 AcABS (Figure S3 and S4, ESI).

122 However, the addition of extra HCl to leachates to induce AcABS formation and the efficient
123 extraction of Co(II) is not realistic from an industrial perspective due to i) the corrosivity of HCl
124 and ii) the increased cost of solution neutralisation after extraction. Furthermore, even small HCl
125 concentrations can inhibit the subsequent electro-deposition of Co(II) due to the narrowing of the
126 electrochemical window caused by the reduction of [H₃O]⁺ (*cf.* Figure S5 in ESI). [P₄₄₄₁₄]Cl was
127 shown to form ABS with a wide range of chloride salts.¹⁹ As such, we propose a mixed ABS-
128 AcABS system using mixtures of HCl/NaCl capable of efficiently separating Co(II) from Ni(II)
129 and Mn(II) from any chloride-containing aqueous solution, even at low HCl concentrations. It is
130 important to stress that some degree of solution acidity is required leach metals and to prevent
131 metal hydrolysis common at the high pH of typical ABS.

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3 132 The binodal curves for [P₄₄₄₁₄]Cl-HCl-H₂O systems containing 1 wt.%, 2wt% and 4wt% of NaCl
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5 133 at $T=298$ K are presented in Figure 1A. As expected from the lower cloud point of the [P₄₄₄₁₄]Cl-
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7 134 NaCl-H₂O system compared to that of HCl,¹⁹ the addition of a small concentration of NaCl results
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10 135 in a large decrease in the corresponding HCl concentration required to induce phase separation.
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12 136 For 15 wt.% [P₄₄₄₁₄]Cl, approximately 21 wt.% of HCl is required compared to 6.5 wt.% HCl for
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14 137 a mixed ABS-AcABS containing 4 wt.% NaCl. An additional benefit of the presented ABS-
15
16 138 AcABS system is the predictable shift in the binodal position with increasing NaCl concentration
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18 139 as shown in Figure 1B. For [P₄₄₄₁₄]Cl concentrations above 5 wt.%, the binodals in Figure 1A are
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20 140 roughly parallel. This allows the following simplification to be made: the addition of 1 wt.% NaCl
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22 141 decreases the HCl requirement by approximately 3.4 wt.%. The proposed linear correlation is only
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24 142 valid for ABS-AcABS containing up to of 4 wt.% NaCl. Addition of NaCl above 4 wt.% does not
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26 143 provide the same relative HCl decrease as below this salt concentration (Figure S6 in ESI). This
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30 144 appears as the limit for the synergistic effect of NaCl with HCl in ABS-AcABS.
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147 **Figure 1. (A)** The effect of NaCl concentration on the binodal curve of [P₄₄₄₁₄]Cl-HCl-H₂O system
 148 at 298 K (binodal data is provided in Table S3 in the ESI). **(B)** Reduction in the HCl concentration
 149 required to induce phase separation at a fixed NaCl concentration for 10 wt.%, 15 wt.% and 20
 150 wt.% [P₄₄₄₁₄]Cl

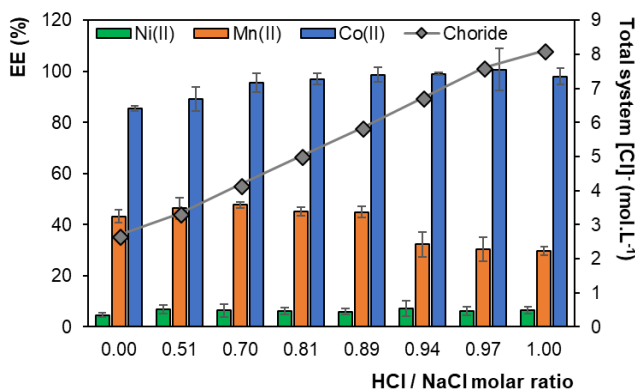
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152 The partition of Co(II), Ni(II) and Mn(II) from a multielement solution containing 0.1 mol.L⁻¹
 153 of each respective metal ion was attempted for eight ABS-AcABS systems at different HCl:NaCl
 154 ratio ($T=298$ K). The system compositions are given in Table S4 of the ESI and their respective
 155 metal extraction efficiency and the concentration of Cl⁻, [H₃O]⁺ and H₂O in the IL-rich phase after
 156 extraction and phase separation are presented in Figure 2-3 and Table S4. The concentration of the
 157 [P₄₄₄₁₄]⁺ cation in the aqueous phase was found to be below the detection limit for all tested systems

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3 158 and is not included. The results in Figure 2 show that for all systems, there is little variation in the
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5 159 extraction efficiency of the studied metal ions as one moves from and ABS to AcABS despite the
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8 160 large variation in the total chloride concentration. Co(II) was extracted to the IL-rich phase whilst
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10 161 Ni(II) remained in the aqueous phase and Mn(II) partitioned between the two, with a slight increase
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12 162 in Mn(II) extraction at higher NaCl concentrations. These results are in accordance with previously
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14 163 reported Co(II) and Ni(II) extraction from [P₄₄₄₁₄]Cl-NaCl-H₂O ABS and [P₄₄₄₁₄]Cl-HCl-H₂O
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16 164 AcABS^{6,8} as well as those using hydrophobic phosphonium based-ILs in traditional liquid-liquid
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19 165 extraction.^{13-14,16,20}
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22 166 ILs incorporating quaternary phosphonium cations are known to extract anionic metal
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24 167 complexes such as those formed by Co(II), Cu(II), Fe(III), Pd(II), or Pt(IV) at high halide
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27 168 concentrations through the formation of a hydrophobic pair between the anionic metal complex
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29 169 and the cation of the IL.^{6,8,13-14,20-21} Ni(II) exhibits a limited coordination with chloride anions,
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31 170 highlighted by the low complexation constant of NiCl⁺ ($k_1^{\text{Ni}^{2+}} = 0.07$).¹⁸ The inability of Ni(II) to
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33 171 form anionic chloro-complexes in water results in low extraction yields due to its inability to form
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35 172 an ion pair with the IL cation. The intermediate complexation constant of Mn(II) with Cl⁻ ($k_1^{\text{Mn}^{2+}}$
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37 173 = 0.33) compared to Ni(II) and Co(II) ($k_1^{\text{Co}^{2+}} = 0.40$)¹⁸ is reflected in its extraction efficiency
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39 174 (Figure 2). The speciation of Co(II) is highly dependent on the ratio of Co(II) concentration to
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41 175 chloride concentration in solution, the anionic species CoCl₃⁻ and CoCl₄²⁻ can be found at high
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43 176 HCl concentrations.¹⁸ This transition from Co(H₂O)₆²⁺ found in aqueous solutions to negatively
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45 177 charged Co(II) complexes can be visually observed as the solution changes color from pinkish red
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48 178 to deep blue, the same as the color of the IL-rich phase after extraction. A previous study on the
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51 179 extraction of Co(II) using [P₄₄₄₁₄]Cl confirmed that Co(II) is predominantly extracted as the
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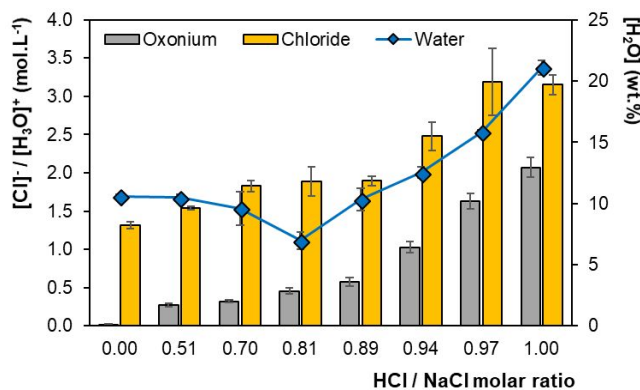
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3 180 CoCl_4^{2-} species within the IL phase.^{6,8} The speciation of Co(II) is highly relevant for its subsequent
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5 181 electrodeposition from IL solutions and will be addressed further on.²²
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26 184 **Figure 2.** Co(II), Mn(II) and Ni(II) extraction efficiencies in ABS-AcABS system with varying
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28 NaCl to HCl concentrations at 298 K. System compositions are provided in Table S4 of the ESI.
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35 187 On a molar basis, significantly less Cl^- is required to induce ABS phase separation and Co(II)
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37 188 extraction when NaCl is employed compared to HCl. NaCl was shown to be a more efficient
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39 189 salting-out agent than HCl for the liquid-liquid demixing of $[\text{P}_{44414}]\text{Cl}$ -based ABS.¹⁹ Extraction of
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41 190 Co(II) is close to quantitative for HCl:NaCl ratio of 0.7 or greater. It is postulated that in such
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43 191 systems, the Cl^- provides the necessary chloride to form anionic chlorocobalt complexes whilst the
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45 192 greater salting-out effect of Na^+ compared to that of $[\text{H}_3\text{O}]^+$ promotes the transition of the less
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47 193 hydrophilic CoCl_3^- and CoCl_4^{2-} species to the IL-rich phase. This supports the claim that a mixed
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49 194 ABS-AcABS system for metal extraction combines the advantages and flexibility of AcABS with
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51 195 those of ABS with no loss in metal extraction efficiency.
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3 196 The partition behaviour of the acid and water to the IL-rich phase in mixed ABS-AcABS
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5 197 presents an interesting behaviour based on the ratio of HCl to NaCl as shown in Figure 3. The
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7 198 water content of the IL-rich phase is low for all the studied systems, decreasing down to a minimum
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9 of 7 wt.% H₂O for an ABS-AcABS composition of 30 wt.% [P₄₄₄₁₄]Cl, 10.8 wt.% HCl and 4.0
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11 wt.% NaCl. The water content increases as NaCl is substituted by HCl from 10.6 wt.% in ABS
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13 and reaching 21.1 wt.% for the pure AcABS in line with the greater salting-out potential of NaCl
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15 compared to HCl.¹⁹ Furthermore, the acid concentration in the IL-rich phase does not significantly
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17 increase whilst NaCl is the primary driver (HCl:NaCl molar ratio <0.89) for the phase separation
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19 of ABS-AcABS. From the presented results, two conclusions can be inferred of great relevance
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21 for the subsequent electrodeposition of Co(II) from a [P₄₄₄₁₄]Cl-rich phase. Firstly, a mixed ABS-
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23 AcABS system can be predictably tuned with little appreciable variation in metal extraction
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25 compared to simple ABS or AcABS systems. Secondly, a compromise is required in the HCl to
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27 NaCl ratio of ABS-AcABS. Higher NaCl concentrations reduce the acid and chloride migration to
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29 the IL-rich phase at the expense of a lower water content compared to simple AcABS. The high
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31 viscosity of loaded [P₄₄₄₁₄]Cl solutions can reduce the diffusion of Co(II) as well as cause losses
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33 during manipulation. However, minimizing the acid concentration will facilitate the deposition of
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35 Co(II) from [P₄₄₄₁₄]Cl solutions. An additional consideration is that the water content, and
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37 therefore the viscosity, of the loaded [P₄₄₄₁₄]Cl-rich phase once isolate can be controlled by dilution
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217 **Figure 3.** Concentration of acid ($[\text{H}_3\text{O}^+]$), chloride anion and water in the $[\text{P}_{44414}]\text{Cl}$ -rich phase
 218 after metal extraction in ABS-AcABS system with varying NaCl to HCl concentrations at 298 K.
 219 System compositions, including the partition behavior of the acid and water to the IL-rich phase,
 220 are provided in Table S4 of the ESI.

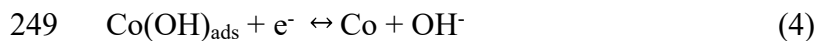
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222 Electrochemical behaviour of Co(II) in ABS-AcABS systems

223 Having demonstrated the separation of Co(II) from Ni(II) and Mn(II) in AcABS and ABS-
 224 AcABS as well as the partitioning of the system components relevant to the subsequent deposition
 225 of Co(II), the electrochemical behaviour of studied system is now investigated. The influence of
 226 the hydrophilic $[\text{P}_{44414}]\text{Cl}$ in aqueous solutions on the reduction potential of Co(II) is presented in
 227 Figure 4. The presence of the IL in aqueous solution lowers the kinetics of water to hydrogen
 228 reduction (*cf.* Figure 4A), in line with the wide electrochemical window of phosphonium-based
 229 ILs.²³⁻²⁴ Co(II) is known to reduce to metallic cobalt at a potential of -0.28 V vs. ENH , this is to
 230 say, $-0.50 \text{ V vs. Ag/AgCl}$.²⁵ In accordance with the literature, the CV of an aqueous 0.1 mol.L^{-1}
 231 Co(II) solution (Figure 4A, dashed line) presents an inset reducing peak at -0.42 V and a minimum
 232 at $-1.0 \text{ V vs. Ag/AgCl}$. A large oxidation peak is also observed from 0.42 to $0.59 \text{ V vs. Ag/AgCl}$,

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3 233 confirming that cobalt can be oxidized reversibly. The addition of increasing amounts of [P₄₄₄₁₄]Cl
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5 234 from 0 to 10 wt. % IL results in a decrease in the cathodic peak potential for cobalt ($E^{\text{Red}}_{\text{Co}}$) from
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7 235 -0.42 to -1.06 V vs Ag/AgCl. When the concentration of IL exceeds 10 wt.%, the reduction peak
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9 236 potential remains constant (*cf.* Figure 4B). This shift in the reduction peak is a strong indication of
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11 237 a change in the complexation of Co(II) in the presence of the chloride anions from the IL. The
12
13 238 anionic cobalt complexes CoCl_3^- and CoCl_4^{2-} are the predominant complexes reported in chloride
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15 239 based ILs.^{13-14,22,26} Furthermore, whilst the CoCl_3^- was shown to be electrochemically active in
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17 240 ILs, the complex CoCl_4^{2-} was not.²² This suggests that a high chloride concentration is inhibiting
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19 241 the deposition of Co(0). This is in accordance with the Nernst law, which states that changes in
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21 242 the speciation has an influence on the standard reduction potential of metallic species.
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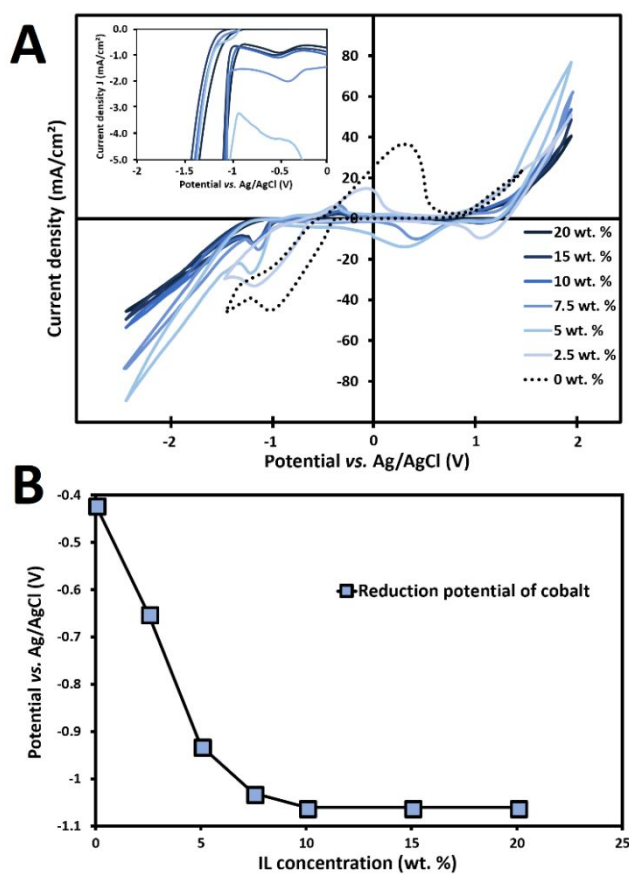
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26 243 However, complexation of chlorides is insufficient to explain the magnitude of the shift in the
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28 244 reduction potential. The electrochemical kinetic behaviour of nickel electrodeposition was
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30 245 previously studied in acidic aqueous phases and lead to the intermediate formation of Ni(OH)
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32 246 adsorbed species.²⁷⁻²⁹ Similarly, cobalt is assumed to present the following reduction mechanism
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35 247 in water:



45 250 Elevated concentrations of ILs could inhibit the formation of the intermediate complex cobalt(I)
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47 251 hydroxide adsorbed species and therefore reduce the kinetic of reduction of Co(II).
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51 252 The intensity of all reduction peaks decreases with the increasing IL concentration due to the
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53 253 higher viscosity and therefore lower kinetics of the IL-concentrated systems compared to the pure
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55 254 water system. Finally, an unveiled trend can be observed for mixtures containing 5 wt. % [P₄₄₄₁₄]Cl
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255 or more with the emergence of a small reduction peak close to -0.5 V vs. Ag/AgCl (Figure 5A,
256 inset). This is attributed to the reduction of Co(II) to Co(I). ILs provide a better environment for
257 the stabilisation of intermediate metal oxidation states compared to water. For example, the
258 presence of water was shown to significantly affect the voltammetric behaviour of Co(II) in the
259 ethylammonium nitrate IL and the oxidation of Co(II) to Co(III).³⁰



261
262 **Figure 4.** (A) CV experiments at a 0.01 V.s⁻¹ scan rate of various solutions containing 0.1 mol.L⁻¹
263 of Co(II) and concentration of [P₄₄₄₁₄]Cl ranging between 0 (black dotted line) and 20 wt. %
264 (light to dark blue colours). (B) Evolution of the inset peak corresponding to the reduction of Co(II)
265 to Co(0) as a function of the concentration of [P₄₄₄₁₄]Cl.

CV analysis at a scan rate of $0.01 \text{ V}\cdot\text{s}^{-1}$ and 298 K on a GC working electrode was carried out in the four systems AcABS, ABS and ABS-AcABS (both undiluted and diluted) after extraction from $0.1 \text{ mol}\cdot\text{L}^{-1}$ Co(II) solutions. The solution compositions of the studied systems are listed in Table S1. The CV scans are presented in Figure 5. Electrodeposition of Co(II) was performed during one hour on a GC electrode under agitation. The electrodes were qualitatively and semi-quantitatively analyzed via SEM-SE and SEM-ESD respectively. The morphology and composition of the obtained deposits are presented in Figure 6 and Table 1 respectively.

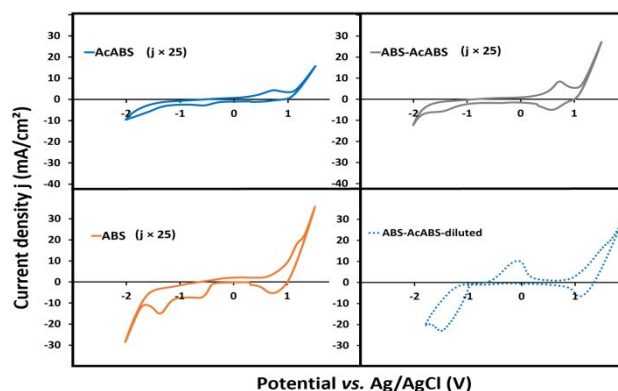


Figure 5. CV of various systems after extraction of cobalt in an aqueous solution containing $0.1 \text{ mol}\cdot\text{L}^{-1}$ Co(II). Scanning rate: $0.01 \text{ V}\cdot\text{s}^{-1}$. Current densities (J) are multiplied by 25 for the ABS, AcABS and ABS-AcABS systems.

Starting with the ABS system, first reported by Onghena et al.⁸ composed of $[\text{P}_{44414}]\text{Cl}-\text{NaCl}-\text{H}_2\text{O}$, a reduction peak (Co(II) to Co(0)) with an onset point at $-1.07 \text{ V vs. Ag/AgCl}$ can be observed (Figure 5, orange line). This is in full agreement with our previous result showing that $E^{\text{Red}}_{\text{Co}} = -1.06 \text{ V vs. Ag/AgCl}$ for systems containing 10 wt. % or more $[\text{P}_{44414}]\text{Cl}$. After inducing a potential

of -2.00 V vs. Ag/AgCl to the solution, EDS analysis of the obtained deposit on the GC electrode surface indicates a high purity cobalt deposit of 98.9 mol.% (Table 1). No significant quantities of chloride or phosphonium are recorded. The morphology of the obtained deposit is that of micrometre-scale dendrites, characteristic of metallic cobalt in aqueous solutions.³¹ Despite the lack of visible Co(0) reduction peak in the [P₄₄₄₁₄]Cl-HCl-H₂O AcABS (Figure 5, purple line), small particles were identified on the GC electrode after electrodeposition. This is a direct consequence of the large concentration of acid after extraction in the top phase ([H₃O]⁺ = 3.0±0.26 mol.L⁻¹). In such an acidic environment, Co(0) particles can be leached back in the aqueous solution after deposition. Two concomitant but opposing phenomena emerge: (i) the reduction of Co(II) at the negative overpotential and (ii) the oxidation of Co(0) due to the HCl concentration. As a result, the particle seen in Figure 6 is composed of only 52.7 mol.% of cobalt and 44.7 mol.% of chloride, characteristic of an ongoing leaching phenomenon.

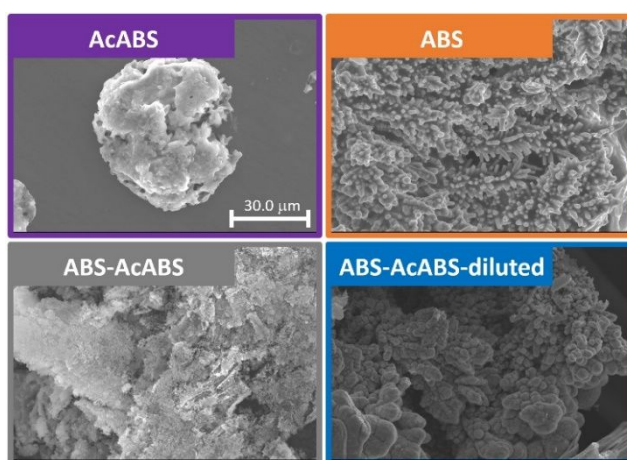


Figure 6. SEM-SE images (magnification $\times 1000$) of working electrodes after 1 hour of electrodeposition at -2.00 V vs. Ag/AgCl.

Table 1. Elemental analysis of the electrodeposited deposits obtained in ABS, AcABS and ABS-AcABS (undiluted and diluted) systems after extraction from solutions containing 0.1 mol.L⁻¹ Co(II).

Systems	Elemental analysis (mol.%)		
	Co	Cl	P
ABS	98.9 ± 12.3	1.1 ± 0.5	-
AcABS	52.7 ± 23.3	44.7 ± 18.3	2.6 ± 1.6
ABS-AcABS	92.6 ± 12.5	6.9 ± 6.3	0.5 ± 0.1
ABS-AcABS-diluted	95.6 ± 16.3	3.3 ± 2	1.1 ± 0.6

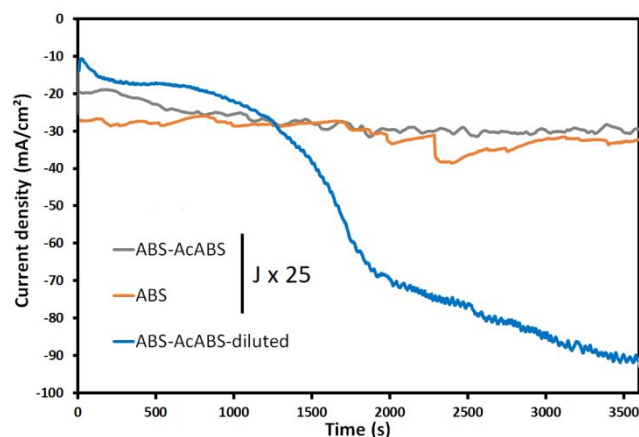
To avoid leaching just after the electrodeposition step, a mixed ABS-AcABS system containing [P₄₄₄₁₄]Cl-NaCl-HCl-H₂O is evaluated (composition provided in Table 1). As shown in Figure 3, the partial substitution of HCl by NaCl reduces the [H₃O]⁺ concentration of the IL-rich phase whilst maintaining the required solution acidity to perform the leaching of metals. This system was studied both in its undiluted and diluted form to establish the impact of water and therefore Co(II) complexation, on the quality of the Co(0) deposits. In the CV of undiluted ABS-AcABS, E^{Red}_{Co} appears at -1.12 V vs. Ag/AgCl (Figure 5, grey line), similar to that obtained in the ABS system. The composition of the obtained deposit is 92 mol.% of cobalt and only 7 mol.% chloride. This represents a significant increase in the deposit purity compared to that obtained in AcABS. The presence of Cl⁻ is assigned to (i) the presence of residual [P₄₄₄₁₄]Cl in the final deposit and (ii) to the small leaching effect from the persistent presence of HCl ([H₃O]⁺ = 0.35±0.04 mol.L⁻¹). SEM-SE analysis of the working electrode surface after deposition reveals its complete coverage by a large layer of deposit (*cf.* Figure 6). The deposit presents a sheet-like structure with no observable

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3 317 dendrites. This is probably due to the etching of the deposit surface by the remaining HCl after
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5 318 oxidation of Co(0) present in the dendritic structures of high surface area.
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9 319 To gain a better understanding on the role of water in the studied system, the IL-rich phase (top
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11 320 phase) of the mixed system ABS-AcABS was isolated after extraction and diluted (0.2 g of water
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13 321 per gram of isolated IL-rich phase). The system was diluted through dropwise addition of water
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15 322 until a shift in the solution colour from blue to light red was observed. By varying the water content
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17 323 of the IL-rich phase after AcABS extraction, essentially transitioning from a water in IL
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19 324 environment to IL as electrolytes in aqueous solutions, the mass transport and interfacial structure
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21 325 at the electrode can be altered resulting in potentially different deposit properties.³²⁻³³ An
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23 326 additional positive effect of dilution on the Faradic efficiency is the change in Co(II) coordination
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25 327 from chlorocobalt complexes to Co(II) hexahydrate. Dilution of the system results in a positive
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27 328 shift in the onset of the reduction peak from -1.12 V vs. Ag/AgCl for ABS-ACABS to -0.90 V vs.
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29 329 Ag/AgCl for ABS-AcABS-diluted. The dilution influences the complexation of cobalt-chloride
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31 330 complexes, thereby increasing the reduction potential in accordance with Nernst's law. A deposit
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33 331 composed of large dendrites was visually observed, further confirmed by SEM-SE (*cf.* Figure 6).
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35 332 Elemental analysis of the deposit highlights a quasi-pure material composed of 95.5 mol.% cobalt.
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37 333 In light of these results, [P₄₄₄₁₄]Cl-NaCl-HCl-H₂O mixture stands out as promising medium for the
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39 334 recovery of metallic cobalt. The morphology and composition of the obtained deposits can be
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41 335 altered by varying the NaCl to HCl ratio and water content, resulting in highly tailored cobalt
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43 336 deposits. However, extraction results displayed in Figure 2 indicate that up to 40 wt.% of Mn(II)
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45 337 can be co-extracted with Co(II). The question of the selectivity of such a process, starting from an
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47 338 aqueous solution containing a mixture of Co(II), Mn(II) and Ni(II) thus arises.
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340 Selective electrodeposition of Co(II) from Ni(II) and Mn(II)

341 After extraction of a mixture of 0.1 mol.L⁻¹ of Co(II), Ni(II) and Mn(II) from ABS and ABS-
342 AcABS systems (Table S1 of the ESI), chronoamperometry experiments at -2V vs Ag/AgCl were
343 carried out to selectively reduce cobalt to its metallic state. Results are given in Figure 7. Current
344 densities for all experiments suffer from some oscillations as a result of hydrogen evolution from
345 the reduction of water and/or of [H₃O]⁺. The current density slowly decreases with time during
346 deposition in all systems, characteristic of metallic deposition. The reduction of a conductive
347 material such as cobalt can increase the surface area of the electrode and thus the current density
348 in absolute value. This phenomenon is particularly pronounced in the ABS-AcABS-diluted system
349 where the current density is multiplied by a factor of 8 in one hour. The lower viscosity and
350 chloride complexation of this system are beneficial for an efficient deposition of metals.
351 Quantitative compositional analysis of the deposits for the systems presented in Figure 7 and their
352 respective Faradic efficiencies are displayed in Table 2.



354
355 **Figure 7.** Chronoamperometry experiments using a potential of -2.00 V vs. Ag/AgCl for 1 hour.
356 Current densities (J) are multiplied by 25 for the ABS and ABS-AcABS systems.

For all studied systems, no trace of Mn(II) and Ni(II) were recorded, confirming that solely Co(II) is reduced as a metallic species. This is to be expected as Ni(II) is not extracted to the IL-rich phase (*cf.* Figure 1), and Mn(II) presents a reduction potential of -1.41 V *vs.* Ag/AgCl, lower than that of Co(II) (-0.5 V *vs.* Ag/AgCl).²⁵ The efficiency of Co(II) reduction is low in the undiluted ABS and ABS-AcABS systems with a final deposit mass of 0.30 mg and 0.29 mg respectively. Faradic efficiencies indicate that around 30 % of the electrons generated by the potentiostat are devoted to the reduction of Co(II) to metallic Co(0) in these systems. Inducing a potential of -2.00 V *vs.* Ag/AgCl results in an important reduction of water and/or proton to hydrogen. The low energetic yields hinder the industrial application for such processes.

Table 2. ICP analysis performed for ABS, ABS-AcABS, and ABS-AcASB-diluted systems. The composition of the deposits and Faraday efficiencies (E_F) are given for all systems.

Deposit Composition	Extraction Systems		
	ABS-AcABS	ABS	ABS-AcABS-diluted
Co (mg)	$0.30 \pm 5 \times 10^{-3}$	$0.29 \pm 5 \times 10^{-3}$	7.2 ± 0.1
Mn (mg)	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$
Ni (mg)	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$
E_F (%)	28.9	31.6	59.7
Co electroplated (mol.%)	0.91	0.82	2.51

Deposition yields are significantly improved after dilution, with close to twenty fourfold increase in the deposit mass to 7.2 mg in the system ABS-AcABS-diluted. This results in a twofold increase

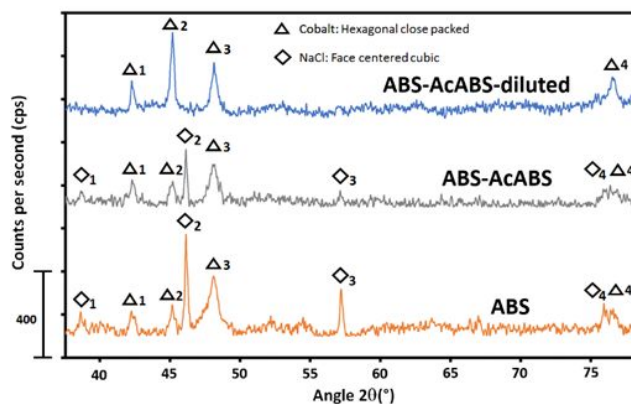
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3 372 in the Faradic efficiency to a value of 59.7 %. The Faradic yields reported here are reasonably
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5 373 satisfying and were obtained without any optimisation of the electrochemical process. At -2 V vs.
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7 374 Ag/AgCl, water or $[\text{H}_3\text{O}]^+$ present in the medium is expected to be reduced significantly. Carrying
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9 375 out the experiments at a more positive potential would most probably lead to better yields due to
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11 376 a less pronounced reduction of water or $[\text{H}_3\text{O}]^+$. Experiments carried out at -1.5 V vs. Ag/AgCl
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13 377 revealed that deposition of Co(II) was possible, whereas assigning a potential of -1 V at the GC
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15 378 electrode did not yield any reduction of Co(II). It is worth highlighting that the electric charge is
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17 379 of 0.3 and 14 C for the undiluted and diluted ABS-AcABS systems respectively. As a result, even
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19 380 if the Faradic yield is twice higher with the ABS-AcABS-diluted, more electrons will be devoted
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21 381 to the reduction of water in the latter system. However, the cobalt deposition kinetic is more than
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23 382 24 times faster in the diluted systems which significantly improves results obtained compared to
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25 383 pure ILs. After 1 hour of chronoamperometric measurements, only 2.5 mol. % of Co(II) ions were
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27 384 reduced. This proves that the bath did not suffer from any significant concentration depletion.
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29 385 Larger surface electrodes are required to recover the metal in an acceptable length of time. The
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31 386 current-time transient for the deposition of Co(II) from the ABS-AcABS-diluted system was
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33 387 studied to determine the nucleation process (Figure S7 of the ESI) and was found to follow a 3D
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35 388 instantaneous nucleation growth process.
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43 389 The crystalline structure of the deposits obtained at the end of the chronoamperometry
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45 390 experiments were analysed by XRD analysis with the spectra depicted in Figure 8. NaCl crystals
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47 391 are highlighted in the ABS-AcABS and ABS systems. This is not surprising as these two solutions
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49 392 contain an important initial NaCl concentration (7.6 wt.%) to induce the formation of two phases.
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51 393 Near the electrode, the deposition of cobalt in ABS-AcABS and ABS systems will most likely
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53 394 release chloride anions from the metallic complexes and locally saturate the solution in NaCl
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3 395 inducing the crystallisation of the latter salt. All deposits are composed of metallic Co(0)
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5 396 crystallised in a hexagonal close packed lattice. However, there are differences in the
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7 397 crystallisation of Co(0) in the ABS and ABS-AcABS compared to the ABS-AcABS-diluted
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10 398 system. Focusing on the cobalt metallic peaks 2 (p_2) and 3 (p_3) at 44.6° and 47.5° respectively, the
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12 399 ratio $R = p_2 / p_3$ differs from one system to another. These two peaks correspond to the crystal
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14 400 orientation (111) and (101) respectively of metallic cobalt.³⁴ Concerning the ABS-AcABS-diluted
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17 401 system, p_2 presents a higher intensity than p_3 resulting in a ratio R of 1.51. The opposite
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19 402 phenomenon is reported for ABS-AcABS and ABS systems leading to a ratio of 0.51 and 0.47
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21 403 respectively. This phenomenon highlights a preferential crystalline orientation of metals
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23 404 electrodeposited in concentrated IL solutions compared to diluted IL solutions. Such changes in
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25
26 405 the crystalline nature of deposits due to the presence of IL was previously reported for the
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28 406 deposition of copper in the presence of $[C_4mim][HSO_4]$ as additive.³⁵
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32 407 The versatility of IL-based ABS and AcABS was recently highlighted for its application in metal
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34 408 extraction^{6,8,36-37} but it is here shown that it can be extended to the electrodeposition of metals. The
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36 409 hydrophilicity of the extracting solution allows to tune and enhance the efficiency of the recovery
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39 410 of pure cobalt and to modify the properties of the resulting deposits.
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413 **Figure 8.** XRD diffractograms of deposits obtained after extraction of metals from a mixed
414 solution containing 0.1 mol.L⁻¹ Co(II), Ni(II) and Mn(II) and electrodeposition at a potential of -
415 2.00 V vs. Ag/AgCl during 1 hour.

416

417 CONCLUSIONS

418 AcABS and its ABS-AcABS derivative stands out as an efficient, flexible and integrated
419 extraction-separation-purification platform for the recovery of critical metals from primary and
420 secondary ores. By varying the HCl concentration and the chloride source (either NaCl or HCl),
421 selective separation of Co(II) from Ni(II) was achieved whilst controlling the partition of the
422 various system constituents. The distribution of HCl was found to have a profound influence on
423 the subsequent electrodeposition of Co(II). To address this, a mixed ABS-AcABS extraction
424 system was proposed which combines the advantages of the AcABS and ABS systems. By varying
425 the water content of the [P₄₄₄₁₄]Cl-rich phase after extraction and separation of Co(II) from Ni(II),
426 high quality dendritic deposits of pure metallic cobalt were obtained in presence of Mn(II)
427 impurities. Furthermore, ABS-AcABS systems can be tailored to obtain metal deposits with varied
428 properties. The results presented in this work demonstrate the applicability of AcABS for a ‘one-

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3 429 pot' approach for the sequential leaching, solvent extraction and electrodeposition of metals.
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5 430 Moreover, this work provides an understanding of the fundamental mechanisms governing the
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7 431 extraction and electrodeposition in AcABS required to extend these findings to the recovery of
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9 432 other critical metals.
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35 442 **ASSOCIATED CONTENT**

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39 443 **Supporting Information.** detailed list of chemicals and instruments used, extraction of Co(II),
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41 444 Ni(II) and Mn(II) in AcABS as a function of HCl concentration, IL-rich phase viscosity before
42
43 445 and after Co(II) extraction, extraction in AcABS as a function of Co(II) concentration, composition
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45 446 of IL-rich phase after extraction in ABS and ABS-AcABS systems, CV of aqueous Co(II) solutions
46
47 447 in the presence of HCl, electrochemical behavior of Co(II) in [P₄₄₄₁₄]Cl aqueous solutions,
48
49 448 chronometric measurements of Co(II) deposition from [P₄₄₄₁₄]Cl-rich phase after extraction in
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51 449 AcABS, ABS and ABS-AcABS, nucleation mechanism of Co(II) in mixed ABS-AcABS-diluted
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53 450 system during electrodeposition.
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19

20 458 ‡ Nicolas Schaeffer and Matthieu Gras are equally contributing authors. The manuscript was
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23 459 written through contributions of all authors. All authors have given approval to the final version
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25 460 of the manuscript.
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28 461 **Notes**
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31 462 The authors declare no competing financial interest.
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569 **TABLE OF CONTENT (TOC)**

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573 **SYNOPSIS**

574 The potential of acidic aqueous biphasic system (AcABS) is extended and proposed as a new
575 extraction-separation platform for the integrated hydrometallurgical treatment of critical metals
576 from leaching to electrodeposition.

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