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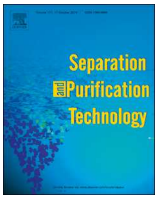

Recovery of metals from spent lithium-ion batteries using ionic liquid $[P_{8888}][Oleate]$

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ABSTRACT

A separation method to selectively recover valuable metals (Co, Ni, Mn and Li) from synthetic spent lithium-ion battery cathodes leachate using a fatty-acid-based ionic liquid, tetraoctylphosphonium oleate $[P_{8888}]$[oleate] is demonstrated. The investigated parameters for this selective separation and recovery process include extraction pH, contact time and composition of the regeneration solution. The benefit of using this ionic liquid is that > 99% of Co and > 99% of the Mn can be separated from the Ni and the Li by a two-stage extraction process. A subsequent single regeneration process separates the Co from the Mn. Finally, Ni and Li are completely separated in an additional regeneration process. An economic potential analysis concludes the paper, revealing that given the current cobalt price, the process outlined here shows a positive zero-order Economic Potential (bases on product sales and raw material cost) when using a 4 M HCl leaching solution and for leachates containing at least 4.5 g Co per liter.

1. Introduction

In lithium-ion battery (LIB) technology, the use of multi-metal cathodes such as lithium-nickel-manganese-cobalt oxide (NMC) has become customary in order to reduce cost, to stabilize raw material supply chains, to increase energy density and battery performance [1–6]. To date, 95% of Li-ion battery waste is landfilled instead of recycled upon reaching end of life [7]. Even though metal recycling is by far the preferable option from the point of view of future economy, environment and human health [8]. Selective metal recovery is however challenging in terms of heterogeneity of the waste material, necessary degree of purity of the recovered metals and sustainability of the overall recycling process [9–11].

Currently, the two most widely used processes for the treatment of spent LIB's are hydrometallurgical and pyrometallurgical in nature. However, hydrometallurgical processes consume less energy, show a higher metal recovery rate with high purity and seem more adjustable for recycling future generations of LIBs [12,13]. After a series of pretreatment steps such as discharging, dismantling, crushing and sieving, the different valuable cathode metals are separated by leaching using strong acids or bases, followed by purification steps like solvent extraction, precipitation, electrolytic processing or a combination of these methods [14,15]. However, the efficiency of (selective) metal precipitation is limited because the process is time-consuming, due to the co-precipitation of other more concentrated metals and finally due to the low yield of metal precipitation (< 50%) [15]. Furthermore, the process may require the use of an additional chemical reagent, e.g. dimethylglyoxime as in the case of nickel recovery [15]. Solvent extraction-based techniques are considered to be more efficient, because they allow operation in the continuous mode, require relatively simple equipment along with relative small quantities of reagents while still achieving a high leachate throughput [16]. In addition, liquid-liquid extraction processes are in general rather flexible towards the nature and concentration of the extractants and the composition of the aqueous and organic phase [17].

Currently used metal extractants include Cyanex 272 (di-isooctyl phosphinic acid), PC88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester), and D2EHPA (di-2-ethylhexyl phosphoric acid) [12,18–20]. The main disadvantage of these commercially available extractants is the required use of a highly toxic diluent like kerosene. Secondly, multiple extractants are needed to selectively recover valuable metals from spent LIBs such as NMC leachates which contain cobalt (Co), manganese (Mn), nickel (Ni) and lithium (Li) [21]. For example, Cyanex 272 and PC88A are mainly used to separate Co from Ni while D2EHPA is used to separate Co from Mn [12,21]. Furthermore, in the extraction of metals by saponified extractants, which show better separation compared to non-saponified ones, stripping with strong acid may convert the saponified extractant into its acid form, which in turn

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Table 1
Comparison of Co/Ni separation factors and cost for various extractants. Selectivity is defined as $\beta_{Co/Ni} = D_{Co}/D_{Ni}$, where D_M is distribution coefficient of metal (M) $= (C_{f,o} - C_{r,i})/C_{f,o}$.

Extractant	Price ($/kg)	$\beta_{Co/Ni}$	Concentrations (g/L)	Diluent	Ref
Cyanex 272	1–160*	750	[Co] = 14 [Ni] = 15	kerosene	[19]
PC88A	6–8*	42	[Co] = 21 [Ni] = 1	kerosene	[23]
D2EHPA	2–30*	14	–	kerosene	[24]
[P_{8888}] [Oleate]	10**	30,000	[Co] = 15 [Ni] = 21	–	This study

* Price according to Alibaba 20 Oct 2019 which varies with supplier, quality and quantity.

** Price for [P_{8888}][oleate] has been calculated based on raw material costs only, as shown in (Appendix A).

will decrease the extraction of metals [22]. Therefore, an additional regeneration step is employed to convert the acid form of the extractant to the saponified form. Considering the wide ranges of specifications and with that realizing the limitation of comparison, Table 1 lists currently employed organophosphorus extractants used in the separation of Co, Mn and Ni. In order to circumvent the use of kerosene, to reduce the number of stages/extractants involved in the process and accordingly to reduce the environmental impact, the present study explores the applicability of an ionic liquid (IL) as a viable alternative to selectively recover Co, Mn, Ni and Li from a synthetic leach solution originating from cathodic material of spent LIBs (NMC). Even though the viscosity of this IL is 0.134 Pa.s, it is applicable in its pure, undiluted form.

As shown in numerous studies already, ILs can be designed accordingly to the metal they need to extract [25–33]. One such IL is tetraoctylphosphonium oleate [P_{8888}][Oleate] (Fig. 1), a metal-binding functionalized fatty-acid-based IL that demonstrates a high and selective extraction efficiency towards transition metals at different pH levels [34]. The presence of bulky, long chained tetraalkylphosphonium cations and hydrophobic oleate anions prevent the loss of IL to the aqueous phase. The latter, anion loss after protonation, occurring when exposed to an acidic feed or an acidic regeneration solution, is a commonly observed feature with IL's composed of a conjugated acid and an anion such as phthalate [25,26]. Because of its bulky nature, protonation of the oleate anion hardly affects its hydrophobicity, thereby preventing its loss to the aqueous phase.

The focus of the present study is on the extraction and regeneration efficiency of [P_{8888}][Oleate] for the four metals Co, Mn, Ni and Li during 2 cycles of operation. Several parameters affecting these efficiencies have been investigated, notably pH, contact time, composition of the regeneration solution and number of required extraction/regeneration stages within one cycle. At the end, the outcome of a (simplified) economic analysis (based on product sales and raw material cost = EP0) of the process outlined here is discussed.

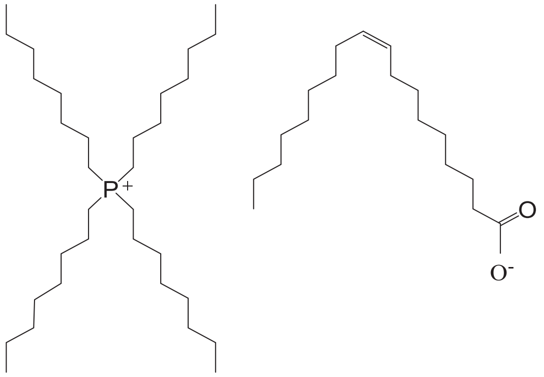

Fig. 1. Tetraoctylphosphonium oleate [P_{8888}][Oleate].

2. Experimental

2.1. Materials and analysis

Tetraoctylphosphonium bromide (> 95%) was purchased from IoLiTec; sodium hydroxide (> 99%), hydrochloric acid (37%), nitric acid (69%), ammonia solution (minimum 25%), ammonium chloride, ammonium carbonate, sodium chloride, sodium hydrogen carbonate and sodium carbonate from VWR Chemicals; oleic acid (90%), nickel (II) chloride hexahydrate (99.95%), cobalt (II) chloride hexahydrate (98%) and ammonium bicarbonate (99.0%) from Alfa Aesar; ammonium sulphate, perchloric acid (70%), lithium chloride (99%) and manganese (II) chloride dihydrate (99%) from BOOM BV. MilliQ water (≥18 MΩ.cm) was obtained from a Millipore Milli-Q® Biocel, which uses a Qgrade® column. All chemicals were used as received, without any further purification.

The aqueous phases after each extraction and regeneration process were analyzed by a Metrohm IC Compact 761 ion chromatograph (detection range: 0.1–80 mg/L) and a Perkin Almer Optima 5300 DV inductive coupled plasma optical emission spectrometry (ICP-OES) (detection range: 0.05–10 mg/L). The organic phase was digested using a Milestone Ethos. The pH of feed, regeneration and raffinate solutions have been measured using a Mettler Toledo pH-meter which works in the range of −2 to 20 with an accuracy of ± 0.002. Recovered metal precipitate were evaluated using Fourier transform infrared spectroscopy (FTIR). Easy microwave digester (Appendix B) and analyzed using the same instruments as applied for the aqueous phase.

2.2. Synthesis and analysis of [P_{8888}][oleate]

Tetraoctylphosphonium oleate [P_{8888}][Oleate] was synthesized according to the procedure described in previous studies [27]. Briefly, sodium oleate was produced by adding oleic acid (52.36 g, 0.19 mol) to 800 mL of sodium hydroxide (12.74 g, 0.32 mol). After stirring at 45 °C for 3 hrs., tetraoctylphosphonium bromide (100 g, 0.18 mol) was added and the stirring continued for 6 hrs. at 75 °C. The organic phase of the mixture was then washed with warm water (8 × 1 L) at 45 °C to remove sodium bromide and excess of sodium hydroxide. A slightly yellow viscous liquid was obtained after drying the ionic liquid under vacuum at 50 °C. The dried [P_{8888}][Oleate] was then saturated with water by mixing 10 wt% of MilliQ water for 24 h at room temperature. After removal of the remaining water, the water content of the saturated [P_{8888}][Oleate] was measured by a coulometric Karl Fischer titrator (Mettler-Toledo, model DL39). The physical properties of the produced ionic liquid at room temperature are density: 0.894 g/ml; pH: 9.7; conductivity: 190 µS/cm; viscosity: 0.134 Pa.s. The purity of the IL was determined using 1H NMR on a 400 MHz Bruker nuclear magnetic resonance (NMR) spectrometer (model: Avance III 400 MHz) and the following was determined within 2% error from theoretical NMR spectra: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm), δ 5.35 (2H, m), ~2.8 (+ ~2H, b, water), 2.40 (12H, m), 2.21 (2H, t, J = 7.7 Hz), 2.01 (4H, m), 1.59 (2H, m), 1.50 (14H, m), 1.30 (50H, d), 0.90 (15H, t, J = 6.8 Hz). Detection of synthesis impurities such as bromide and sodium were accomplished via Milestone Ethos Easy microwave digester and

Table 2
Main components, accounting for ~60% of total mass, in the spent lithium ion battery cathodes [35]. Oxygen (not shown) contributes for another 21 wt%, other elements for the remaining part.

Element	Co	Li	Ni	Mn
Wt.%	14.88	5.75	21.87	16.96

Metrohm IC Compact 761 Ion Chromatograph (measuring range: 0.10–80 mg/L).

2.3. Metal extraction and regeneration procedure

The Co concentration in the (synthetic) feed solution was set at 1 g/L (in line with previous experimental work) [27]. As for the other metals, we followed the weight ratios presented by Hu *et al.* (Table 2) [35], resulting in 1.14 g/L Mn, 1.40 g/L Ni and 0.39 g/L Li. All the metals were added as chloride salts. Unless stated otherwise, standard feed solution with the above composition was prepared without pH adjustment. Then, 5 mL of the feed solution was added to 5 mL of the water-saturated $[P_{8888}][Oleate]$ (around 10 wt% water) and mixed for 5 min at 40 rpm unless stated otherwise (Appendix C). After centrifugation for 10 min at 3750 rpm (22 °C), in an Allegra X-12R Centrifuge of Beckman Coulter. The loaded IL was regenerated with 5 mL of various concentrations single or multi sodium and ammonium salt solutions for 2 hrs. and centrifuged (3750 rpm; 10 min, 22 °C). Sodium salts used as regeneration solutions are sodium carbonate Na_2CO_3, sodium nitrate $NaNO_3$, sodium phosphate Na_3PO_4 and sodium sulphate Na_2SO_4. Ammonium salts are ammonium hydroxide NH_4OH, ammonium chloride NH_4Cl, ammonium carbonate $(NH_4)_2CO_3$, ammonium sulphate $(NH_4)_2SO_4$, ammonium bicarbonate NH_4HCO_3. Concentrations and compositions are defined in more detail in (Appendix D).

The extraction efficiency ($\eta_{E,i}$), with equal volumes of aqueous and organic phase, in cycle i is calculated by:

$$\eta_{E,i} = \frac{(C_{f,o} - C_{r,i})}{C_{f,o}} \times 100\% \tag{1}$$

Where $C_{f,o}$ is the metal concentration in the initial feed and $C_{r,i}$ the metal concentration in the raffinate in cycle i.

The regeneration efficiency ($\eta_{R,i}$) is calculated by:

$$\eta_{R,i} = \left(1 - \frac{C_{IL,R,i}V_{IL,i}}{(C_{f,o} - C_{r,i})V_{f,i} + C_{IL,R,(i-1)}V_{IL,i}}\right) \times 100 \tag{2}$$

Where $C_{IL,R,i}$ is the metal concentration in the IL after regeneration in cycle i, $C_{IL,R,(i-1)}$ the metal concentration in the IL after regeneration in cycle $(i-1)$, $V_{IL,i}$ and $V_{f,i}$ are the volume of the feed and the IL in cycle i respectively.

3. Results and discussion

3.1. Overall separation and recovery process

Fig. 2 shows a flow diagram of the overall metal extraction and recovery process, which will be discussed in more detail in the next sections. It is important to mark the difference between cycle and stage. Here, cycle refers to (repeating) the whole process of extraction and regeneration, whereas stage refers to (repeating) a single step more than once (each time using fresh organic phase in extraction or fresh regeneration solution in regeneration) during a cycle to enhance either the extraction or regeneration efficiency. The entire process was carried out for two subsequent cycles with 5 min and 2 hrs for each extraction and regeneration stage, respectively. The regenerated IL from the first extraction stage was reused in the extraction stage of the 2nd cycle. Abbreviations, like E-1, R-1-A, Rf-1, used throughout the text refer to Fig. 2.

3.1.1. Extraction of Co and Mn (E-1)

Even though the literature reports higher leaching efficiencies at lower pH, there is no consensus regarding the optimum acid concentration [28–30]. Therefore, the extraction efficiency was explored over a broad pH range of −1 to 5 (Fig. 3). The extraction of cobalt, manganese, nickel and lithium with chloride as the counter anion was investigated at different feed pH levels. Chloride as a medium has been selected because it results in a higher metal leaching efficiency compared to their nitric and sulfuric acid counterparts [13,28,36,37]. This is even in the absence of H_2O_2 or any other reducing/oxidizing agents because of its chlorine ions, which promote the dissolution of metal ions.

At pH 5, Co, Mn and Ni are extracted as aqua complexes with high efficiency of nearly 100% via the anionic part of the IL (oleate) as suggested by Parmentier *et. al.* (2016) for an ammonium-based ionic liquid (Eq. (3)), while Li is essentially not extracted at all [38]. Compared to the extraction at pH 5, the lower extraction observed at pH 0.43–0.1 reflects an effect most likely due to the high HCl concentration in the feed and the consequential increased extraction of HCl into $[P_{8888}][Oleate]$ [31]. As a result, the oleate anions of the IL become protonated and with that are no longer available for extraction [34]. Using 8 M HCl, the extraction efficiency of Co and Mn, but not of Ni, starts to increase again at pH $<$ 0 to reach 99% and 89% for Co and Mn, respectively. This behaviour reflects the formation of negatively charged tetrachlorocobaltate(II) and tetrachloromanganate(II) complexes in the presence of excess chloride ions and the extraction of these metal complexes by the cationic part of the IL (Eq. (4)) [34]. The same behaviour has been observed in the extraction of copper using carboxylic acid based hydrophobic eutectic solvents as reported by Nicolas Schaeffer et al. [33].

pH > 0.5

$$M^{2+}{}_{aq} + 2Cl^{-}{}_{aq} + 3[P_{8888}][oleate]_{IL} \rightleftharpoons [P_{8888}][M(oleate)_3]_{IL} + 2[P_{8888}][Cl^{-}]_{IL} \tag{3}$$

pH < − 0.5

$$MCl_4{}^{2-}{}_{aq} + 2H^{+}{}_{aq} + 2[P_{8888}][oleate]_{IL} \rightleftharpoons [P_{8888}]_2[MCl_4]_{IL} + 2[oleicacid]_{IL} \tag{4}$$

In contrast, the stability of the negatively charged nickel-tetrahedral chloro-complex is relatively low compared to Co and Mn based on the stability constant as shown in Table 3 [39,40], This results in a very low extraction efficiency of Ni around 3% (Fig. 3). Note that in the pH range studied Li is essentially not extracted at all, in accordance with a previous study showing that the extraction of alkali metals like Li require alkaline conditions [34]. This differential behaviour towards pH thus offers the possibility to effectively separate Co and Mn from Ni and Li. Therefore, the extraction of Co and Mn was carried out starting from a highly acidic 8 M HCl feed solution of pH $<$ 0.

Table 4 shows extraction efficiencies during the two subsequent cycles of 99% and 89–84% for Co and Mn, respectively. The overall extraction of Ni and Li remains < 2%. Compared to Co, the extraction efficiency of Mn is relatively modest. As will be discussed in the 'process optimization' section 3.3, a second extraction stage can recover the residual Mn remaining in Raffinate-1 (Rf-1).

The data clearly show that during two subsequent cycles of operation, the extraction efficiency of Co remains essentially unaffected whereas the extraction of Mn lowers by about 5%. Most likely, this reduction is (partly) caused by a slightly lower IL: feed ratio, due to the IL sample taken for analysis. Apparently, the Co extraction efficiency is less sensitive to the IL: feed ratio. While the extraction efficiencies of Ni and Li remain less than 4%. From these results we conclude that the $[P_{8888}][oleate]$ is fairly stable, even during exposure to feed solutions of pH $<$ 0. By implication, $[P_{8888}][oleate]$ can be used during subsequent extraction and regeneration stages.

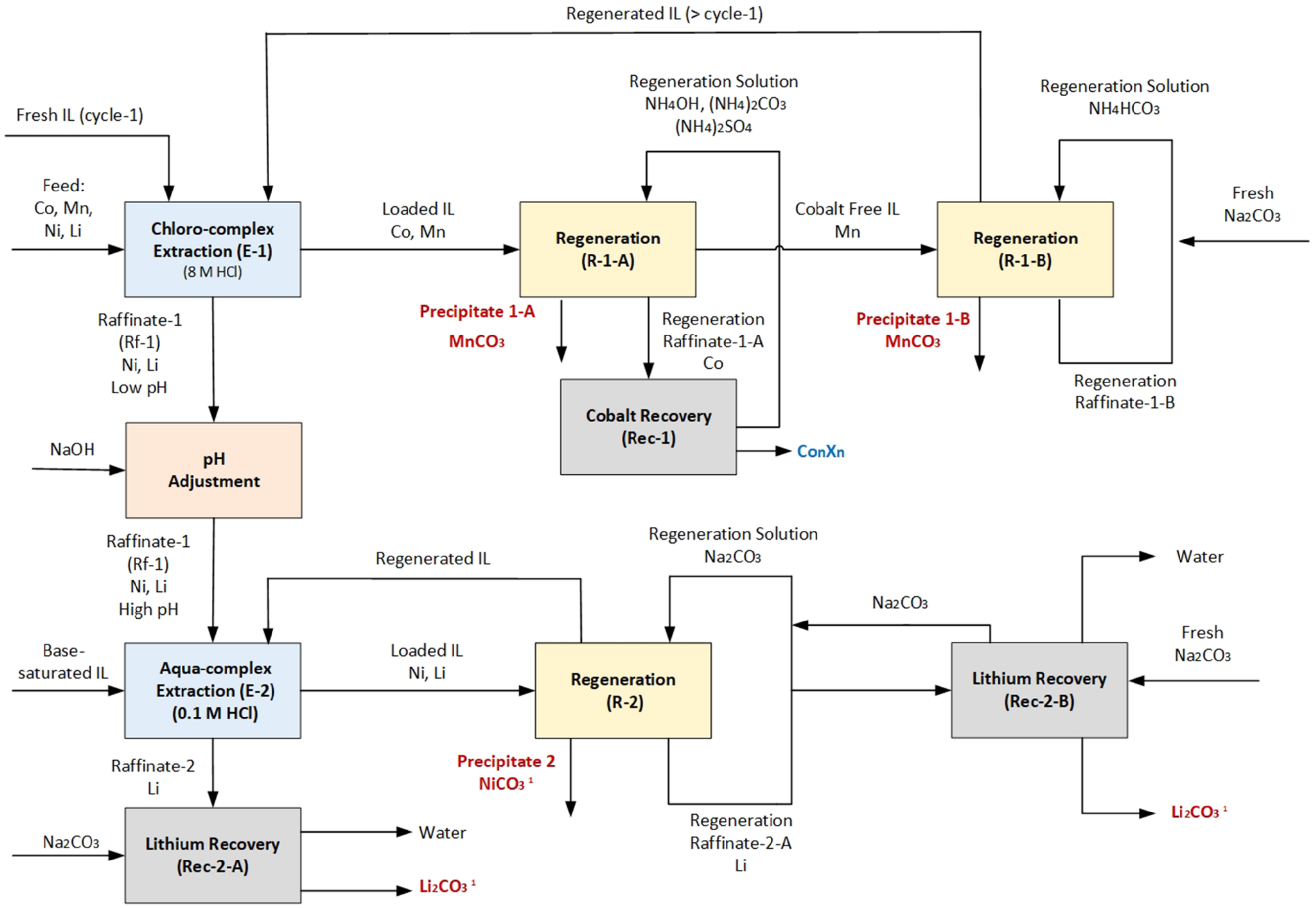

Fig. 2. Flow diagram of the overall metal extraction and recovery process. Precipitates (i.e., process end-product) are indicated in red. With Co harvested in the form of Co_nX_n (printed in blue), X_n depends on the technology used (see text). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

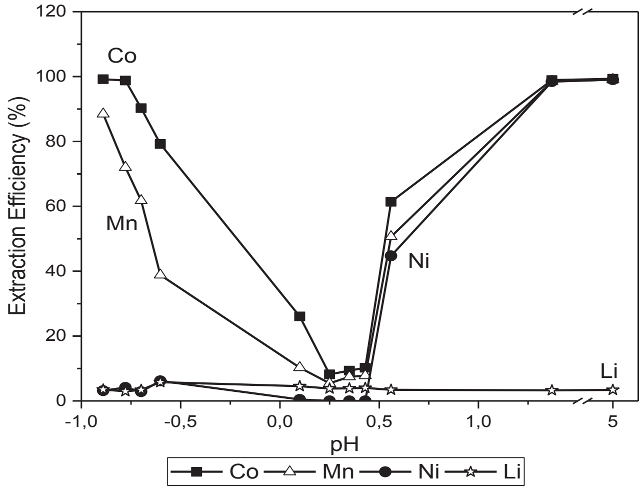

Fig. 3. Extraction efficiency of cobalt, manganese, nickel and lithium using $[P_{8888}]$[Oleate] as a function of the pH of initial metal feed solution.

Table 3
Overall stability constants of metal chloro-complexes in aqueous feed solution [40].

Metal chloro-complex	$[CoCl_4]^{2-}$	$[MnCl_4]^{2-}$	$[NiCl_4]^{2-}$
log β4	8.2	6.7	2.8

Table 4
Single stage extraction efficiencies of metals from a highly acidic chloride medium (8 M).

	$\eta_{E,i}$			
Metal	Co	Mn	Ni	Li
Cycle 1	99	89	4	3
Cycle 2	99	84	2	2

3.1.2. Separation and recovery of cobalt and manganese (R-1-A & B)

Regeneration solutions of different composition and ionic strength were tested for their regeneration efficiency. The finally selected regeneration solution is a composite of 1 M NH_4OH, 1.2 M $(NH_4)_2CO_3$ and 1 M $(NH_4)_2SO_4$. The selection of this particular composite required the screening of a range of single and multi-salt solutions for their regeneration efficiency, including the effect of their (relative) concentration. For brevity and in order not to hamper the flow of the paper, these data are summarized in (Appendix D). Fig. 4 shows the results of four promising regeneration solutions. After establishing the ideal combination, the relative amounts were fine-tuned. A distinction was made between the relative amount of the recovered metal appearing in solution and as precipitate. Clearly, solution RS-2 is the regeneration solution of choice because it combines 100% efficiency for Co (purity 97%) with > 90% of Mn of which by far the largest part precipitates (purity 94%), thereby separating the two metals. Even though the two metals thus can be effectively separated, 90% recovery of Mn requires a two-stage regeneration, whereas for Co a single stage suffices for 100%

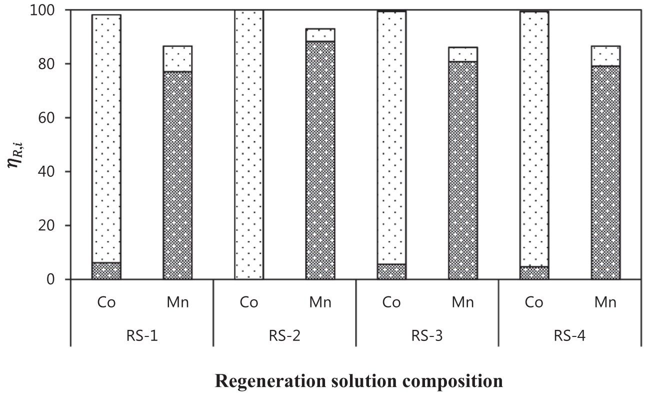

Fig. 4. Two-stage (total) regeneration efficiency for Co and Mn using regeneration solutions (RS) possessing a combination of three salts: NH_4OH, $(NH_4)_2CO_3$ and $(NH_4)_2SO_4$ differing in (relative) concentration. RS-1: 1 M NH_4OH, 1.1 M $(NH_4)_2CO_3$ and 0.9 $(NH_4)_2SO_4$. RS-2: 1 M NH_4OH, 1.2 M $(NH_4)_2CO_3$ and 1 $(NH_4)_2SO_4$. RS-3: 1 M NH_4OH, 1.3 M $(NH_4)_2CO_3$ and 1.1 $(NH_4)_2SO_4$. RS-4: 1 M NH_4OH, 1.4 M $(NH_4)_2CO_3$ and 1.2 $(NH_4)_2SO_4$. Light and dark bar areas indicate metal in solution and metal as precipitate, respectively.

yield. RS-2 recovers Co in the form of an (dissolved) aqueous amino complex and Mn as a precipitate of $MnCO_3$.

Regeneration solution RS-2 (1 M NH_4OH, 1.2 M $(NH_4)_2CO_3$ and 1 $(NH_4)_2SO_4$.) not only serves to recover the metals (and regenerate the IL) but also to separate the two metals Co and Mn. Reaction schemes 4–8 outline a possible scenario of complex formation and conversion during regeneration. The sequence of complex formation is based on color identification as described in the literature and shown in Fig. 5. It all starts with metal chloro-complexes (blue in Fig. 5-B IL) changing to aqua complexes (purple in Fig. 5-C IL), indicating ligand exchange between the IL and the alkaline regeneration solution [41–43]. The ligand exchange reaction, essentially the neutralization of the organic phase, can be expressed as:

$$[P_{8888}]_2[MCl_4]_{IL} + 2[oleicacid]_{IL} + 2NH_4OH_{IL} \rightleftharpoons$$

$$2[P_{8888}][oleate]_{IL} + [M(H_2O)_2]Cl_{2IL} + 2NH_4Cl_{IL} \quad (5)$$

Once in the ammonia-ammonium containing regeneration solution, the metal complexes undergo further ligand exchange. The cobalt aqua complex exchanges water for ammonia - (Eqs. (6) and (7)) to form hexamminecobalt (II) complex, initially pink in colour (Fig. 5-C RRf). This complex forms a deep-red solution after full regeneration of loaded ionic liquid (Fig. 5-D RRf) which is soluble in Regeneration Raffinate (RRf-1-A) [44,45]. The manganese aqua complex reacts with carbonate forming a manganese carbonate precipitate (PPT-1-A), thereby phase-separating from the cobalt-containing raffinate:

$$[Co(H_2O)_2]^{2+}_{aq} + 6NH_{3aq} \rightarrow [Co(NH_3)_6]^{2+}_{aq} + 2H_2O \quad (6)$$

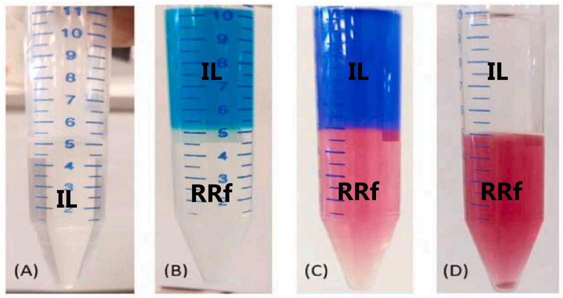

Fig. 5. Ionic liquid in different states. (A) pure IL, (B) loaded IL with $[CoCl_4]^{2-}$ and $[MnCl_4]^{2-}$ complexes, (C) neutralized loaded IL (first 5 min of regeneration) and (D) fully regenerated IL. RRf: regeneration raffinate.

Table 5

Regeneration efficiency of Co and Mn as dissolved complex in the regeneration raffinate (RRf) and as solid precipitate (PPT) during the first stage (1-A) and second stage (1-B) regeneration for two cycles.

$\eta_{R,i}$	RRf-1-A		PPT-1-A		RRf-1-B		PPT-1-B	
Metal	Co	Mn	Co	Mn	Co	Mn	Co	Mn
Cycle 1	100	2	–	80	–	3	–	9
Cycle 2	100	4	–	75	–	4	–	8

$$[Mn(H_2O)_2]^{2+}_{aq} + (NH_4)_2CO_{3aq} \rightarrow MnCO_{3s} + 2NH_4{}^{+}_{aq} + 2H_2O_{aq} \quad (7)$$

Table 5 shows the regeneration efficiency of Co and Mn during two consecutive cycles. Using RS-2, in the first regeneration stage (R-1-A), the regeneration efficiency of Co and Mn is 100% and 80%, respectively. In order to enhance the Mn regeneration, a second regeneration stage was deployed, using 2 M $(NH_4)_2CO_3$ (R-1B), resulting in a total (RRf + PPT) Mn regeneration efficiency of 93% for the first cycle versus 92% for the second cycle. Precipitates in Fig. 2 are indicated in red. FTIR spectra of $MnCO_3$ precipitate matches that found in literature (see Appendix E) [46]. Even though not included in this study, as for harvesting Co in the form of metallic Co or Co_nX_n (printed in blue in Fig. 3), X_n depends on the technology used for the Co recovery section. For example, electrodeposition renders metallic Co, roasting CoO and heating in acidic conditions $CoCl_2$ [47,48].

3.1.3. Extraction of Ni (E-2)

With Ni and Li left behind in raffinate Rf-1 (Fig. 2), the next step is to separate these two metals. Prior to the second extraction process, a pH adjustment to less acidic conditions (pH 1–2) with NaOH is needed to prevent the protonation of oleate during extraction. This leaves way for Ni to be extracted by interacting with the anionic part of the IL, as discussed in section 3.1.1.

Table 6 shows that a single stage extraction of 5 min duration is sufficient to extract all the Ni from Rf-1. Remarkably and in contrast to the data shown in Fig. 3, a substantial amount of Li is co-extracted. For now, the most plausible explanation is that the extraction of Li reflects the salting out effect of Na which results from the addition of NaOH for pH adjustment. Finally, Li can be recovered as Li_2CO_3 from Rf-2 via evaporation using saturated Na_2CO_3.

3.1.4. Separation and recovery of Ni and Li (R-2)

The regeneration of Ni and Li from the loaded IL was accomplished using 1 M Na_2CO_3 in a single stage for 2 hrs. This regeneration process resulted in the separation of Ni from Li via the formation of $NiCO_3$ precipitate (PPT-2 in Table 7) leaving the co-extracted Li in the regeneration Raffinate 2 (RRf-2). This is due to the difference in solubility product of $NiCO_3$ (1.42×10^{-7}) and Li_2CO_3 (8.15×10^{-4}) [49]. In order to increase the precipitation of $NiCO_3$, the IL used in the first extraction cycle (E-2, cycle 1) needs to be pre-saturated with Na_2CO_3. Without this initial saturation step of the IL with Na_2CO_3, Ni extraction leads to a lower regeneration efficiency of 80% and reduces precipitation to 51%. The purity of the produced $NiCO_3$ precipitate is around 100% and its FTIR spectrum is in line with that obtained for standard sample (see Appendix E).

The regeneration raffinate (RRf-2), containing Na_2CO_3 and Li_2CO_3,

Table 6

Extraction efficiency of Ni and Li at pH = 1.

	$\eta_{E,i}$	
Metal	**Ni**	**Li**
Cycle 1	100	33
Cycle 2	100	25

Table 7
Regeneration efficiency of Ni and Li, partly dissolved in the regeneration raffinate (RRf-2) and partly precipitated (PPT-2).

$\eta_{R,i}$	RRf-2		PPT-2	
Metal	Ni	Li	Ni	Li
Cycle 1	4	81	94	3
Cycle 2	4	88	94	–

can be recycled over the regeneration process to increase the lithium concentration to a value close to its solubility limit. The lithium salt in the regeneration raffinate (RRf-2) could be obtained via evaporation of water.

3.2. Selectivity and capacity of [P_{8888}][Oleate]

As shown, with 1 g of Co/L and 1.14 g of Mn/L present in the feed, [P_{8888}][Oleate] extracts Co about 10% more efficient than Mn (Table 4), resulting in an extraction ratio of Co and Mn of around 10:9. Increasing the feed concentrations of both metals to 5 g/L Co significantly shifts this ratio in favor of Co, resulting in a Co:Mn extraction ratio of approximately 2:1. This ratio further increases to 5:1 with 10 g/L Co and to 6:1 with 15 g/L Co in the feed (Fig. 6). The corresponding Mn concentrations are given in the legend of Fig. 6.

In brines containing higher concentrations of both metals this behavior can be exploited as it (partly) shifts the separation of Co and Mn from the regeneration to the extraction phase. The preference for Co points to an intrinsic (concentration-dependent) Co over Mn selectivity of [P_{8888}][Oleate]. The reason for this preference goes back to the atomic level. Even though they are very similar, Co and Mn do differ in crystal and Stokes radius as well as charge density [50,51]. With 7.3 nm (Co) and 8.2 nm (Mn), Co is the smallest of the two and with that has the highest charge density. Because of this and because Co is slightly more electronegative (25.28) than Mn (24.40), Co may have a higher propensity to form complexes with Cl as shown in Table 3, which are, in addition, more stable than those based on Mn [50,51]. Fig. 6 also indicates the high capacity of this IL to take up metals, especially, Co. With 15 g/L Co present in the feed and an extraction efficiency of around 61%, the uptake of Co amounts to 9 g per liter IL.

3.3. Process optimization

Discussing ways to optimize the process demands, first, a definition of optimization, is it in terms of extraction efficiency, cost or, for example, environmental impact. Obviously, these different definitions and approaches may lead to a totally different outcome. A hundred percent extraction is preferred, of course, but against what cost? Cost reduction might be achieved by one-stage instead of two-stage extraction and limited regeneration processes, but the compromise is a metal containing waste stream. From the point of view of environmental impact, it is also not evident how to optimize the process. Including a second extraction or regeneration stage may prevent metals ending up in a waste stream but what about the impact of the other chemicals needed to achieve this?

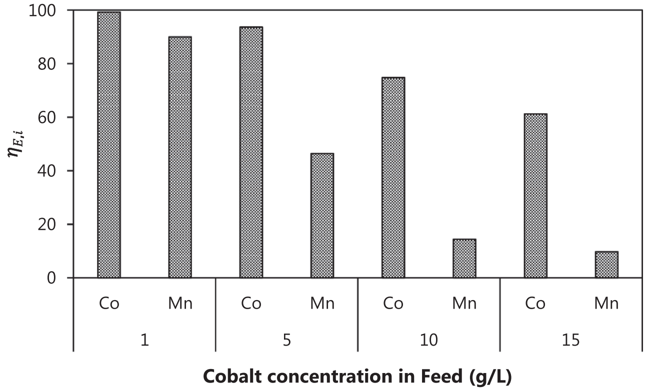

Fig. 6. Extraction efficiency of Co and Mn at different initial feed concentrations of both ion species: 1, 5, 10 or 15 g/L (Co) and 1.14, 5.7, 11.4 and 17.1 g/L (Mn). Experimental conditions: 8 M HCl, T = 22 °C.

Therefore, process optimization was performed via reducing the amount of HCl to minimize the environmental impact and costs without compromising the extraction efficiency. A set of experiments were performed using different HCl concentrations of 4, 5, 6 and 8 M. Table 7 shows that when employing a single stage, the extraction efficiency increases from 79% using 4 M HCl to 99% using 8 M HCl for Co and from 39% to 90% for Mn. As previously remarked, this enhancing effect of increased acid molarity reflects the formation of negatively charged chloro-complexes in the presence of excess chloride, which in turn promote metal extraction [39]. As shown in Table 7, a second extraction stage can partially compensate for the lower extraction efficiency resulting from lowering the HCl concentration. This effect becomes more prominent at lower HCl molarity. For instance, when using 4 M HCl, introduction of a second stage increased the Co and Mn extraction efficiency from 79% to 89% and from 39% to 46%, respectively. In industry, this can be achieved by implementing multiple counter-current stages. An additional benefit of a second extraction stage is the reduction of metal impurities in Rf-1. When employing two-stage extraction, the extraction efficiency of both Ni and Li remained below 4%. From the economical point of view, a process including two-stage (or more) extraction at 4 M HCl may turn out the preferred option. However, because [P_{8888}][Oleate] expresses its highest extraction efficiency during single stage at 8 M HCl, this higher HCl concentration has been selected for the experiments in this explorative study at laboratory scale.

4. Economic analysis

Even though the emphasis of the previous paragraph was on the optimization in terms of extraction efficiency, it is instructive to perform a (brief, high level) Economic Potential analysis (EP0), with EP0 defined as the difference between Sales and Feedstock cost.

$$EP0 = Sales - Feedstock\ \ cost \tag{8}$$

Sales and feedstock values are obtained by multiplying the process capacity/requirement (ton/year) by the sales price of cobalt and chemicals ($/ton) respectively [52]. In the present study, metals other than Co were excluded from the EP0 analysis whereas the feedstock costs include leaching and neutralization reagents (HCl and NaOH respectively). As shown in Table 8 and discussed in the previous paragraph, both feed pH and number of extraction stages have a distinct effect on the (total) extraction efficiency.

Wang et al. argued that leaching 1 ton of spent LIB requires 50 m^3 of

Table 8
Extraction efficiency for Co and Mn at various HCl concentrations performed in two stages.

HCl (M)	pH	Metal	$\eta_{E,i}$		
			Stage-1	Stage-2	Total
4	−0.6	Co	79	47	89
		Mn	39	11	46
5	−0.7	Co	89	90	97
		Mn	46	62	73
6	−0.8	Co	97	99	99
		Mn	73	72	86
8	−0.9	Co	99	93	100
		Mn	90	100	100

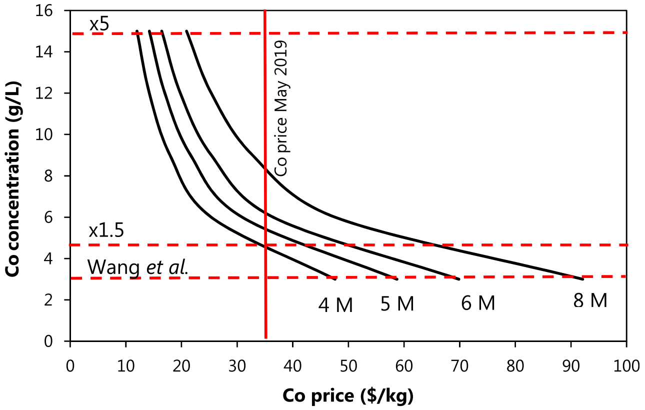

Fig. 7. Co concentration (g/L) in the leachate as function of the Co price ($/kg) needed for EP0 = 0, at different molarities of the HCl used. Presented molarities refer to the value reached after the leaching process. The red solid line indicates the Co price as per May 2019 [54]. Red dashed lines present the Co concentration studied by Wang *et al.* [53] and the Co concentrations obtained after a volume reduction by a factor 2 and 5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4 M HCl [53]. Based on this, the total cost for leaching and neutralization using 4 M HCl and NaOH becomes 7.1 k$/ton spent LIB. The total income from recovered Co per ton spent LIB is 5.3 k$ as based on a Co price of 35 $ per kg (Investment Mine 6 month report, May 2019) and a Co concentration in the leachate solution of 3 g/L [54]. In this scenario, EP0 turns positive at a Co price of at least 48$ per kg. Fig. 7 presents the minimum Co price needed to obtain zero EP0 levels as function of the Co concentration, for four different leachate acidities. Evidently, apart from the molarity of the HCl used, increasing Co concentration in the leachate will also shift the price of Co required for EP0 = 0 to a lower value. For example, and as indicated in Fig. 7, using 4 M HCl, reducing the volume by 33% (and with that increasing the Co concentration from 3 to 4.5 g/L), shifts the demanded minimum Co price from 48 to 33 $ per kg. A further Co concentration increase by a factor 5 lowers the needed Co price to 12 $ per kg.

Table E.1 (Appendix E) shows the economic potential analysis (EP0) for 1 ton spent lithium ion battery leached in 10 and 50 m^3 4–8 M HCl (acidity after leaching). Note that the income from the recovery (for instance a gate fee for the spent LIB) and of other metals present (Ni for instance) is neglected. On the other hand, EP0 does not take utility costs and depreciation into account. Even though the EP0 analysis indicates that the process outlined here can in principle be transformed into economically feasible technology, up-scaling demands further optimization, for instance, in terms of utilizing counter current stages for both extraction and regeneration.

5. Conclusions

Using the phosphonium-based ionic liquid $[P_{8888}]$[Oleate], Co, Mn, Ni and Li can be successfully separated and recovered from a simulated spent lithium-ion battery HCl-based leachate.

In a single-stage extraction at 8 M HCl (pH = −0.9), > 99% of the Co and 89% of the Mn can be extracted. The subsequent separation of Mn from Co can be achieved by a regeneration process using a composite solution containing ammonia, ammonium carbonate and ammonium sulphate and in which Co remains in the raffinate and Mn precipitates as $MnCO_3$. The extraction efficiency of Mn can be improved to 99% by deploying a two-stage instead of a single-stage extraction process.

Next, using the same ionic liquid, the extraction of Ni can be achieved after increasing the pH to about 1, resulting in a low co-extraction of Li. Complete separation of Ni and Li can be accomplished by using a Na_2CO_3 solution during regeneration, due to the difference in the solubility product of both carbonate salts. The regenerated ionic liquid can be directly re-used in the subsequent extraction cycles.

The three key parameters defining the (possible) economic feasibility of the process outlined here are the Co concentration in the leachate solution, the molarity of the HCl used and the market price of Co. An EP0 analysis taking into account these parameters reveal that in terms of economics the use of 4 M HCl is preferred despite the fact that 8 M HCl showed the highest extraction efficiency for both Co and Mn. Furthermore, the break-even point, i.e. EP0 = 0 (at a current Cobalt price of 35 $/kg) can be reached by reducing the leachate volume by at least 33% and consequently increasing the cobalt concentration by 50% to 4.5 g/L or once the cobalt price exceeds 48 $ per kg.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2020.117435.

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