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Solvent extraction fractionation of Li-ion battery leachate containing Li, Ni, and Co

Sami Virolainen^{a,*}, Mojtaba Fallah Fini^a, Antero Laitinen^b, Tuomo Sainio^a

^aLappeenranta University of Technology, Laboratory of Separation Technology, P.O. Box 20, FI-53851 Lappeenranta, Finland

^bTechnical Research Centre of Finland, P.O. Box 1000, FI-02044, Espoo, Finland

**Corresponding author. Tel.: +358 40 7093444, E-mail address: Sami.Virolainen@lut.fi*

Abstract

In this research, the separation of Li, Ni, and Co by solvent extraction was studied from synthetic Li-ion battery waste leachate. The purpose was to propose a process for producing all the metals with over 99.5% purities, as the purity demands for battery grade metals are high. Emphasis was also placed on obtaining pure Li raffinate in the early stage of the process, as societal interest in Li is growing rapidly. Thus, the purpose was to first extract Co and Ni selectively yielding pure Li raffinate, and consequently separating Co and Ni as pure products in the stripping stage. The equilibrium behavior of the separation system was studied by constructing the pH isotherms as well as loading and stripping isotherms. Bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) and (2-ethylhexyl)phosphonic acid mono-2-ethylhexyl ester (PC-88A) were used as extractants, both as unmodified and modified with 5% v/v TOA or TBP. Based on the equilibrium results, bench-scale continuous counter-current separation experiments were designed and conducted using 1.0 M Cyanex 272 modified with 5% v/v TOA. Co and Ni were loaded in two stages from the sulfate feed solution containing 2.8 g/L of Li, 14.4 g/L of Co, and 0.5 g/L of Ni. In this step, over 99.6% yields for Co and Ni were achieved, giving 99.9% pure Li raffinate. However, 17–26% of Li was co-extracted, but efficient scrubbing with NiSO_4 was designed with equilibrium experiments and demonstrated in continuous operation. In the stripping step, 99.5% pure aqueous Ni solution and 99.2% pure organic Co solution were obtained using two counter-current stages. Adding one more stage increased the Ni and Co purities to 99.7 and 99.6%, respectively. In addition to the high

purities of the metals, the suggested process has fewer process steps compared to previously suggested flowsheets for similar fractionation.

Keywords

Lithium; Cobalt; Battery waste; Solvent extraction; Continuous counter-current operation

1. Introduction

Li-ion batteries typically contain 2–15% Li, 15–30% Co, and up to 10% Ni (Zeng et al., 2014). They are the most popular ones among rechargeable batteries (Jacobi, 2003), and their demand will likely increase significantly due to their use in electric vehicles (Cabeza et al., 2015). This has led, and will continuously lead to a strong increase in the demand for Li and Co, as 31% and 25% of their production, respectively, is used in the batteries (Dewulf et al., 2010; Jansen, 2013; United States Geological Survey, 2015). However, as the Li-ion batteries come to the end of their life within under 10 years, it is also evident that the amount of used batteries available as a secondary metals' resource will increase at the same time (Goodenough and Park, 2013). For example, in 2011, the recycling rate of Li was only 3%, meaning that there is a huge potential for increased utilization of the waste as its raw material (Talens Peiró et al., 2013). Although the share of Ni used in batteries is not as high as for Li and Co (United States Geological Survey, 2015), its share in battery waste may be significant (Zheng et al., 2014), and as a valuable base metal it would also be a viable target metal in the hydrometallurgical fractionation of battery waste leachate.

After mechanical and possibly some other pretreatment, battery waste is usually leached with acid (Ekberg and Petranikova, 2015). Various acids have been proposed for the task,

yet the most commonly used ones are H_2SO_4 and HCl , which both have high leaching efficiencies at moderate concentrations (Zeng et al., 2014). In addition to the previously discussed Li, Ni, and Co, Li-ion batteries contain significant amounts of Cu (7–17%), Al (3–10%), and Fe (up to 20%) (Zeng et al., 2014), which are also leached with the conventional methods used. They can be removed by precipitation (Granata et al., 2012) or solvent extraction (Suzuki et al., 2012), but their separation was not in the scope of this research.

The solvent extraction fractionation of Co, Ni, and Li from H_2SO_4 and HCl solutions has been researched extensively for the last 20 years. Table I presents the most important of these studies. Only the solvent extraction separation in pure acid solutions is discussed here. Other methods such as precipitation are seen as more viable recovery methods if, for example, organic acids are used as additives in the leaching (Zeng et al., 2014).

As Table I shows, the H_2SO_4 media has clearly been much more popular than HCl in the leaching–solvent extraction process for recovering valuable metals from battery waste. Only two process proposals deal with the HCl media, and only one of these has Ni included. Moreover, in the proposal by Niinae et al. (2014), the metal concentrations are very low, and only the solvent extraction was studied.

Table I. Previous research on the solvent extraction fractionation of Co, Ni, and Li from battery waste leachates. The diluent of the organic phase in all studies has been some conventional commercial kerosene, except for those where sulfonated kerosene is mentioned.

Aqueous feed	Extraction	Scrubbing	Stripping	Reference
HCl Co 17.3 g/L Li 1.7 g/L pH 0.6	99.99% Co and 13% Li, 0.9 M PC-88A, pH 6.7, O/A 0.85:1	CoCl ₂ +HCl (Co 30 g/L), pH 1.0, O/A 10:1	2 M H ₂ SO ₄ , O/A 5:1, >99.99% purity Co	(Zhang et al., 1998)
HCl Co 0.12 g/L Ni 0.12 g/L Li 0.01 g/L	10% v/v Cyanex 272, O/A 1:1, Co pH 4.5-5.0, Ni pH 5.5-6.0	-	0.1 M HCl, Co 98%, Ni 94%, O/A 1:1	(Niinae et al., 2014)
H ₂ SO ₄ Co 16.7 g/L Ni 11.0 g/L Li 1.4 g/L	>96% Co at pH 5.1-5.5 and 96% Ni at pH 6.3-6.5, 1.0 M Cyanex 272, 10 w-% saponified, 1 min, O/A 1:1	-	2 M H ₂ SO ₄ , 1 min, O/A 1:1	(Nan et al., 2005 and 2006)
H ₂ SO ₄ Co 7.2 g/L Ni 4.3 g/L Li 1.5 g/L	Sulfonated kerosene, 99.9% Co, <1% Ni and Li, 20 v/v-% Mextral 272P, O/A 2:1, pH 4.5, 5 min	5 g/L Na ₂ CO ₃ , 100% Li, A/O 1:1, 10 min, 25 °C	0.1 M H ₂ SO ₄ , 99% Co, O/A 2:1, 5 min, 25 °C	(Chen et al., 2015)
H ₂ SO ₄ Co 13.8 g/L Ni 15.0 g/L Li 2.0 g/L	99.9% Co, 1% Ni and Li, 0.4 M Cyanex 272, 50% saponified by NaOH, 25 °C, O/A 2:1, pH 5.5- 6.0, 30 min	-	2 M H ₂ SO ₄ , O/A 11.7:1, >99.9% purity Co	(Kang et al., 2010)
H ₂ SO ₄ Co 20.6 g/L Ni 0.5 g/L Li 2.5 g/L pH 3.5	95% Co, <5% Ni and Li, 25 w- % P507 in sulfonated kerosene, TBP modifier, 70% saponified by NaOH, 25 °C, O/A 1.5:1, pH 4.2, 10 min	-	3 M H ₂ SO ₄ , O/A 4:1	(Chen et al., 2011)

Aqueous feed	Extraction	Scrubbing	Stripping	Reference
H ₂ SO ₄ Co 0.12 g/L Li 0.01 g/L pH 3.5	90% Co and <1% Li, 10 v/v-% PC-88A + 5 v/v-% TOA, 25 °C, pH 5.4, O/A 1:1	-	3 M H ₂ SO ₄ , O/A 1:1, >98% Co	(Suzuki et al., 2012)
H ₂ SO ₄ Co 11.0 g/L Ni 13.0 g/L Li 1.6 g/L	99.9% Co, 5.4% Ni and 3.1% Li, 1 M Cyanex 272	15 g/L Co	2.2 M H ₂ SO ₄ , Co purity >99.8%	(Nogueira and Margarido, 2012)
H ₂ SO ₄ Co 25.1 g/L Ni 2.5 g/L Li 6.2 g/L pH 2.0	99.8% Co, 4.3% Ni and 12.9% Li, 0.56 M PC-88A, 60% saponified by 12 M NaOH, O/A 3:1, pH 4.5, 25 °C, 10 min	2.0 g/L CoSO ₄ , pH 4.8	0.2 M H ₂ SO ₄ , OA 1:1, 10 min, 25 °C, 99.9% purity Co	(Nguyen et al., 2014)
H ₂ SO ₄ Ni 2.5 g/L Li 4.8 g/L pH 2.0	99.6% Ni and 6.8% Li, 0.15 M PC-88A, O/A 1:1, pH 6.5, 10 min, 25 °C	0.1 M Na ₂ CO ₃ , O/A 2:3	0.2 M H ₂ SO ₄ , O/A 1:1, 10 min, 25 °C, 99.9% purity Ni	(Nguyen et al., 2015) <i>Note: Continuing the previous process after extraction of Co</i>

The general approach in all the processes described in Table I is to extract the Co and Ni in separate solvent extraction circuits, and the Li remains in the final raffinate after Ni extraction. In addition, in many of the given processes, emphasis has not been placed on the nowadays more and more significant Li product. Thus, often the yields of the Co and Ni extraction are incomplete and impure Li raffinate is produced. Alternatively, the process is not optimized to obtain pure Ni, which obviously causes some losses of the valuable Co and Li. Nguyen et al. (2014 and 2015) have suggested the only process in which the Co and Ni are both produced as 99.9% pure. A scrubbing stage is needed in both Co and Ni extraction steps, causing two streams to be treated or recycled back to the feed. The Li purity obtained with this suggested process is 99.8%.

Organophosphorus reagents bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272, Mextral 272P, P507) and 2-ethylhexyl hydrogen (2-ethylhexyl)phosphonate (PC-88A) are exclusively used for the fractionation due to their good Co/Ni selectivity. They are often modified with TOA (trioctylamine) or TBP (tributyl phosphate) mainly to affect the selectivities (Niinae et al., 2010; Suzuki et al., 2012). TBP is also in general known to improve poor phase behavior in solvent extraction, which in this case can be caused by the high Co concentration in the organic phase. C.Y. Cheng et al. (2011) have stated that the phase modifying properties of the TBP are related to formation of more surface active complexes in the organic phase. Thus it is possible that also TOA, having similar interaction properties with complexes, could act as phase modifier in this separation system.

In addition to the academic research literature, the methods for recovering valuable metals from battery waste by hydrometallurgy have been extensively patented. For example, in

Sonu et al.'s (2012) method, Mn, Co, and Ni are selectively recovered from purified battery waste leachate, respectively, by D2EHPA (di-(2-ethylhexyl)phosphoric acid), Cyanex 272, and Versatic 10 (neodecanoic acid). The method used by Yang et al. (2010) is similar; Mn is extracted with D2EHPA and Co is extracted with P507, but the separation of Ni and Li has not been described. In J. Cheng et al.'s (2011) method, Cu is first selectively extracted for a product, after which Co and Ni are extracted and selectively stripped.

In this research article, we propose a process in which all three valuable metals are produced with very high yields and purities (>99.5%). The battery manufacturers state that they prefer to use the purest raw materials available (Yoshio et al., 2009). For example, the purity demand for battery grade Li_2CO_3 has been stated to be 99.9% (Moreno, 2013). The production of very pure fractions early in the hydrometallurgical process leads to the efficient use of raw materials and separation facilities, as with this kind of process a minimum amount of waste is produced and no additional purification steps are needed to treat impure intermediate products.

The novelty in this work lies in simplifying the process so that the whole multicomponent separation process could be done in a single loading-scrubbing-stripping solvent extraction circuit instead of having separate circuits for Co and Ni extractions. Moreover, none of the previously suggested processes (Table I) have been demonstrated, either on a larger scale or in continuous counter-current processing. This research article demonstrates the process in bench-scale continuous counter-current operation as well.

2. Experimental

2.1 Materials and reagents

Table II. Chemicals used in the experiments to design the Co+Ni+Li fractionation process for sulfuric acid leachate of Li-ion battery waste.

Chemical	Manufacturer/supplier	Purity
CoSO ₄ · 7H ₂ O	Outokumpu OY	Technical grade, 22% Co content
NiSO ₄ · 6H ₂ O	Sigma-Aldrich Co.	99%
Li ₂ SO ₄ · H ₂ O	Alfa-Aesar	99%
H ₂ SO ₄ 95-97%	Merck KGaA	Pro analysi
HNO ₃ 65%	Merck KGaA	Pro analysi
NH ₃ 25%	Merck KGaA	Pro analysi
Exxsol D80	ExxonMobil Chemical	-
Cyanex 272	Cytec Solvay Group	88%
PC-88A	Daihachi	>95%
Trioctylamine (TOA)	Sigma-Aldrich Co.	98%
Tributylphosphate (TBP)	Sigma-Aldrich Co.	97%

Details of the chemical used in the experiments are given in Table II. The organic phases were composed of the extractant (1 M Cyanex 272 or 1 M PC-88A), phase modifier (TOA or TBP), and diluent (Exxsol D80). TBP is generally widely used as a phase modifier for organophosphorus extractant. Here TOA was chosen as alternative having similar solvating properties than TBP, and as being used as equilibrium modifier in studies of Niinae et al. (2010 and 2014) and Suzuki et al. (2012). The organic phases were washed twice with H₂SO₄ and once with pure water, and after this the aqueous traces were removed by centrifugation.

Synthetic aqueous feed solution for the experiments was made by dissolving the corresponding sulfate salts to purified water. The composition (Co 14 g/L, Ni 0.5 g/L, and Li 2.8 g/L) was chosen based on the authentic leachate of Chen et al. (2011), but the amount of Co was reduced for experimental reasons.

All metal analyses, both from the batch experiments and pilot runs, were carried out from 14% or 1 M HNO₃-media using a Thermo-Scientific iCE™ 3300 AAS Atomic Absorption Spectrometer. The organic phase metal concentrations were analyzed after stripping them with 14 wt% or 1 M HNO₃ (A/O = 10:1).

2.2 *Equilibrium experiments*

The effect of pH on the extraction of Co, Ni, and Li with Cyanex 272 and PC-88A, both as unmodified and modified with 5% v/v TOA, was studied in a jacketed 1000 mL glass reactor at 23 °C. The pH of the aqueous phase was adjusted by bubbling ammonia gas with nitrogen into the reactor, and before sampling, the mixing was continued for 15 min to ensure equilibrium. The aqueous phases were analyzed to construct the Co and Ni isotherms. The Li isotherm was constructed based on the organic phase analysis because relatively small extracted amounts were more accurately detected from the organic phase. The extent of extraction for metal *i*, E_i , was used to represent the effectiveness of the solvent extraction. Since the organic phase loading was zero in the initial state, E_i can be calculated as

$$E_i = \frac{q_i}{c_i^{\text{feed}}} \frac{V_{\text{org}}}{V_{\text{aq}}} \cdot 100\% = \frac{c_i^{\text{feed}} - c_i}{c_i^{\text{feed}}} \cdot 100\% \quad (1)$$

where q stands for the organic phase concentration and c for the aqueous phase concentration, c^{feed} is the initial concentration in the aqueous phase, and V_{org} and V_{aq} are the volumes of the organic and aqueous phases, respectively.

Loading isotherms of Co and Ni were constructed for the same four organic phases as the pH-isotherms. The reagents were pre-neutralized with NH_3 to extents of 48% and 70%, respectively, for Cyanex 272 and PC-88A to obtain equilibrium pH values of 7.0 and 6.5, which were chosen based on the pH isotherms. The phases were equilibrated at 23 °C in 50–100 mL separation funnels for 10 min. The organic to aqueous phase ratio O/A was varied in range of 5:1–1:5. The metals were analyzed from both phases.

To investigate Li scrubbing, an equilibrium study was done for Cyanex 272 modified with 5% TOA at two equilibrium pH values (i.e., 6.0 and 6.5). 0.3 g/L NiSO_4 solution was chosen as the scrubbing agent because it should be suitable to do the task without scrubbing any desired Co and Ni. In the suggested process in which both Co and Ni are extracted to the organic phase, the conventionally used CoSO_4 would likely scrub the Ni as well. The experiments were performed in a jacketed 120 mL glass reactor at 23 °C, and the agitation time was 10 min. The phase ratio O/A was varied in range of 10:1–1:10. The pH adjustment was done with a few drops of 95–97% H_2SO_4 . The organic phase, Cyanex 272 modified with 5% v/v TOA, contained 10.1 g/L of Co, 0.420 g/L of Ni, and 0.356 g/L of Li, and it was prepared by extracting simulated sulfate leachate of Li-ion battery waste.

Stripping isotherms were constructed for all four organic phases. The organic phases were prepared by extracting simulated sulfate leachate of Li-ion battery waste with a 1:1 phase ratio in a pH of 6.5 (Cyanex 272) and 7.0 (PC-88A), and thus the metal contents could be

assumed to be similar to the scrubbing isotherms. This organic phase was mixed with phase ratios O/A 1:1, 1:1.5, 1:2, and 1:3. Acidities of the stripping solutions (0.025 M for Cyanex 272, 0.1 M for PC-88A) were chosen based on pH isotherms and preliminary experiments so that the equilibrium pH with a 1:1 phase ratio would be the highest possible, still having 100% stripping efficiency for Ni.

2.3 *Continuous counter-current experiments*

Continuous counter-current solvent extraction for the fractionation of metals in Li-ion battery waste leachate was performed in bench-scale pilot equipment provided by SX Kinetics Inc. The same equipment has been previously used for studying purification of Li brine (Virolainen et al., 2016). The volumes of each mixer and settler are 270 and 1050 mL, respectively, and the settlers are jacketed for adjusting the temperature. The recycling of the phases is possible to accurately adjust the actual phase ratio in the mixer, which was monitored by sampling next to the impeller. Peristaltic MasterFlex pumps (model 07528-30) were used for feeding the aqueous and organic phases. Semi-open six-bladed impellers with rotation speeds of 700–900 rpm were used for agitation. The flowsheet of the equipment (for two stages) is given in Fig. 1.

The temperatures and pH values of each mixing stage were monitored online. The pH control was done by pre-neutralization of the organic phase using aqueous ammonia (25%), or the dropwise addition of concentrated H₂SO₄ (95-97%) into the aqueous streams. The organic phase in these continuous counter-current runs, chosen based on the equilibrium experiments, was 1 M Cyanex 272 in ExssoI D80 containing 5% v/v of a phase modifier (TOA or TBP). The total flowrate in the system varied was 27 mL/min ($\pm 2\%$) in every run,

yielding 10 min ($\pm 2\%$) residence time in the mixer. The effect of the residence time on the performance of the process stages was not studied here but, based on the literature, the used residence time is well high enough to reach equilibrium. All the experiments were performed at temperatures close to 23 °C. For chemical analyses, to monitor the actual behavior of the fractionation, samples were taken from the outlet of each stage several times during the run.

The selective loading of Co and Ni to the organic phase, the scrubbing of Li, and the selective stripping of Ni were studied in separate experiments. Three runs were made to the loading step, one for the scrubbing, and five for the stripping. In addition, the scrubbing of co-extracted Li was studied with one continuous run. The extraction runs all had two counter-current stages, in the scrubbing run, one stage was used, while in two of the stripping runs three stages were used. The other varied run parameters were the phase ratio and the pH. The exact run parameters are given with the results in Tables III and IV. Some results are given as the phase purity of a certain metal *i*, which is defined as the share of that metal from the total amount of metals:

$$Purity_i = \frac{c_i}{c_{tot}} \cdot 100\% \quad (2)$$

Figure 1. Continuous counter-current setup to study the fractionation of metals in Li-ion battery waste leachate.

3. Results and discussion

3.1 Equilibrium studies for designing the continuous experiments

In all four studied organic phases, modified and unmodified 1 M Cyanex 272 and 1 M PC-88A had similar selectivity for Co and Ni over Li (Fig. 2). That is, based on the pH-isotherms, it is not possible to avoid significant co-extraction of Li while having a high extent of extraction for the Co and Ni. Modifying the Cyanex 272 with 5% TOA shifted all the isotherms toward higher pH, but did not affect the selectivities between the metals. When PC-88A was modified with 5% TOA, the Ni isotherm shifted toward a higher pH, while for Co and Li the modification did not have a clear effect. Thus, the modification of the PC-88A increased the desired Co/Ni selectivity, but decreased the more important (Co+Ni)/Li selectivity.

The previously described observations about the weaker extraction of metals in presence of TOA modifier are consistent with the literature. According to Suzuki et al. (2012) TOA affects the equilibrium of the metal complex formation in two different ways. The TOA molecules have electric interactions with the organophosphorous reagents, and thus the complex formation is hindered. In sulfate solutions, Co forms a complex with two organophosphorous reagent dimers, Ni with three, and Li with two (Preston, 1982; Zushi et al., 2000). Thus, the availability of the reagent molecules (or dimers) has significant effect on the uptake of the metals. According to Suzuki et al. (2012) it is also possible that the TOA molecules repulse the metal ions in the phase interface.

The known fact in the hydrometallurgical industry, that Cyanex 272 has better Co/Ni selectivity than the PC-88A, was confirmed with the current data (Fig. 2), and it makes the Cyanex 272 a more attractive choice for the suggested Co+Ni+Li fractionation process from the selectivity point of view. However, based on these data, it seems that the fractionation could also be feasible with the PC-88A if its other properties are significantly better.

Figure 2. Dependence of the metal extraction on the pH from the simulated sulfate leachate of Li-ion battery waste. Symbols: circles Co, squares Ni, and diamonds Li. Organic phases: a) unmodified Cyanex 272, b) unmodified PC-88A, c) Cyanex 272 modified with 5% v/v TOA, d) PC-88A modified with 5% v/v TOA.

In Fig. 3, loading isotherms for all four studied organic phases are presented. It can be seen that the PC-88A has clearly better capacities than Cyanex 272 for both Co (19-20 g/L vs. 14-15 g/L) and Ni (0.48 vs. 0.35 g/L). Adding the TOA modifier reduces the loading capacities of Co significantly, but for Ni it does not have an effect. As discussed in connection with the pH isotherms, TOA weakens the extraction of all metals. However, in high loadings the extraction of Ni might be exclusively limited by the competition with Co and thus the TOA does not have a notable effect. The loading curves of Co are very steep for all the organic phases, and the maximum loadings are achieved in under 2 g/L aqueous phase concentrations. Thus, it is evident that the Co removal could be done in a single-stage operation. However, when the Co loading approaches saturation, it starts to displace

Ni. The phenomenon behind this is simple competition for the available reagent molecules. When the loading of Co is not very high, there is still plenty of room for Ni as well, but when the Co loading increases there starts to be lack of available reagent molecules. Uptake of Co is favored both because of its much higher affinity and because of more favorable stoichiometry, and it begins to displace Ni. This is clearly seen in Fig. 3b as decrease of the Ni loading curves at higher metal concentrations. Moreover, the Ni uptake curves are not very steep, and thus it is suggested to use at least two loading stages to obtain a high yield for Ni, and consequently high purity for the Li raffinate. Due to the shape of the Ni loading curves, accurate McCabe-Thiele analysis is not possible, and thus the number of needed equilibrium stages should be studied in actual continuous counter-current operation.

Figure 3. Loading isotherms of a) Co and b) Ni for the four organic phases (circles unmodified Cyanex 272, squares Cyanex 272 modified with 5% TOA, diamonds unmodified PC-88A, hexagrams PC-88A modified with 5% TOA) used in the equilibrium experiments for the simulated sulfate leachate of Li-ion battery waste.

Another remarkable conclusion from the loading curves in Fig. 3 is that having such a high Co concentration in the feed aqueous phase (14 g/L) sets in this case actual limits for the applicable phase ratio. For example, with the 1 M Cyanex 272, a phase ratio A/O over 1:1 cannot be used, and the reagent concentration cannot be increased either due to the phase behavior issues. Thus, the A/O of 1:1 was chosen as the starting point for the continuous counter-current runs.

Figure 4. a) Scrubbing isotherms of Li, and b) co-scrubbing of Ni, with 0.3 g/L NiSO_4 solution at an equilibrium pH of 6.5 (squares) and 6.0 (circles). The dashed arrows indicate the McCabe-Thiele analysis.

As indicated from the pH isotherm data in Fig. 2, there would always be a significant amount of co-extracted Li in the organic phase after Co+Ni loading. Thus, a scrubbing stage is needed to obtain a higher yield for the Li and a higher purity for the consequent Ni and Co products. To study the scrubbing, an isotherm was constructed only for the

modified Cyanex 272 (Fig. 4a), as it was believed to reveal the optimal conditions and operation mode. The scrubbing was more efficient in a pH of 6.0, but then a significant amount of Ni was also scrubbed, while in a pH of 6.5, no Ni scrubbing was observed (Fig. 4b). Moreover, at a higher pH, scrubbing is efficient in a single step yielding a ca. 20 ppm Li impurity level with O/A 1.5:1. Thus, the scrubbing was first attempted in the bench-scale in a single stage.

To study the number of needed stages and phase ratio O/A, stripping isotherms for Ni with H_2SO_4 were constructed (Fig. 5a). Several initial stripping acidities were tested to have isotherm points so that the Ni stripping equilibrium would be in the 0% extraction efficiency area of the pH isotherms. The organic phases did not differ in their Ni stripping isotherms (Fig. 5a), but the stripped Co amounts were much higher for PC-88A than for Cyanex 272 (Fig. 5b), as a higher acidity was needed for Ni stripping, as indicated from the pH isotherms as well (Fig. 2).

Purpose of the McCabe-Thiele analysis shown in Fig. 5a was to find decent run parameters to begin the continuous counter-current operation, not to optimize them accurately. Also, the McCabe-Thiele analysis is not well suited to predict the performance of the selective stripping step because the performance in terms of achieved purities is more dependent on the amount of stripped Co than on the yield of Ni. Even small amount (*e.g.* 1%) of stripped Co would give impure Ni to the aqueous phase, but already as low as 90% Ni yield would give over 99% pure Co. Thus, the purity of Ni is expected to be sensitive to the pH, which might be slightly different in the continuous operation compared to the batch isotherm data. This would also make the McCabe-Thiele analysis inaccurate.

Unity was chosen as phase ratio for the McCabe-Thiele analysis in Fig. 5a because with a higher value the operating line would rise above the isotherm in the relevant Ni organic concentration range (>600 mg/L). The starting point (650 mg/L Ni in organic phase) was adopted from the loading experiments discussed later. For simplicity the end point of (0, 0) was chosen as the goal would be to have close to 100% yield for the Ni. It can be seen that even though the acidity was set to a higher side, neglecting perfect selectivity (high Co co-stripping), the stripping efficiency of Ni, even for a fairly low Ni concentration of 650 mg/L, would not be very high with only a single stage and phase ratio close to unity. Thus, based on this analysis, it was determined to have at least two stages in the stripping, and consequently a slightly higher phase ratio O/A 1.5:1 was suggested.

Figure 5. a) Stripping isotherms of Ni, and b) co-stripping of Co, with 0.025 (Cyanex 272) and 0.1 M (PC-88A) H_2SO_4 solutions from the four organic phases (circles unmodified Cyanex 272, squares Cyanex 272 modified with 5% TOA, diamonds unmodified PC-88A, hexagams PC-88A modified with 5% TOA). The dashed arrows indicate the McCabe-Thiele analysis.

3.2 Continuous counter-current processing

The purpose of the continuous counter-current experiments was to suggest an improved flowsheet for the previously given approach where the metals (Co and Ni) are recovered one by one, leaving Li to the raffinate. In this process, there is need for loading, scrubbing, and stripping steps in each metal's recovery. In this work an approach, in which the fractionation of these three metals is achieved in a single process having loading, scrubbing, and two stripping steps, was explored (Fig. 6). The additional purpose was to demonstrate the process in bench-scale and real counter-current operation, which has not

been previously done for this separation task and is also generally rare in academic literature concerning solvent extraction.

Although the PC-88A had a higher loading capacity, Cyanex 272, modified with 5% TOA or 5% TBP, was chosen as the organic phase for the continuous counter-current experiments due to its superior Co/Ni selectivity. It was observed immediately in the continuous runs that without the modifier the operation is physically impossible. This is because the organic phase becomes very viscous, and consequently the phase disengagement is very poor without a modifier. On the other hand, a disadvantage of adding the modifier is lowered extraction capacity of the organic phase (see equilibrium results in Section 3.1).

Figure 6. Proposed flowsheet for the continuous counter-current solvent extraction fractionation of metals in Li-ion battery waste leachate.

Extraction of cobalt and nickel

In the first and second loading runs (Table III) 5% v/v TOA was used as the modifier, and in the third run the modifier was 5% v/v TBP. Two counter-current stages were used in every run, and the actual changed run parameters were the pH and the phase ratio A/O. The run time in each run was at least 660 min, allowing ≥ 66 mixer volumes to pass the system. Based on the measured conditions and metal extraction trends (Fig. 7), the system can be

assumed to be in steady state before the end of the run. Although, in the depicted Run #2, the pH of the 2nd loading stage counting from the aqueous inlet slightly increased until the end of the run, the metal extraction trends were constant for the last hour (6.0 mixer volumes). Otherwise the run parameter curves in Fig. 7a were smooth, indicating the successful operation of the system.

Figure 7. Continuous counter-current extraction of Co and Ni from simulated battery waste sulfuric acid leachate (Co 14.5 g/L, Ni 0.51 g/L, Li 2.7 g/L) with 1 M Cyanex 272 modified with 5% TOA (Run #2). a) Trends of the run parameters, and b) metal extraction efficiencies. The temperature in the 1st stage was 23.5–24.0 °C, and in 2nd stage 22.0–22.8 °C. Symbols: black triangle pH of the 1st stage, white triangle pH of the 2nd stage, dark blue square A/O in 1st stage, light blue square A/O in 2nd stage, blue circles Co, red squares Ni, and green diamonds Li.

Table III. Run conditions, parameters, and extraction efficiencies in continuous counter-current extraction of Co and Ni from Li-ion battery leachate. The feed concentration of the metals were Co 14.2–14.5 g/L, Ni 0.49–0.51 g/L, and Li 2.7–2.9 g/L. The temperature was 22–24 °C.

Run #	Phase modifier % v/v	Run time (min)	pH		Phase ratio A/O		Extraction, %		
			1 st	2 nd	1 st	2 nd	Co	Ni	Li
1	5% TOA	720	5.0	7.2	0.96	0.94	100	80.1	7.6
2	5% TOA	700	6.8	7.1	0.77	0.77	100	99.6	17.3
3	5% TBP	660	6.7	7.0	0.78	0.76	100	99.9	26.2

As expected, the extraction of Co to the organic phase was easy and practically complete in all the loading runs (Table III). In Run #1, the pH in the first extraction stage (counting from the aqueous feed) was only 5.0, and thus the Ni extraction was not complete. In Run #2, the pH was increased also in the first stage to near seven. At the same time, the phase ratio was decreased from near unity to A/O 0.77:1. Consequently, the Ni extraction was quantitative, but at the same time the Li co-extraction also increased to 17.3%. Changing the modifier from TOA to TBP increased the Li co-extraction up to 26.2%. This result corresponded to the observations of Suzuki et al. (2012), Niinae et al. (2010, 2014), and Ahn et al. (2012). Thus TOA is clearly a better phase modifier. The performance of the two-stage loading was satisfactory, but significant Li losses could not be avoided by adjusting the run parameters. Thus, either more loading stages at a lower pH or a Li scrubbing stage should be added. The latter was chosen in this research, as it was expected that the quantitative Li scrubbing without Co or Ni losses would be fairly easy in a single stage.

Scrubbing of lithium

Based on the scrubbing isotherms presented in Section 3.1 (Fig. 4), a continuous single-stage scrubbing run with a phase ratio O/A close to 1.5:1 was done. Fig. 8 shows the pH of the aqueous phase as well as the Ni and Li contents of the organic phase during the run. The Li content in the organic outlet leveled within 200 min (20.3 mixer volumes) to under 9 mg/L, which is a satisfactory result. The Ni concentration was fairly stable during the run, and this level increased to over the feed concentration of 480 mg/L after 140 min (*i.e.*, 14.2 mixer volumes), which is important since the goal is not to scrub any desired Ni. The increment of the equilibrium pH to a desired value of 6.5 took 200 min (20.3 mixer volumes). The purity of the organic phase with respect to the Co+Ni mixture increased from 98.7% to >99.9%. Overall, the single-stage scrubbing in the described conditions fits very well with the proposed fractionation process.

Figure 8. Continuous scrubbing of Li from the organic phase loaded from simulated battery waste sulfuric acid leachate. The organic feed contained 14.4 g/L of Co, 0.48 g/L of Ni, and 0.193 g/L of Li. The aqueous feed was 0.30 g/L of NiSO_4 solution at a pH of 1.3 adjusted with H_2SO_4 . The measured average values of O/A and temperature were 1.47 and 23 °C, respectively. Symbols: red squares Ni, green diamonds Li, and black triangles pH.

Selective stripping of Ni

In total, four continuous counter-current bench-scale runs were made to study the selective stripping of Ni from the organic phase (Table IV). It should be noted that the loading, scrubbing and stripping stages were studied in separate experiments, but the organic phase used in the stripping experiments was the one obtained in the continuous scrubbing run discussed above. Two stripping runs were made with two stages, and two with three stages. The runs lasted over 660 min (65 mixer volumes). When looking at the trends of the run parameters and metal extraction efficiencies (Fig. 9), it can be concluded that the three-stage system in Run #8 was in a steady state at least in the end of the run, perhaps even after 480 min. Since it can be expected that the two-stage run achieved the steady state even earlier than the three-stage runs, steady state operation can be assumed in every stripping run. It can be also seen from Fig. 9a that the trends of the adjusted run parameters,

pH and phase ratio O/A, were fairly stable, again indicating the successful operation of the system.

Table IV. Run parameters and results of the continuous counter-current solvent extraction bench-scale experiments for selective Ni stripping from the organic phase loaded from simulated Li-ion battery waste leachate. The temperature in the runs was 22.2–23.6 °C.

Run #	Run time (min/mixer volumes of feed)	Organic feed concentration, g/L		pH			Phase ratio O/A			Phase purity, %	
		Co	Ni	1 st	2 nd	3 rd	1 st	2 nd	3 rd	Co, org	Ni, aq
5	660/66	14.7	0.74	6.3	5.2	-	1.55	1.50	-	99.6	97.6
6	720/71	14.4	1.14	6.3	5.4	-	1.47	1.50	-	98.7	99.6
7	660/65	14.3	1.60	6.3	6.1	5.4	1.52	1.48	1.46	98.2	99.9
8	690/68	14.4	1.07	6.0	5.8	5.0	1.61	1.47	1.50	99.6	99.7

Figure 9. Continuous counter-current bench-scale stripping of Ni from the organic phase loaded from simulated battery waste sulfuric acid leachate (Run #8). a) Trends of the run parameters, and b) metal stripping efficiencies. The temperature in the 1st stage was 23.2–23.6 °C, in 2nd stage 23.2–23.6 °C, and in 3rd stage 22.5–22.9 °C. Symbols: black triangle pH of the 1st stage, white triangle pH of the 2nd stage, grey triangle pH of the 3rd stage, dark blue square O/A in the 1st stage, light blue square O/A in the 2nd stage, turquoise square O/A in the 3rd stage, blue circles Co, and red squares Ni.

Based on the pH isotherms and stripping isotherms presented in Section 3.1, the operation conditions given in Table IV were chosen for the first continuous stripping run (#5). Since fairly good results—99.6 % and 97.6% pure Co and Ni phases, respectively—were obtained, it was decided just to increase the pH slightly to reduce the co-extraction of Co, and thus to obtain higher Ni purity. Also, at the same time the possibility of having a slightly higher Ni concentration was tested. The changes improved the Ni purity in the

aqueous phase in Run #6 to a very good 99.6%, although the Co purity in the organic phase decreased slightly because the Ni was not stripped with as high of a yield as in the Run #5.

Although the results of the two-stage runs were satisfactory, it was decided to test whether the three-stage operation mode would produce even better purities (Table IV). Again, the run parameters in the first three-stage run were close to optimal, yielding 98.2% and 99.9% pure Co and Ni phases, respectively. Still, it was expected that a better purity for Co could be obtained, and thus it was decided to lower the pH slightly to remove the Ni to an even greater extent. Of course, at the same time, a lower purity for Ni was expected, but as illustrated in Table IV, the reduction was small (from 99.9% to 99.7%). When the Co purity simultaneously increased to 99.6%, the operation conditions were concluded to be as optimal as they could be achieved with this bench-scale experimental approach.

4. Conclusions

A solvent extraction process for the fractionation of Co, Ni, and Li from the sulfuric acid leachate of Li-ion battery waste was designed. The most suitable reagent, operating pH, phase ratio, and number of equilibrium stages were determined based on batch equilibrium experiments. The loading, scrubbing, and stripping steps of the process were verified by bench-scale continuous counter-current experiments. In the proposed process, Co and Ni are selectively extracted together, yielding 99.9% pure Li_2SO_4 raffinate at the same time. The small amount of co-extracted Li is scrubbed, after which the Co and Ni are separated in a selective stripping step.

While Cyanex 272 was chosen as the extractant, PC-88A was found to be not significantly worse. It was shown that with Cyanex 272 undesired formation of a viscous organic phase can be eliminated by adding 5% v/v TOA as phase modifier. Two-stage extraction at pH of 6.8–7.1 with a phase ratio $A/O = 0.77$ is suggested for extraction of Co and Ni. Single stage scrubbing for removing the co-extracted Li from the organic phase with 0.3 g/L of NiSO_4 at a pH of 6.5 ($O/A \approx 1.5:1$) is suggested for increasing the purity of Co and Ni product streams. Selective stripping of Co and Ni was successful in three stages at a pH of 5.0–6.0 with a phase ratio $O/A \approx 1.5:1$. Purities of 99.6 and 99.7% were obtained for the organic Co solution and aqueous NiSO_4 solution. The benefit of using three-stage counter-current stripping is not marginal as using two stages yielded 98.7 and 99.6% purities for Co and Ni respectively, and it is known that the for example battery manufacturers tend to use as pure (up to 99.9%) Co and Li salts as possible.

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