

Process for the separation of metals by solvent extraction

The present invention is in the field of recycling of Li-ion batteries or their waste and describes an efficient process for the recovery of lithium (Li), and one or more of nickel (Ni), manganese (Mn) and cobalt (Co) from aqueous acidic solutions.

- 5 The development of lithium-ion batteries, and specifically the use of nickel-manganese-cobalt (NMC) cathode materials, has increased the demand for high-purity nickel sulfate, cobalt sulfate and manganese sulfate, either as a solid or in solution. Recycling of these raw materials from industrial scrap and end-of-life products is preferred over primary mining in terms of resource efficiency and
10 environmental burden.

Streams originating from battery recycling typically contain Li. Li is an alkali metal and difficult to separate from other metal ions, especially if chemically very similar, such as sodium (Na). Yet, sodium hydroxide (NaOH) is the most common base reagent used for neutralization operations in refining flowsheets, including
15 (hydrolysis) precipitation, solvent extraction and ion exchange. As a result, Li typically ends up in the process effluent, together with Na. A Na-Li separation is required to valorize Li from the effluent.

Commonly known processes for Li-recovery are often based on precipitation, with long process times, low Li recovery rates and low quality of the obtained lithium
20 salts. Therefore, solvent extraction processes, also known as SX-processes, gained more attention for the recovery of Li.

Hung Shu-Hui et al. ("Recovery of metal ions from spent Lithium Ion Batteries (LIBs) using sodium salts of D2EHPA or P507: performance evaluation and life cycle assessment", Research Journal of Chemistry and Environment, vol. 18,
25 2014) describe the solvent extraction of Li, Co, Mn and Ni from spent Li-Ion Batteries using sodium-di-(2-ethylhexyl)-phosphoric acid (Na-D2EHPA) and mono-2-ethylhexyl ester (Na-P507) dissolved in kerosene. Both the D2EHPA and P507 extractants were saponified using NaOH solution, and kerosene was used as the diluent. The extraction percentage for the metal ions including Li, Co, Mn
30 and Ni increased with increasing equilibrium pH. NaOH was introduced and the Na ended up as Na₂SO₄ in the raffinate, in stoichiometric exchange for the extracted metals.

JP2019169306 discloses a method for producing a battery electrode material in a slurry state to be coated over a sheet-shaped collector and containing an aqueous binding agent and an electrode active substance comprising electrolytic Mn dioxide. The process of kneading and mixing the electrode raw material with water
5 as solvent comprises steps of mixing the electrode active substance, mixing the binding agent, and mixing with a neutralization agent. LiOH is used as neutralization agent, yet not in the context of a hydrometallurgical refining process in which solvent extraction is used as technology to separate metals from each other.

10 Han Zhejie et al. describe a solvent extraction process using acidic solvent and investigate the extraction mechanism systematically ("Recycling of lithium and fluoride from LiF wastewater from LiF synthesis industry by solvent extraction", Journal of Environmental Chemical Engineering, vol. 11, 2023) . The result shows that Li was extracted by a cation exchange mechanism with D2EHPA (di-2-
15 ethexylphosphoric acid). 99.72% Li recovery and battery-grade LiCl solution (3.40 g/L) were achieved by mixing LiF (aqueous) with the NaOH-saponified D2EHPA at 25 °C for 6 min at pH 4.60. The Li-loaded solvent was however not used as such for extraction of metals.

US2021130927 teaches an extraction process for Li and optionally Ni from a
20 Ni(II)/Li(I) solution, thereby producing a lithium-poor solution. Such method requires a Li-selective extractant to separate Li, rather than extracting impurities with conventional systems and concentrating Li in the raffinate stream.

WO23175157 provides a method for processing a black mass to battery chemicals. The black mass is leached, followed by removing impurities from the
25 first process solution using LiOH, to produce a second process solution, separating Li from the second process solution using chromatographic separation, producing Li₂SO₄ and a third process solution. Finally, the process converts the Li₂SO₄ produced by electrodialysis to LiOH and H₂SO₄. LiOH is used as neutralization agent for hydrometallurgical refining by ion exchange technology
30 according to the chromatography principle, yet not in the specific context of solvent extraction.

JP2023100269 teaches a method for recovering metals from Li-ion battery waste by reducing the use of NaOH as pH adjusting agent. Instead, a LiOH solution is used for pH corrections after leaching and during solvent extraction operations. The extraction includes separate steps for Mn extraction, Co extraction, Ni
5 extraction. The aqueous Li₂SO₄ solution is hydroxylated to obtain an aqueous LiOH solution for recycling and reuse in previous refining steps. Reusing the regenerated LiOH solution for saponification of the solvent is not mentioned.

CN108517422 teaches a method for recovering Li from a lithium-containing polymetallic solution. The solution is adjusted to a pH of 3-7 and extracted with a
10 saponified organic phase to obtain a lithium-rich raffinate. The saponified organic phase is obtained by mixing an organophosphorus extracting agent with a non-sodium saponification agent.

“Saponification” is the conversion of the acidic form of an acidic extractant molecule to the neutralized form. In a typical reaction with NaOH, the extractant
15 protons are released and exchanged for Na⁺ ions, according to the following reaction: $R - H + NaOH \rightarrow R - Na + H_2O$ (with R as the organic extractant). Industrial applicability of LiOH as neutralization agent in solvent extraction processes is not evident from the available prior art.

Saponification of an organic solvent with LiOH solution may result in a two-phase
20 system. Separation of an aqueous phase from an organic phase can be done by different technologies. These include coalescing devices, settling devices, parallel plate separation, membrane filtration, centrifugal technologies, etc. But any such process step obviously increases the overall cost of the process.

Another approach is a direct injection of NaOH or LiOH solution into the extraction
25 reactor. Such an approach can be chosen for processes in which direct pH control is preferred, for example to optimize selectivity, but it requires pH-adjustments during the extraction process.

It appears that most refining flowsheets make use of NaOH for neutralization, which then unavoidably also results in the mixture of Na and Li when processing
30 Li-bearing NMC streams.

Faced with the problems described in the prior art above, it is therefore an objective of the present invention to provide an alternative process for the recovery

of Li on one hand, and one or more of Ni, Mn and Co on the other hand, using solvent extraction and upfront saponification with LiOH. This results in a simplification of existing refining flowsheets.

5 In the present approach, an upfront saponification, i.e. conversion of the organic solvent mixture with LiOH solution, is performed. Using LiOH for neutralization avoids contamination with Na ions, originating from NaOH. With a neutralization of the organic solvent mixture upfront, there is also no need for pH adjustments in the extraction step. Solvent flow, dissolution capacity, and properties of the saponified organic extractant are more consistent and predictable, which is an
10 advantage in an industrial setup. Such an approach is preferred in capacity-driven processes.

More specifically, in a separate reaction an organic extractant in acidic form is mixed with LiOH, resulting in an emulsion, which is then used for neutralization.

Any formation or separation of an aqueous phase during the process would result
15 in a fluctuating input to the extraction reactor. The emulsion needs to remain stable when pumped from the saponification reactor to the extraction section of the industrial plant. A micro-emulsion, which is a single stable, homogeneous and clear organic phase, fulfills this requirement well.

The invention is further detailed in the following embodiments.

- 20 1. Process for the separation of metals by solvent extraction, comprising the steps:
- providing a first aqueous phase comprising an aqueous acidic Li-bearing solution further comprising one or more of Ni, Mn and Co;
 - providing a first organic phase comprising an organic extractant in
25 acidic form, and a diluent;
 - saponifying at least partially the organic extractant by mixing the first organic phase with an aqueous solution containing LiOH, thereby obtaining a second organic phase;
 - mixing the first aqueous phase with the second organic phase under
30 conditions suitable for solvent extraction, thereby obtaining a third organic phase containing a major part of one or more of the Ni, Mn

and Co, and a second aqueous phase containing a major part of the Li; and,

- separating the third organic phase and the second aqueous phase; characterized in that in the step of saponifying, mixing the first organic phase with an aqueous solution containing LiOH is performed until a homogeneous and clear micro-emulsion is obtained.
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2. Process according to item 1, wherein the first organic phase further comprises a modifier.
 3. Process according to items 1 or 2, wherein the organic extractant comprises an organophosphinic according to the formula bis(2,4,4-trimethylpentyl)phosphinic acid.
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4. Process according to any one of items 1 to 3, wherein the step of saponifying is performed using an aqueous solution containing LiOH in a concentration of 90 to 120 g/L, preferably of 100 to 110 g/L.
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5. Process according to any one of items 1 to 4, wherein the micro-emulsion is free of Na.
 6. Process according to any one of items 3 to 5, wherein the organic extractant contains more than 95% by weight of an organophosphinic, and wherein the saponification level is 60% or less.
- 20
7. Process according to any one of items 3 to 5, wherein the organic extractant contains less than 90% by weight of an organophosphinic, and wherein the saponification level is 20% or less.
 8. Process according to any one of items 1 to 7, wherein the micro-emulsion comprises 1 to 10% by volume of water.
- 25
9. Process according to any one of items 1 to 8, wherein the concentration of Ni in the first aqueous phase is less than 125 g/L.
 10. Process according to any one of items 1 or 9, wherein the concentration of Co in the first aqueous phase is less than 120 g/L.
 11. Process according to any one of items 1 to 10 wherein the concentration of Mn in the first aqueous phase is less than 130 g/L.
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12. Process according to any one of items 1 to 11, wherein the concentration of Li in the first aqueous phase ranges from 0.1 to 35 g/L.
 13. Process according to any one of items 1 to 12, wherein the first aqueous phase is obtained by acidic leaching of Li-ion batteries or their waste.

14. Process according to any one of items 1 to 13, further comprising the step: recovering one or more of Ni, Mn and Co from the third organic phase by stripping with an acidic aqueous solution, thereby obtaining a metal-bearing aqueous phase and a metal-depleted organic phase.
- 5 15. Process according to any one of items 1 to 14, further comprising the step: subjecting the second aqueous phase to electrodialysis, thereby obtaining an acidic aqueous solution and an aqueous solution containing LiOH.
16. Process according to item 15 wherein the acidic aqueous solution is used in the step of recovering one or more of Ni, Mn and Co according to item 10 14.
17. Process according to item 15, wherein the aqueous solution containing LiOH is used in the step of saponifying according to item 1.

The first embodiment relates to a process for the separation of metals by solvent extraction, comprising the steps:

- 15 ▪ providing a first aqueous phase comprising an aqueous acidic Li-bearing solution further comprising one or more of Ni, Mn, and Co;
- providing a first organic phase comprising an organic extractant in acidic form, and a diluent;
- 20 ▪ saponifying at least partially the organic extractant by mixing the first organic phase with an aqueous solution containing LiOH, thereby obtaining a second organic phase;
- mixing the first aqueous phase with the second organic phase under conditions suitable for solvent extraction, thereby obtaining a third organic phase containing a major part of one or more of the Ni, Mn and Co, and a 25 second aqueous phase containing a major part of the Li; and,
- separating the third organic phase and the second aqueous phase;

characterized in that in the step of saponifying, mixing the first organic phase with an aqueous solution containing LiOH is performed until a homogeneous and clear micro-emulsion is obtained.

- 30 A specific embodiment relates to a process for the separation of metals by solvent extraction, comprising the steps:

- providing a first aqueous phase comprising an aqueous acidic Li-bearing solution further comprising one or more of Ni, Mn and Co;
 - providing a first organic phase comprising an organic extractant in acidic form, and a diluent;
 - 5 ▪ partially saponifying the organic extractant by mixing the first organic phase with an aqueous solution containing LiOH, thereby obtaining a second organic phase;
 - mixing the first aqueous phase with the second organic phase under conditions suitable for solvent extraction, thereby obtaining a third organic
 - 10 phase containing a major part of one or more of the Ni, Mn and Co, and a second aqueous phase containing a major part of the Li; and,
 - separating the third organic phase and the second aqueous phase;
- wherein in the step of saponifying, mixing the first organic phase with an aqueous solution containing LiOH, is performed with an organic extractant being an
- 15 organophosphorus-based acid until a saponification level of at least 1% and up to 60% has been reached and one homogeneous phase comprising a clear and transparent micro-emulsion is obtained.

Yet another specific embodiment relates to a process for the separation of metals by solvent extraction, comprising the steps:

- 20 ▪ providing a first aqueous phase comprising an aqueous acidic Li-bearing solution further comprising one or more of Ni, Mn and Co;
- providing a first organic phase comprising an organic extractant in acidic form, and a diluent;
- partially saponifying the organic extractant by mixing the first organic phase
- 25 with an aqueous solution containing LiOH, thereby obtaining a second organic phase;
- mixing the first aqueous phase with the second organic phase under conditions suitable for solvent extraction, thereby obtaining a third organic phase containing a major part of one or more of the Ni, Mn and Co, and a
- 30 second aqueous phase containing a major part of the Li; and,
- separating the third organic phase and the second aqueous phase;

wherein in the step of saponifying, mixing the first organic phase with an aqueous solution containing LiOH is performed with an organic extractant being an organophosphinic acid comprising more than 5% of phosphine oxide, in particular an organophosphinic oxide, until a saponification degree of at least 1% and up to 5 20% has been reached and a homogeneous phase comprising a clear and transparent micro-emulsion is obtained.

An "extractant" is the active component capable of extracting a metal species by chemically binding with it and forming a metal-extractant complex that is better soluble in the organic phase than it is in the aqueous phase. Specifically, the 10 extractant is an organic extractant. The organic extractant particularly is an organophosphorus-based acid, which includes organophosphoric acids, organophosphonic acids and organophosphinic acids. Suitable organic extractants are, for example, phosphinic acids, which should be named more correctly organophosphinic acids because they are carrying organic substituents, 15 but which can be used as synonyms as far as the term actually relates to the same chemical compounds e.g. [bis(2,4,4-trimethylpentyl)phosphinic acid], sold under the commercial names of Cyanex 272, Ionquest 290, C272, etc., organophosphoric acids, e.g. D2EHPA [di(2-ethylhexyl) phosphoric acid], organophosphonic acids, e.g. PC88A [2-ethylhexyl phosphonic acid mono-2- 20 ethylhexyl ester], DIDA [diisopropyl dithiophosphinic acid, or versatic 10 acid [neodecanoic acid]. These can be used according to the invention, provided that they are dosed in concentrations which allow for the formation of a homogeneous and clear micro-emulsion.

An important aspect of the invention is that the organic extractant, which is 25 originally in its acidic form, is saponified before use. The term "saponifying" means that the acidic proton of the acid is replaced by another cation. In the present invention, the proton is replaced by a Li cation.

The "saponification level" is defined as the fraction, expressed in %, of the acidic protons of the extractant that is replaced by an alkali metal, which, in the present 30 case, is Li and is given in molar percent (mole%). Saponification levels can be up to 20%, up to 50% or up to 60%. Saponification levels above 60% are not recommended due to the risk of gel formation, which is undesired in an industrial

process. As a lower limit, the saponification level is at least 1 mole%, or at least 5 mole%, in particular at least 10 mole% or 20 mole% or is 20% or below.

It should be noted that NaOH is the most common base used for saponification or other neutralization operations in refining flowsheets. When aiming for the separation and recovery of Li, it is advantageous to avoid any contamination of the reaction solution with Na. Typically, Na and Li would end up together in the same solution and their separation is difficult or at least requires additional process steps. Saponifying with Li instead of with Na therefore leads to a more efficient and overall shorter process. In addition, any Li used for saponification is not lost, but contributes to the total amount of recoverable Li. This advantageous combination makes LiOH the most preferred saponification reagent in the present process.

Another key aspect of the invention is the obtention of an emulsion, and more specifically of a homogeneous and clear micro-emulsion. An "emulsion" is a mixture of two or more liquids that are usually immiscible but, under specific transforming processes, will adopt a macroscopic homogeneous aspect and a microscopic heterogeneous one. In an emulsion, one liquid is dispersed in the other. In the present invention, the emulsion comprises saponified organic acid combined with an aqueous phase. In the present process, a clear micro-emulsion is obtained. Micro-emulsions are defined as thermodynamically stable isotropic liquid mixtures. Visually, a micro-emulsion appears as a single clear phase. This clear or transparent appearance is due to the small size of the dispersed droplets, typically smaller than the wavelength of light (400 to 800 nm), thus avoiding scattering. Such a small droplet size ensures the stability of the micro-emulsion and may enhance the reaction kinetics of the extraction process.

The solvent extraction process, also known as SX, is a hydrometallurgical separation technology in which two immiscible phases, an organic phase and an aqueous phase, are contacted with each other. In suitable conditions, specific metals are transferred between the phases. Such suitable conditions for SX are well known to the skilled person.

In the above embodiments, the term "diluent" means an organic molecule or a mixture of different organic molecules added to the organic phase to dilute the

extractant and allow for the dissolution of the metal complexes, to improve the physical properties of the organic phase (especially phase-separation phenomena) and to decrease its cost, given that diluents are usually cheaper than extractants. Diluents are frequently kerosene fractions, such as aliphatic or aromatic hydrocarbons and naphthenes, or mixtures thereof. Commercial products include ShellSol™, Elixore™ and Escaid™.

In any process step, the terms “containing a major part of an element” means that more than 50% by weight of that element is contained, with respect to the total weight of that element entering that process step.

More particularly, the third organic phase preferably contains more than 80%, and more preferably more than 90% of one or more of the Ni, Mn and Co. The second aqueous phase preferably contains more than 80%, and more preferably more than 90% of the Li.

In another embodiment, the first organic phase further comprises a modifier. A “modifier” is often added to improve the solubility of metal complexes in an organic phase, to alter the physical properties of the solvent to avoid formation of solid residues or third-phase formation. These phenomena are indeed undesired in solvent extraction. A modifier can also be added to prevent chemical degradation of extractant or diluent. However, modifiers may impair the selectivity of the organic phase, as these may participate in the complex formation of the metals with the extractant.

In another embodiment, the organic extractant comprises an organophosphinic according to the formula bis(2,4,4-trimethylpentyl)phosphinic acid. This extractant lends itself well for the extraction of Co and Mn from aqueous solutions.

In another embodiment, the step of saponifying is performed using an aqueous solution containing LiOH in a concentration of 90 to 120 g/L, preferably of 100 to 110 g/L. It is generally preferred to work with more concentrated LiOH solutions to limit the amount of water introduced in the system. Concentrations below 90 g/L are therefore less favorable. On the other hand, solutions of more than 120 g/L LiOH may reach a saturation limit. The precipitation of Li-crystals during saponification or later in the process is obviously to be avoided.

In another embodiment, the micro-emulsion is free of Na. One of the goals of the present invention is to recover Li while avoiding contamination with other alkaline elements such as Na. Neutralizing or saponifying with NaOH is thus preferably avoided.

- 5 In another embodiment, the micro-emulsion contains a limited amount of aqueous phase. This amount is preferably in the range of 1 to 10 vol%.

In another embodiment, the organophosphinic has a purity of more than 95%. Such an acid can e.g. be obtained under the commercial name of IONQUEST® 290. Using such a high purity agent, the saponification level can advantageously
10 reach 60 mole% while still obtaining a clear or transparent micro-emulsion. The level of saponification is at least 1 mole%, or at least 5 mole%, in particular at least 10 mole%. After the saponification, a step of separation of excessive water may be needed.

In another embodiment, the organophosphinic has a purity of less than 90%. Such
15 an acid can e.g. be obtained under the commercial name of CYANEX® 272. Using such an agent, the saponification level can only reach 20 mole% while still obtaining a clear or transparent micro-emulsion, in particular the level of saponification is at least 1 mole%, or at least 5 mole%, in particular at least 10 mole%. Since the impurities present largely consist of phosphine oxides, or an
20 organophosphine oxide, a purity of less than 90% can be rephrased as the organophosphinic comprising more than 5% of phosphine oxides but is less than 10%. This has the technical effect of obtaining one homogeneous phase comprising a clear and transparent micro-emulsion. Consequently, a step of separation of excessive water will not be needed in this case.

25 To ensure the stability of the solutions, it is preferred to keep the concentration of Ni in the first aqueous phase to less than 125 g/L. It is also preferred to keep the concentration of Co in the first aqueous phase is less than 120 g/L. It is furthermore preferred to keep the concentration of Mn in the first aqueous phase is less than 130 g/L. It is also advantageous if the accumulated concentration of
30 Ni, Co and Mn in the first aqueous phase is less than 130 g/L. These maximal concentrations also correspond to what can be typically expected when the first

aqueous phase originates from an acid leaching step of Li-ion batteries or their waste.

The invented process is of special interest if the first aqueous phase contains an economically viable Li concentration, rendering its separation and recovery
5 worthwhile. However, too high Li concentrations will again put the stability of the solutions at risk. Therefore, a Li concentration of 0.1 to 35 g/L in the first aqueous phase is preferred. The mentioned Li concentration range also corresponds to what can be typically expected when the first aqueous phase originates from the acidic leaching of Li-ion batteries or their waste.

10 The process of the invention is therefore particularly suitable for treating solutions coming from the acidic leaching performed on Li-ion batteries or their waste.

By "Li-ion batteries or their waste" is meant for example waste Li-ion batteries, spent or end-of-life batteries, production or battery scrap, industrial scrap, electrode materials or other pre-processed battery materials.

15 The valuable metals such as Ni, Mn, and Co can advantageously be recovered from the metal-loaded third organic phase by stripping. This is typically performed using a 0.1 to 10 M acidic solution of HCl or H₂SO₄. Once in an aqueous solution, the metals can be isolated and refined according to usual hydrometallurgical methods. These metals can then be re-used in Li-ion battery cathodes. The
20 stripped organic phase is then again available as the first organic phase of the process.

Li can be advantageously recovered from the second aqueous phase, e.g. by electrodialysis, membrane electrolysis, solvent extraction, or ion exchange. A fraction of this Li can be converted to LiOH and recycled to the saponifying step
25 in the form of an aqueous solution containing LiOH. The remainder of the Li can be recovered for re-use in Li-ion batteries cathodes or anodes.

It is preferred to subject the second aqueous phase to electrodialysis, thereby obtaining an acidic aqueous solution and an aqueous solution containing LiOH. The acidic aqueous solution may then be used in the step of recovering the one
30 or more of Ni, Mn and Co by stripping. The aqueous solution containing LiOH may then be used in the step of saponifying the organic extractant in acidic form.

The following examples illustrate the invention.

Example 1

The stability of a micro-emulsion with 30 vol% Cyanex® 272 or lonquest® 290 and LiOH has been studied. The diluent used was Escaid 110 (70 vol%). Saponification was done with a 105 g/L LiOH solution. The reagents were stirred for 15 min at 25 °C.

Table 1: Stability of different saponified emulsion prepared using Cyanex® 272 and lonquest® 290

	Saponification (%)	LiOH solution (vol%)	Li loading (g/L)	Clear emulsion	Water excess
Cyanex® 272 (> 5% phosphine oxides)	10	2.0	0.30	Yes	No
	20	3.9	0.88	Yes	No
	30	5.9	1.1	No	Yes
	40	7.8	2.0	No	Yes
	50	9.8	2.4	No	Yes
lonquest® 290 (< 5% phosphine oxides)	10	2.1	0.57	Yes	Yes
	20	4.3	1.2	Yes	Yes
	30	6.4	1.9	Yes	Yes
	40	8.6	2.4	Yes	Yes
	50	10.7	2.9	Yes	Yes
	60	12.9	3.2	Yes	Yes

10 A clear micro-emulsion typically indicates a homogeneous and stable micro-emulsion, meaning that the water contained in it does not separate afterwards, e.g. when pumping this solution. Any phase separation would alter the organic:aqueous ratio (O/A ratio) during processing, which needs to be avoided.

It appears that a clear emulsion can be achieved for all saponification levels up to 60%, in particular with Ionquest® 290, whereas for Cyanex® 272, the saponification level window is limited to the saponification range of 20% or below. This is presumably due to the difference in purity of these commercial products,
5 of respectively 98% and 85%.

Saponification levels above 60% are not recommended because of a risk of gel formation, which is undesired in an industrial process.

Excess water can form a separate phase during saponification. This does not alter the stability of the micro-emulsion itself. It is however required to separate this
10 water phase from the micro-emulsion before use. This phase always forms for the two compounds above, except when using Cyanex® 272 at low saponification levels of up to 20%, which is thus preferred.

Example 2

This example illustrates the solvent extraction step using 30 vol% Cyanex® 272
15 and 70 vol% Escaid 110. The solvent is saponified upfront with a LiOH solution. A solvent capacity of 10 g/L Mn was targeted, corresponding to a saponification level of 42.5%. To this end, 116 mL of LiOH a 75 g/L LiOH solution was added per liter of organic solvent. To obtain a clear micro-emulsion, the diluted solvent and the LiOH solution were mixed for about 15 min at 25 °C.

20 The extraction was performed in 6 steps, mixing in each step the aqueous phase from a preceding step with an equal volume of fresh, saponified organic phase according to an O/A ratio of 1. A total of 702 mL of LiOH solution was thus added over the course of the extraction process, resulting in a total volume of raffinate of 1.70 L. The aqueous phases and the micro-emulsions were stirred for 5 min at 40
25 °C to ensure equilibrium.

In the first 5 steps, the Li in the organic extractant became exhausted: this resulted in a slight decrease in the pH and in the automatic termination of the extraction process. In step 6, however, the Mn was exhausted in the aqueous phase. The pH remained at its nominal value of about 4.6.

30 In Table 2, the initial (first) aqueous phase is labeled "Feed", while the second aqueous phase is labeled "Raffinate". The feed originates from an upfront process comprising bulk removal of Ni and Co (as sulfates) and hydrolysis/neutralization.

To use this feed according to the invention, the neutralization is performed for example with LiOH, Li₂CO₃, Ca(OH)₂ or CaCO₃, but avoiding NaOH. The reported pH is the pH after this neutralization.

5 **Table 2:** Metal compositions of feed and raffinate solutions, before and after six extraction steps with an organic phase comprising 30 vol% Cyanex-272 that is 42.5% saponified

	Volume (L)	Co (mg/L)	Ni (mg/L)	Mn (g/L)	Mg (g/L)	Li (g/L)	Na (mg/L)	pH
Feed	1.00	500	930	54	9.4	15	1	4.5
Raffinate	1.70	< 2.5	420	< 0.0025	0.69	17	1	4.6

10 This example shows that excellent yields of more than 99% are obtained for the extraction of Co and Mn. Ni displays a lower yield due to the selected working pH of about 4.5, which is not particularly suited for Ni extraction. This example also demonstrates that the pH of the aqueous phase remains remarkably stable during extraction, at about 4.5. This feature is due to the ion exchange mechanism between the metals, in this example essentially between Mn and Li. This contrasts
15 with the need for constant neutralization when extractants are used in their acidic form.

If a higher Ni is desired, the same extractants can be used at a slightly higher pH, such as 5.0 to 5.5.

CLAIMS

1. Process for the separation of metals by solvent extraction, comprising the steps:
 - providing a first aqueous phase comprising an aqueous acidic Li-bearing solution further comprising one or more of Ni, Mn and Co;
 - providing a first organic phase comprising an organic extractant in acidic form, and a diluent;
 - partially saponifying the organic extractant by mixing the first organic phase with an aqueous solution containing LiOH, thereby obtaining a second organic phase;
 - mixing the first aqueous phase with the second organic phase under conditions suitable for solvent extraction, thereby obtaining a third organic phase containing a major part of one or more of the Ni, Mn and Co, and a second aqueous phase containing a major part of the Li; and,
 - separating the third organic phase and the second aqueous phase;wherein in the step of saponifying, mixing the first organic phase with an aqueous solution containing LiOH, is performed with an organic extractant being an organophosphorus-based acid until a saponification level of at least 1% and up to 60% has been reached and one homogeneous phase comprising a clear and transparent micro-emulsion is obtained.
2. Process according to claim 1, wherein the micro-emulsion exhibits a size of the dispersed droplets of about 400 to about 800 nm.
3. Process according to claim 1 or 2, wherein the first organic phase further comprises a modifier.
4. Process according to any of claims 1 to 3, wherein the first organic phase further comprises a modifier, which is a phosphine oxide compound, in particular an organic phosphine oxide compound.

5. Process according to any of claims 1 to 3, wherein the first organic phase further comprises a phosphine oxide compound, in particular an organic phosphine oxide compound, as a modifier in an amount of more than 5 percent.
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6. Process according to any of claims 1 to 5, wherein the organic extractant comprises an organophosphinic acid, in particular according to the formula bis(2,4,4-trimethylpentyl)phosphinic acid.
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7. Process according to any one of claims 1 to 6 wherein the step of saponifying is performed using an aqueous solution containing LiOH in a concentration of 90 to 120 g/L, preferably of 100 to 110 g/L, and/or in a relative amount of 1 vol% to 5 vol%, preferably 2 vol% to 4 vol%.
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8. Process according to any one of claims 1 to 7, wherein the micro-emulsion is free of Na.
9. Process according to any one of claims 1 to 8, wherein the organic extractant contains more than 95% by weight of an organophosphinic acid, and wherein the saponification level is 60% or less and at least 1%.
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10. Process according to any one of claims 1 to 8, wherein the organic extractant contains less than 90 mole% by of an organophosphinic acid, and wherein the saponification level is 20% or less and at least 1 %.
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11. Process according to any one of claims 1 to 10, wherein the micro-emulsion comprises 1 to 10% by volume of water.
12. Process according to any one of claims 1 to 11 wherein the accumulated concentration of Ni, Co and Mn in the first aqueous phase is less than 130 g/L.
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13. Process according to any one of claims 1 to 12, wherein the concentration of Li in the first aqueous phase ranges from 0.1 to 35 g/L.

14. Process according to any one of claims 1 to 13, wherein the first aqueous phase is obtained by acidic leaching of Li-ion batteries or their waste.
- 5 15. Process according to any one of claims 1 to 14, further comprising the step: recovering one or more of Ni, Mn and Co from the third organic phase by stripping with an acidic aqueous solution, thereby obtaining a metal-bearing aqueous phase and a metal-depleted organic phase.
- 10 16. Process according to any one of claims 1 to 15, further comprising the step: subjecting the second aqueous phase to electrodialysis, thereby obtaining an acidic aqueous solution and an aqueous solution containing LiOH.
- 15 17. Process according to claim 16 wherein the acidic aqueous solution is used in the step of recovering one or more of Ni, Mn and Co according to claim 15.
- 20 18. Process according to claim 16, wherein the aqueous solution containing LiOH is used in the step of saponifying according to claim 1.
- 25 19. Process for the separation of metals by solvent extraction according to one or more of claims 1 to 18, comprising the steps:
- providing a first aqueous phase comprising an aqueous acidic Li-bearing solution further comprising one or more of Ni, Mn and Co;
 - providing a first organic phase comprising an organic extractant in acidic form, and a diluent;
 - partially saponifying the organic extractant by mixing the first organic phase with an aqueous solution containing LiOH, thereby obtaining a second organic phase;
 - mixing the first aqueous phase with the second organic phase under conditions suitable for solvent extraction, thereby obtaining a third organic phase containing a major part of one or more of the Ni, Mn and Co, and a second aqueous phase containing a major part of the Li; and,
- 30

- 5 ▪ separating the third organic phase and the second aqueous phase;
wherein in the step of saponifying, mixing the first organic phase with an
aqueous solution containing LiOH is performed with an organic extractant
being an organophosphinic acid comprising more than 5% of phosphine
oxide, in particular an organophosphinic oxide, until a saponification degree
of at least 1% and up to 20% has been reached and a homogeneous phase
comprising a clear and transparent micro-emulsion is obtained.