

PROCESS FOR EXTRACTING A METAL SPECIES BY LIQUID-LIQUID REACTIVE EXTRACTION

The present invention relates to a process for extracting a metal species from an aqueous solution using liquid-liquid reactive extraction.

5 “Extraction” generally designates any separation method in which one or more components are separated from a mixture of substances using an extractant. In liquid-liquid extraction, a solute is extracted from a liquid by a liquid extractant, in which the different solubilities of the components to be separated in two immiscible solvents are utilized. Usually, a hydrophilic phase, such as water, and a hydrophobic organic solvent serve as said
10 immiscible solvents. One application of liquid-liquid extraction is the selective separation of metal ions, which is increasingly gaining importance within the scope of electromobility and the reprocessing of used batteries.

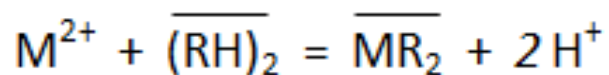
In general, the principle of reactive extraction is based on the so-called extraction isotherms, which indicate the distribution of a metal species between an aqueous phase (AP) and an organic phase (OP) for a related pH value. The degree of extraction, E, represents the
15 proportion of metal species M in the organic phase as a ratio based on the total amount of the metal species in both phases, wherein E can theoretically adopt all values between 0 and 1, or 0% and 100%:

$$E = \frac{C_{OP} \cdot V_{OP}}{C_{OP} \cdot V_{OP} + C_{AP} \cdot V_{AP}}, E \in (0; 1)$$

20 Especially in the field of battery recycling, the separation of cobalt, nickel and manganese as well as lithium from aqueous solutions is of great importance. The prior art describes a number of approaches of how the separation can be optimized.

The extraction of metals is based on a specific form of extraction, the so-called reactive extraction. In this form of solvent extraction, the compound to be extracted is
25 transferred into the other phase by a reaction with a substance dissolved in the extractant. The

following equation shows the underlying chemical reaction and the distribution of the different species to the aqueous and organic phases, marked by an overstrike as usual.



$$K = \frac{[\overline{MR_2}] [H^+]^2}{[M^{2+}] [\overline{(RH)_2}]}$$

5 wherein M represents the metal ion, R represents an acid residue, and K represents the equilibrium constant.

As can be seen from the formulation of the equilibrium constant, such equilibria are pH-dependent. Thus, metals having a high affinity, represented by high values of the equilibrium constant K, are extracted already at low pH values, i.e., from aqueous mediums
10 with a high acidity, while the metals having a low affinity can be extracted from the aqueous phase only at higher pH values. The setting of the pH value can be accomplished, for example, by adding alkaline compounds, such as NaOH, which capture the protons formed during the reaction.

The reactive extraction for separating metal ions is generally known. Thus, in their
15 paper “Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D2EHPA”, issued in Hydrometallurgy 77 (2005) 227-238, D. Darvishi et al. describe the advantages that could be achieved in the separation of cobalt and nickel by activating the complexing agent D2EHPA by Cyanex 272 and Cyanex 302.

P.K. Parhi et al. report the separation of nickel and cobalt in an ammoniacal sulfate
20 solution using Cyanex 272. Their results were issued in “Separation of cobalt and nickel from ammoniacal sulphate solution using Cyanex 272”, Separation and Purification Technology 59 (2008), 310-317.

In “Extraction/Separation of Cobalt by Solvent Extraction: A Review”, Appl. Chem. Eng. Vol. 26, No. 6, 2015, 631-639, B. Swain et al. give a survey of different methods for separating cobalt.

5 In their publication “New Cationic exchangers for the recovery of cobalt(I), nickel(I) and manganese(I) from acidic chloride solutions: Modelling of extraction curves”, issued in Hydrometallurgy 180 (2018) 96-103, K. Omelchuk et al. describe novel extractants for separating the mentioned metal species.

10 N.B. Devi et al. describe the separation of cobalt(II) and nickel(II) using the sodium salts of D2EHPA, PC 88A and Cyanex 272 in “Separation and recovery of cobalt(II) and nickel(II) from sulphate solutions using sodium salt of D2EHPA, PC 88A and Cyanex 272”, Hydrometallurgy 49 (1998) 47-61.

EP 2 614 868 discloses the use of a liquid-liquid extraction unit to contact an aqueous phase with an organic phase, to separate them, and to obtain a desired extract from the thus separated aqueous phase and/or organic phase.

15 In “Simultaneous recycling of nickel metal hydride, lithium ion and primary lithium batteries: Accomplishments of European Guidelines by optimizing mechanical pre-treatment and solvent extraction operations”, issued in Journal of Power Sources 212 (2012) 205-211, G. Granata et al. describe the solvent extraction of Co and Mn, wherein the extraction of Co Cyanex 272 is effected at a ratio of Cyanex/Co of 4 at a pH of 5, and the extraction of Mn
20 D2EHPA is effected at a ratio of D2EHPA/Mn of 2 at a pH of 5-6.

In another publication “Product recovery from Li-ion battery wastes coming from an industrial pre-treatment plant: Lab scale tests and process stimulations”, issued in Journal of Power Sources 206 (2012) 393-401, G. Granata et al. describe the recovery of Co and Li using Cyanex 272 and D2HEPA that were partially saponified with NaOH.

25 In their paper “Separation of cobalt and nickel via solvent extraction with Cyanex-272: Batch experiments and comparison of mixer-settlers and an agitated column as contactors for continuous counter-current extraction”, in Separation and Purification Technology 296 (2022) 121326, I.R. Rodrigues et al. deal with the separation of Co and Ni by solvent extraction using Cyanex-272, wherein a pH of 6 was set.

US 3,666,446 discloses a pH-regulated process for separating Cu and Co, wherein the regulation of the pH value is effected by ion-exchange reactions.

US 4,353,883 describes the separation of Co and Ni from an aqueous solution in the presence of an extractant, wherein said extractant is a phosphinic acid having at least 6 carbon
5 atoms.

From “Resource recovery of critically-rare metals by hydrometallurgical recycling of spent lithium ion batteries” by R. Sattar et al., issued in Separation and Purification Technology 209 (2019) 725-733, a two-stage solvent extraction with Cyanex 272 at a pH of 5.0 is known, wherein the Cyanex was saponified at 50%.

10 All these approaches have the fact in common that despite the uncertainty associated with the significance of the pH, the separation is performed on the basis of extraction isotherms at a pH established to be “optimal”, in which the latter often has to be adjusted elaborately. A further disadvantage in the known methods is the fact that usually a great excess of extractant is required.

15 The pH is generally defined as the negative decadic logarithm of the hydrogen ion activity of a given solution:

$$\text{pH} = -\lg_a(\text{H}^+)$$

The described technology for separating metal ions uses the pH as a control variable, which is generally acknowledged, although the measurement of the pH is subject to many
20 uncertainties in practice.

In particular, this means that a measured pH value is not suitable for concluding therefrom the actual H^+ concentration of a solution, i.e., the pH in this respect is an unsatisfactory, uncertainty-prone specific control variable in connection with the reactive extraction as herein described, in order to run the process stably. This is true, in particular,
25 when the operating range comprises a maximum of only a few tenths pH units.

Therefore, before this background, there is a need for an improved method for separating metal species and obtaining them in a very pure form from aqueous solutions, which preferably can dispense with the pH as a control variable.

Within the scope of the present invention, it has been surprisingly found that the liquid-liquid reactive extraction of metal species from aqueous solutions by using the activated extractant and by setting a defined stoichiometric ratio of the activated extractant to the metal species to be extracted can dispense with the pH as a control variable.

5 Therefore, the present invention firstly relates to a process for extracting a metal species from an aqueous solution using liquid-liquid reactive extraction, said process comprising the steps of:

a) providing an aqueous phase comprising at least one metal species to be extracted;

10 b) providing an organic phase comprising an extractant for extracting the metal species to be extracted;

c) activating the extractant in the organic phase with an activating agent;

d) contacting the aqueous phase and organic phase from step c);

e) separating the aqueous phase and the organic phase comprising at least part of the extracted metal species,

15 wherein said activated extractant and said metal species to be extracted are in a defined mutual stoichiometric ratio,

characterized in that an active control of the pH does not take place.

Without being bound to theory, it is assumed that the extractant promotes the transition of the metal species from the aqueous to the organic phase. Thus, the extractant is activated
 20 according to the invention. Because a predefined stoichiometric supply of activated extractant based on the metal species to be extracted, adapted to the separation problem, is provided, the pH as a control variable for the operating point can be dispensed with, and the uncertainty associated with the determination of the pH can be avoided. The ratio of activated extractant to the metal species to be extracted is representative of the ratio of activating agent, for
 25 example, Na^+ , to the amount of metal species to be extracted, which are matched to one another according to the invention.

In an extraction, it is a general object to find an acceptable compromise between the quality and purity of the species to be extracted and the yield. Within the scope of the process

according to the invention, it has surprisingly been found that the species to be extracted could be recovered in high purity and yield because of the process control, which is independent of pH.

Within the scope of the process according to the invention, the extractant is activated by the activating agent. The activation of the extractant is preferably effected before contacting the aqueous phase and the organic phase. Thus, the activating agent is preferably added already in the necessary amount, matched to the amount of the metal species to be extracted, to the organic phase before contacting it with the aqueous phase. Such precontacting can be done either continuously or in a batch mode.

The process according to the invention provides that the activated extractant is provided in a defined ratio to the metal species to be extracted. Surprisingly, it has been found that the separating performance and selectivity of the extraction can be controlled by adjusting this ratio, and the process can thus preferably be performed independently of an active pH control. Therefore, in a preferred embodiment, the process according to the invention further comprises a step in which the stoichiometric ratio of activated extractant to the metal species to be extracted is adjusted according to a previously defined ratio.

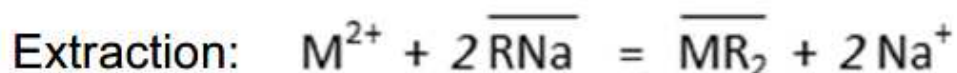
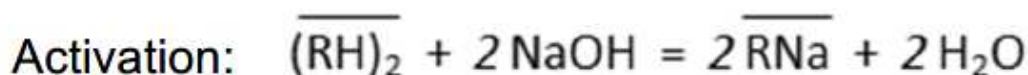
The adjusting of the defined stoichiometric ratio can be effected, for example, on the basis of the concentration of the metal species to be extracted. Therefore, an embodiment of the process according to the invention is preferred in which the concentration at least of the metal species to be extracted in the aqueous phase is determined in an upstream step.

The extractant is preferably selected from the group of complexing agents and liquid ion exchangers, and accordingly it can form a complex with the metal species to be extracted. In a particularly preferred embodiment, the extractant is selected from the group of organophosphinic acids, organophosphonic acids, and organophosphoric acids. Even more preferred extractants are selected from the group consisting of bis(2-ethylhexyl)phosphoric acid (D2EHPA), bis(1,3-dibutoxypropan-2-yl)phosphoric acid (Bidiopp), bis(1,3-diisobutoxypropan-2-yl)phosphoric acid (IPA), bis(5,8,12,15-tetraoxanonadecan-10-yl)phosphoric acid (TPA), bis(undecan-6-yl)phosphoric acid (UPA), bis(1,3-dioctyloxypropan-2-yl)phosphoric acid (OPA), bis(1,3-di-2-ethylhexyloxypropan-2-yl)phosphoric acid (EHPA), and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272). Also, the use of mixtures of the above listed extractants has proven particularly advantageous,

as well as the use of a mixture of branched monocarboxylic acids, as well as other organic acids, which are accordingly used preferably within the scope of the present invention.

Corresponding products are commercially available, for example, under the designation of Versatic™ Acid.

- 5 The activating agent activates the extractant, for example, by deprotonating it. Accordingly, the activating agent is preferably matched to the extractant. Said activating agent can be selected, for example, from the group of alkali hydroxides and/or ammonia. In particular, said activating agent is sodium hydroxide or lithium hydroxide. In this case, the activation of the extractant and the subsequent extraction of the valuable metal can be
- 10 formulated in accordance with the following two equations, in which the amount of activated extractant is matched to the amount of metal species to be extracted.



- For this process control, it has surprisingly been found that when the extractant is activated with aqueous sodium hydroxide, the latter can be absorbed completely by the
- 15 organic phase. The use of aqueous sodium hydroxide at a concentration of at least 40 mass % or more has proven particularly advantageous. Good results could be achieved already with the use of 20 mass % D2EPAH in Escaid™, as obtainable, for example, from Exxon Mobil, with diluted aqueous sodium hydroxide of 20 mass % at 50°C, and in addition, activation with 40 mass % aqueous sodium hydroxide surprisingly resulted in a single phase, which remained
- 20 stable even after cooling to room temperature. This behavior simplifies the technical realization significantly. A phase separation does not occur, the activation stoichiometry can be adjusted in an exactly defined way through exact mass flows, without having to rely on the pH or other control variables. The desired activation proportion of the extractant can be adjusted directly, or also subsequent to the activation by mixing in a non-activated organic
- 25 phase.

The process according to the invention aims at separating metal species, wherein especially transition metals and rare earth metals are preferred. The metal species are preferably selected from the group consisting of cobalt, nickel, manganese, iron, copper, magnesium, aluminum, and lithium. In particular, said metal species is cobalt, nickel,
5 manganese, and aluminum.

The organic phase is immiscible with the aqueous phase. Therefore, aliphatic and aromatic hydrocarbons and mixtures thereof are preferably used as said organic phase within the scope of the process according to the invention. Among these, in particular, kerosine or Escaid™ 120 as commercially available from Exxon Mobile have proven particularly
10 suitable.

The process according to the invention is mainly adapted to the industrial large scale, and is preferably performed in multistage countercurrent as a continuous process. In an alternatively preferred embodiment, the process according to the invention is performed in a batch mode.

The process according to the invention not only allows a metal species to be extracted from an aqueous solution, but may also be employed for the selective separation of several metal species from one another. Therefore, an embodiment is preferred in which the aqueous phase comprises at least one other metal species that at least in part remains in the aqueous phase. Adjusting a corresponding stoichiometric ratio not only can increase the separating
15 performance, but also can define the amount of other metal species that is co-transferred into the organic phase, so that a desired ratio of the metal species in the organic phase is achieved. In order to ensure the purity of the main component, the extraction may be followed by a washing step, more preferably in terms of an enhancing extraction, in which the charged organic phase is contacted, for example, with a pure solution of the main component and/or
20 mineral acids, especially sulfuric acid, whereby the minor components are driven out of the organic phase again, such as in the separation of transition metals in the sulfate system. Accordingly, the process according to the invention further includes a washing step subsequent to the extraction.

The process according to the invention is an improvement over conventional
30 separation methods, which rely on the pH as a control variable. Accordingly, an embodiment is preferred in which the process is not subject to any pH-dependent control. Although the pH

may be measured within the scope of the process according to the invention as an indicator, the required amount of activating agent is preferably dosed at the desired positions through exact gravimetric dosing, preferably by Coriolis mass flowmeters. Especially when utilizing extraction columns, the approach with an activated extractant and defined stoichiometric ratios is to be preferred.

The process according to the invention may be performed in mixer-settler batteries, or in extraction columns, the performance in extraction columns being preferred. Suitable extraction columns are known to those skilled in the art, and preferably have material exchange elements for increasing the contact area and mixing between the organic and aqueous phases.

The present invention further relates to a device for performing the process according to the invention, wherein said device includes a reactor for contacting an aqueous phase with an organic phase, and wherein said reactor has at least one discharge port for collecting the aqueous and/or organic phase.

Suitable reactors in the device according to the invention include, in particular, mixer-settler batteries and extraction columns, in which the extraction columns are preferred. The space requirement can be significantly reduced by using an extraction column, and the circulating amounts of organic and aqueous phase can be kept low. Further, the use of the extraction columns ensures some continuity of countercurrent, in which only one phase boundary at the column head or at the column bottom has to be regulated. Also, the construction costs for a column are significantly lower as compared to large mixer-settler batteries.

In a further preferred embodiment, the device according to the invention further has a module for precontacting the organic phase with the activating agent.

The present invention is further explained by means of the following Examples and Drawings, which should by no means be understood as limiting the idea of the invention.

FIGURES

Figure 1 schematically shows an exemplary course of the degree of extraction in the separation of Mn, Cu, Co and Ni ions, wherein for $E = 0$, the corresponding metal species remains in the aqueous phase completely, and $E = 1$ indicates a complete transition into the

organic phase. Thus, for example, an organic phase containing a majority of the Cu and Mn ions and an aqueous refined product in which the majority of the Co and Ni ions remain can be obtained as a function of the acidity of the solution. Thus, depending on the prevailing acidity, the separation of the different metal species from each other can be selectively controlled.

Figures 2 and 3 show experimentally determined extraction isotherms for cobalt and nickel. Figure 2 shows the individually recorded isotherms, while Figure 3 shows the extraction isotherms of an aqueous solution containing both metals in equal concentrations. A competitive behavior for the short supply of extractant in accordance with the process according to the invention can be clearly observed. Because of its higher affinity for the extractant, cobalt pushes back the co-extraction of nickel, and the isotherms are drastically shoved apart. The organic phase thus charged with the two metals can be freed from the undesirable nickel fractions subsequently by a contact with a washing solution that contains only cobalt, or by washing with a mineral acid, such as sulfuric acid. It is to be noted that a single extraction stage is shown here. Then, high yields with a simultaneously high purity can be realized by countercurrent operation for both the extraction process and the washing process. Suitable devices include mixers-settlers and columns.

EXAMPLES

The process according to the invention was tested in a first batch set-up.

600 ml of a solution containing equimolar Co and Ni with 40 g/l of Co and 39.88 g/l of Ni was prepared from the respective chloride salts, and contacted with 1576 ml of an organic solution containing 20 mole % bis(2-ethylhexyl)phosphoric acid (DEHPA) as the extractant with stirring. A 50% NaOH solution was used as the activating agent at 40°C. Table 1 shows the stoichiometric ratio of extractant, aqueous sodium hydroxide and the Co to be extracted. After the phase separation was complete, the content of Co and Ni was determined respectively in the organic and aqueous phases. Table 2 summarizes the results of the analysis.

Table 1:

Starting material	moles
Co (in aqueous phase)	0.407

DEHPA (in organic phase)	0.819
NaOH	0.876

Table 2:

	Co	Ni
organic phase	13.30 g/l	1.84 g/l
aqueous phase	2.78 g/l	30.31 g/l
D(M)*	4.77	0.060

* Partition coefficient: $D = M_{OP}/M_{AP}$ with $M = \text{Co, Ni}$; OP: organic phase; AP: aqueous phase

- 5 As can be seen from the Table, the process according to the invention achieves an efficient separation of Co and Ni by a reactive extraction of the Co from the aqueous phase. From the partition coefficients D determined on the basis of the measured concentrations, a separating factor ($\omega = D_{\text{Co}}/D_{\text{Ni}}$) of 79 is obtained. Comparable experiments at a pH of 3.5 with the same extractant and under the same extraction conditions suggest a separating factor of 3.
- 10 Thus, a significant increase of selectivity can be achieved by the process according to the invention.

Thus, the process according to the invention is a simple and efficient alternative to a pH-controlled extraction, since only the amount of the metal species to be extracted has to be known.

- 15 The separating performance could be increased further by a continuous process mode. Therefore, the above described experiment was repeated in a continuously operated mixer-settler plant. The experiment was repeated with 6 mixer-settler units, each with a volume of 350 ml, in which the organic phase was precontacted with a 200 g/l NaOH solution.

- 20 After a test duration of 16 hours, partition coefficients of $D(\text{Co}) = 20.77$ and $D(\text{Ni}) = 0.011$ could be calculated according to the concentrations of Co and Ni as measured in Table 3. On this basis, a separating factor ($\omega = D_{\text{Co}}/D_{\text{Ni}}$) of 1888 is obtained.

Table 3:

	Co	Ni
organic phase	13.50 g/l	0.3 g/l
aqueous phase	0.65 g/l	28 g/l
D(M)*	20.77	0.011

CLAIMS

1. A process for extracting a metal species from an aqueous solution using liquid-liquid reactive extraction, said process comprising the steps of:

a) providing an aqueous phase comprising a metal species to be extracted;

5 b) providing an organic phase comprising an extractant for extracting the metal species to be extracted;

c) activating the extractant in the organic phase with an activating agent;

d) contacting the aqueous phase and organic phase from step c);

10 e) separating the aqueous phase and the organic phase comprising at least part of the extracted metal species,

wherein said activated extractant and said metal species to be extracted are in a defined mutual stoichiometric ratio,

characterized in that an active control of the pH does not take place.

15 2. The process according to claim 1, characterized in that the activation of the extractant is performed before contacting the aqueous and organic phases.

3. The process according to at least one of the preceding claims, characterized in that said process further includes a step in which the stoichiometric ratio of activated extractant to the metal species to be extracted is adjusted.

20 4. The method according to at least one of the preceding claims, characterized in that the concentration at least of the metal species to be extracted in the aqueous phase is determined in an upstream step.

5. The process according to at least one of the preceding claims, characterized in that the extractant is selected from the group of complexing agents and liquid ion exchangers.

25 6. The process according to at least one of the preceding claims, characterized in that said process further includes a step of washing the separated organic phase.

7. The process according to at least one of the preceding claims, characterized in that the extractant is selected from the group of organophosphinic acids, organophosphonic acids, and

organophosphoric acids, especially selected from the group consisting of bis(2-ethylhexyl)-phosphoric acid (D2EHPA), bis(1,3-dibutoxypropan-2-yl)phosphoric acid (Bidiopp), bis(1,3-diisobutoxypropan-2-yl)phosphoric acid (IPA), bis(5,8,12,15-tetraoxanonadecan-10-yl)phosphoric acid (TPA), bis(undecan-6-yl)phosphoric acid (UPA), bis(1,3-

5 dioctyloxypropan-2-yl)phosphoric acid (OPA), bis(1,3-di-2-ethylhexyloxypropan-2-yl)phosphoric acid (EHPA), bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272); mixtures of the mentioned extractants, and mixtures of branched monocarboxylic acids with other organic acids.

8. The process according to at least one of the preceding claims, characterized in that said

10 activating agent is selected from the group of alkali hydroxides, and especially sodium hydroxide or lithium hydroxide.

9. The process according to at least one of the preceding claims, characterized in that said metal species are selected from the group of transition metals and rare earth metals, especially selected from the group consisting of cobalt, nickel, manganese, iron, copper, magnesium,

15 aluminum, and lithium, in particular, said metal species is cobalt, nickel, manganese, and aluminum.

10. The process according to at least one of the preceding claims, characterized in that the organic phase is selected from the group of aliphatic and aromatic hydrocarbons, and mixtures thereof.

20 11. The process according to at least one of the preceding claims, characterized in that said process is operated as a batch process or continuous process.

12. The process according to at least one of the preceding claims, characterized in that the aqueous phase includes at least one other metal species, wherein said other metal species at least in part remains in the aqueous phase.

25 13. The process according to at least one of the preceding claims, characterized in that the process is not subject to any pH-dependent control, especially characterized in that a measurement of the pH does not take place.

14. The process according to at least one of the preceding claims, characterized in that said process is performed in an extraction column.

15. A device for performing the process according to the invention, wherein said device includes a reactor for contacting an aqueous phase with an organic phase, and wherein said reactor has at least one discharge port for collecting the aqueous and/or organic phase.

16. The device according to claim 15, characterized in that said reactor is an extraction
5 column, and/or the device further includes a module for precontacting the organic phase with the activating agent.