

Additive-free Cu Electrowinning

Many cobalt and nickel containing raw materials and intermediates also contain quantities of copper that end up in leaching solutions after dissolving these materials. Examples are, among others, mattes
5 from primary smelting of ores, intermediate hydroxide and sulfide products from Cu, Co and Ni mining, certain metallic deep-sea nodules containing Co, Ni and Mn, white alloys produced during smelting of Co and Ni products, as well as wastes and production scrap generated during production or use of lithium-ion or nickel metal hydride batteries.

10 Especially the amount of lithium-ion batteries or their waste is expected to grow enormously, mainly due to the ongoing worldwide electrification of the automotive industry. Lithium-ion batteries or their waste comprises new or waste Li-ion batteries, spent or end-of-life batteries, production or battery scrap, battery constituents, such as electrode foils, electrolytes, separators, casing material and electrode materials, or pre-processed battery materials, resulting in very complex waste streams. Key
15 metals in such waste streams are typically copper, nickel and cobalt.

The separation or removal of copper from aqueous solutions containing cobalt, nickel and other metals is therefore a frequent hydrometallurgical operation.

20 WO2019121086 describes the removal of Cu, based on selective precipitation by cementation with a reducing agent. Cu in such a process is precipitated in its metallic form. This is typically applied when the quality and value of the Cu product is of less importance. In such a cementation-based operation, the Cu containing solution is brought in contact with a reducing agent. The effect is a reduction of soluble Cu^{2+} or Cu^{1+} ions to insoluble elemental copper, which then precipitates in solid metallic form.

25 Another option for the removal of copper is electrowinning (EW), but this requires more investments than a cementation. Moreover, process conditions need to be adapted.

C. G. Anderson (Book chapter: Optimization of Industrial Copper Electrowinning Solutions. In: Prime
30 Archives in Chemical Engineering. Hyderabad, India, Vide Leaf, 2019) describes electrowinning of Cu directly on Cu and Ni containing industrial solutions ("direct electrowinning"), with cathodes that are immersed into the solution. By applying an electrical current, Cu is deposited on the cathode, separating it from other elements in solution, such as Co, Ni, Fe or Mn. The robustness of direct electrowinning is

limited, and therefore typically only applied to systems that favor a good Cu-deposition, such as when working at a high Cu concentration.

In other cases, electrowinning is combined with solvent extraction ("SX-electrowinning"). This combination makes Cu-EW more robust, i.e. more tolerant to process variations, but also much more costly in an industrial setup. Examples are found in Cheng et al. (The recovery of nickel and cobalt from leach solutions by solvent extraction: Process overview, recent research and development; Proceedings of ISEC 2005). In such a scheme, Cu is first extracted from an impure feed solution by solvent extraction (SX), which is typically highly selective for Cu. The extracted Cu ions are then transferred to a separate secondary Cu solution, from which copper is harvested in a subsequent electrowinning operation that is not limited by the presence of elements like Co, Ni, Mn and especially Fe, in the primary solution.

In conventional copper electrowinning ("Cu-EW"), dense and smooth Cu deposits with high chemical quality are produced. The process is typically performed at Cu-concentrations of about 35 to 55 g/L Cu, H₂SO₄ concentrations of about 160 to 190 g/L, temperatures of 44 to 56 °C and current densities of 200 to above 450 A/m² (M.E. Schlesinger et al.; Chapter 17 - Electrowinning, Extractive Metallurgy of Copper, Fifth Edition, Elsevier, p. 349-372, 2011; N.T. Beukes, J. Badenhorst, Copper electrowinning: theoretical and practical design, Hydrometallurgy Conference 2009, The Southern African Institute of Mining and Metallurgy, 2009). Permanent cathodes comprising 316 L stainless steel are mostly used, from which the Cu deposits are removed via stripping (T.G. Robinson et al.; Copper Electrowinning: 2013 World Tankhouse Operating Data, Proceedings of Copper 2013, Santiago, Chile, 2013).

In both direct EW and SX-EW, the Cu in the electrolyte is replenished in the process, for example by feeding a Cu-rich leach solution to the EW circuit or by sending the electrolyte from the EW operation back to the stripping section of a Cu-SX process. The Cu concentration thus remains on a high level throughout the process, and even variations in the concentration at entry and exit of the EW-cell are limited.

Alternatively, EW can also be applied with the goal to deplete the Cu content in a Cu-bearing solution. Rather than replenishing the Cu concentration as outlined above, a series of electrowinning cells are put in cascade, each operating at a decreasing Cu concentration (B.C. Wesstrom and O. Araujo, Optimizing a Cascading Liberator, T. T. Chen Honorary Symp. Hydrometall., Electrometall. Mater. Charact. Proc., 151, 2012). In this case, the primary objective is to remove the Cu from the stream, rather than producing a pure and valuable Cu product. A term used for this is "depletion Cu-EW". The physical quality of the deposited Cu is usually very poor, especially at lower Cu concentrations, and thus requires further

refining. The decreasing Cu concentration results in very porous, non-coherent deposits that can disintegrate easily. This way, a substantial part of the deposit usually detaches from the cathode and collects at the bottom of the EW-cell as cathode sludge (Shijie Wang, Recovering copper using a combination of electrolytic cells, JOM, 54, 51–54, 2002).

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Depletion Cu-EW is often embedded in larger hydrometallurgical process schemes where downstream operations can only tolerate limited incoming Cu concentrations. A typical application is the recovery of Cu from bleed streams in which impurities are purged from the main circuit in conventional Cu electrorefining and EW operations. Typically, also the acid concentration in such process schemes is rather high, such as from 350 to 400 g/L (A. Siegmund, S. Gadia, G. Leuprecht, P. Stantke, Proceedings of Copper 2013, 275-283). Cu electrorefining entails electrochemically dissolving copper from impure anodes into an electrolyte, and electrochemically plating pure copper from the electrolyte onto a cathode.

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Also other flowsheets dedicated to battery recycling can involve a depletion Cu-EW step. WO19102765 describes a process, in which an alloy containing Cu, Ni and Co is used as anode in an electrolytic purification process. In this process, Cu, Ni and Co are dissolved into the electrolyte, followed by a deposition of Cu onto a cathode. In one example the Cu concentration is reduced from 10 to 1 g/L in a batch process by applying a very high current density of 1500 A/m^2 , resulting in a Cu product with a chemical purity of 99.9%. The physical characteristics of the Cu deposit are, however, not described. Under these high current densities, typically Cu powders are produced rather than dense deposits.

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The physical quality of a Cu deposit is mainly defined by the compactness of the sheet cathode (absence of porosity, cracks and voids) and by the smoothness of its surface (absence of dendrites, nodules and other protrusions).

One typical way to mitigate above-mentioned issues with regards to the physical quality of the deposit is the use of specific organic additives in the EW process. More information about such additives can, for example, be found in Moats et al. (M.S. Moats, A. Luyima and W. Cui, Examination of copper electrowinning smoothing agents. Part I: A review, Minerals & Metallurgical Processing, Vol 33, pp 7–13, 2016). Organic additives, such as Guar gum, modified starches or polyacrylamides are essential to promote the plating of dense and smooth Cu deposits.

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Working without the typical organic additives may lead to the formation of dendrites or nodules, especially at the edges of the cathode, which are undesired. Their formation may even lead to short circuits in the EW-cells.

5 Cifuentes et al. (L. Cifuentes, M. Mella, On the physical quality of copper electrodeposits obtained on mesh cathodes, Canadian Metallurgical Quarterly, Vol 45, no. 1, 9-16, 2006) investigated the effect of process parameters on the Cu electrodeposition process in a reactive electrodialysis ("RED") cell in absence of additives. At high Cu concentration (9 g/L), a deposit with nodulation at the cathode edges was obtained, while at low Cu concentration (3 g/L), a deposit without nodulation at the cathode edges
10 and with a homogeneous coverage was obtained. Contrary to conventional Cu-EW, cathode geometries other than sheets or blanks are used, such as copper granules or copper mesh. Also, the cell-geometry in the non-conventional RED-cell differs from classic design in having two compartments, separated by a membrane. In these cases, the chemical quality of a Cu-deposit is determined in exactly the same way as in the conventional case, but the parameters for the physical quality needed to be redefined. New
15 quality criteria for Cu-electrodeposits on a copper mesh cathode are proposed, among others also to solve the issue of a co-deposition of arsenic, present in the electrolyte. In this non-conventional Cu-EW the physical quality of the electrodeposit increased markedly with increasing cell current density, leading to the definition of a "base case" for a suitable current density of 290 A/m^2 . For lower current densities, such as 225 A/m^2 , deposit-free zones at the center of the cathode and greater nodulation
20 near the edges was observed. At 150 A/m^2 even larger areas without deposit at the center and sharp nodulation occur. Both are characterized as physically bad deposits with a low coverage ratio. While using a mesh cathode, Cifuentes remains generally silent about how to achieve a sufficiently coherent Cu-deposit on a sheet or blank, which does not disintegrate.

25 It is therefore an objective of the present invention to form a coherent and uniform Cu-deposit on a sheet or blank cathode in a Cu-EW process at low current densities without using additives, and without significant edge effects, such as the formation of dendrites or nodules. This ensures that the risk of short circuits is minimized and that the deposit doesn't disintegrate from the cathode during the process, allowing for easy harvesting.

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A first embodiment therefore describes a process for electrowinning of Cu from an aqueous acidic solution containing Cu and one or more of Ni and Co onto a cathode starting sheet, comprising the steps:

- providing a copper electrowinning cell;

- electrowinning of Cu from an aqueous sulfuric acid solution at a temperature of 50 to 70 °C, wherein the concentration of sulfuric acid is 20 to 100 g/L, wherein the concentration of Cu is at least 2 g/L and at most 15 g/L, and wherein the aqueous acidic solution is free of organic additives;
 - applying means for agitating the electrolyte; and,
- 5 - applying a current density of 100 to 210 A/m²,
thereby obtaining a Cu-deposit on the cathode starting sheet.

Electrowinning is the electrodeposition of metals that have been put in solution via a process commonly referred to as leaching done in a separate operation.

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To achieve a uniform Cu-deposition in standard EW-cells with parallel electrodes in absence of additives, the Cu-EW process is performed at low current densities and low Cu concentrations.

- However, the Cu concentration cannot be too low, otherwise no coherent deposit is formed. This
- 15 requires a minimum concentration of Cu of about 2 g/L. On the other hand, a maximum concentration of Cu of about 15 g/L should not be exceeded, because otherwise a deposit with significant edge effects will be formed.

- Under the chosen conditions, current densities above 225 A/m² do not work because these result in the
- 20 formation of non-coherent, highly porous deposits that easily disintegrate. Current densities below 100 A/m² lead to too low capacities of the Cu EW installation, which then becomes economically unfeasible.

- By “organic additives” we mean product families such as poly- and oligosaccharides (e.g. guar gum and modified starches), (poly)peptides (e.g. gelatin), poly(meth)acrylic acid, poly(meth)acrylate salts and
- 25 esters, polyethers, fluoropolymers, polyacrylamides, alkyl sulfonates and other organosulfur and organonitrogen compounds, including their degradation products. In certain flowsheets, the use of additives is very problematic, if not impossible, as these can hamper subsequent steps such as hydrolysis, solvent extraction (“SX”) or crystallization. Also the selective removal of such additives from the electrolyte prior to downstream processing is difficult. Consequently, these additives often end up in
- 30 the final product, which is undesired. The same is true for their degradation products.

A second embodiment describes a process, wherein the cathode starting sheet is a copper starter sheet or a stainless steel or titanium blank.

“Cathode starting sheets” are used in electrowinning cells to deposit metals such as copper on a flat surface. Such cathode starting sheets are typically in the form of thin copper starter sheets or blanks, made of stainless steel or titanium.

- 5 Cu deposited on a copper starter sheet can be harvested and be collected directly, ready for further processing. Copper deposited on a stainless steel or titanium blank is typically stripped (lifted) from this blank and then collected. In both cases it is important that the Cu-deposit is coherent and doesn't disintegrate, which would interfere with a proper and quantitative collection of the metal.
- 10 In a further embodiment, the current density is below 200 A/m^2 , more preferably below 150 A/m^2 and even more preferably at 140 A/m^2 or less.

Working at a current density below 150 A/m^2 or even at 140 A/m^2 or less is preferred to ensure a coherent and uniform Cu-deposit under the present process conditions.

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In a further embodiment, the means for agitating comprise sparging with air or nitrogen, mechanical or ultrasonic agitation or forced circulation.

- “Means for agitating” is meant in the broadest possible way. Air sparging is frequently used, but air can
20 be replaced by nitrogen or any other non-reactive gas, as the type of gas is less important than the effect it creates when flushed through the electrolytic solution. Gases which react with copper or any other compound of the solution obviously should be avoided in the EW-process.

- Alternatively, agitating can also be achieved with ultrasound or mechanical stirring or a forced
25 circulation, for example by an optimized electrolyte injection, which results in whirling and mixing of the electrolyte solution. An example for “forced circulation” can be found in Cooper et al. (W.C. Cooper, J. Appl. Electrochem. 15, 789–805, 1985). Yet another option is a periodic current reversal (PCR). Air sparging is the preferred means for agitating.

- 30 In a further embodiment, the copper electrowinning cell is a parallel plate cell. This cell type comprises a rectangular cell containing flat plate anodes and cathodes, which are placed alternately in the cell. Flat plates generally facilitate the recovery of copper.

In a further embodiment, the H_2SO_4 has a preferred concentration of 40 to 80 g/L.

Sulfuric acid is the preferred choice, because it is most often used in leaching operations, and most typically used in Cu-EW.

Compared to other Cu-EW processes, which typically apply rather acidic conditions (e.g., 180 to 400 g/L H_2SO_4), the present invention works in significantly milder conditions (20 to 100 g/L H_2SO_4), preferably 40 to 80 g/L. This allows to treat leaching solutions, having mild acidities, and without the need for further acidification. It is also an advantage when having to neutralize Cu-depleted process solutions.

Industrial leach solutions from battery recycling often have concentrations of 1 to 20 g/l acid. This will typically lead to acid concentrations of 40 to 80 g/L in the present EW-process, depending on the amount of Cu removed by electrowinning, as acid is produced due to this process.

In a further embodiment, the aqueous acidic solution containing Cu and one or more of Ni and Co is obtained by leaching of starting materials comprising Li-ion batteries or their waste.

Modern waste streams for battery recycling can be very complex. Leaching solutions originating from the recycling of batteries typically contain appreciable amounts of copper, as well as nickel and/or cobalt. The present process is therefore particularly advantageous to treat such leaching solutions.

In a further embodiment, the aqueous sulfuric acid solution has a Ni concentration of at least 20 g/L.

In a further embodiment, the aqueous sulfuric acid solution has a Co concentration of at least 5 g/L.

Typical leach solutions from battery recycling have concentrations of Ni of at least 20 g/L, and of Co of at least 5 g/L. Such concentrations make them a valuable source for recovering the metals.

In a further embodiment, the aqueous acidic solution containing Cu and one or more of Ni and Co is free of arsenic. Co-deposition of As together with Cu is a recurring problem for streams containing both, leading to a reduced chemical quality of the Cu-deposit. Li-ion batteries and their waste typically do not contain arsenic.

When performing Cu-EW, the following three main deposit types have been observed and characterized. In the following examples the obtained Cu-deposits will be classified accordingly.

Type-1: The deposit is coherent and dense (low porosity), showing very limited formation of nodules or dendrites at the edges. The Cu is uniformly deposited on the cathode surface.

Type-2: The deposit is coherent and dense, but shows pronounced formation of nodules or dendrites at the edges. Thus, the Cu is not uniformly deposited on the cathode surface.

- 5 Type-3: The deposit is porous and non-coherent. It adheres poorly to the cathode and can easily disintegrate.

The following examples illustrate the invention.

Examples 1 to 3

- 10 Examples 1 to 3 were performed as batch processes.

Cu-EW beaker cell tests were performed in a beaker cell of 2.8 L connected to circulation tanks, containing 50 L of electrolyte. A flow rate of 4,2 L/h and a temperature of 60 °C were selected. Synthetic electrolyte with a composition as indicated in Table 1 was used (Cu and H₂SO₄ not shown).

- 15 In the beaker cell, one anode (PbCaSn, 9 x 2 cm²) and cathode (Cu starter sheet, 14 x 10 cm²) was placed. The cathodic current density was set at 140 A/m² and the experiments ran for 7 days.

During such a process, Cu is removed from the electrolyte and deposited on the cathode, and H₂SO₄ is produced.

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This resulted in a decrease in the Cu concentration by about 7 g/L and an increase of H₂SO₄ concentration by about 10 g/L. The starting and final Cu and H₂SO₄ concentrations are indicated in Table 2.

- 25 Table 1 – Synthetic electrolyte composition

Electrolyte composition		
Co	18	g/L
Fe	1.3	g/L
Mn	0.9	g/L
Ni	60	g/L
Ca	48	mg/L
Cr	29	mg/L
Si	28	mg/L
Zn	23	mg/L

Table 2 – Cu-EW beaker cell experiments with synthetic electrolyte

	Concentration (g/L)						Deposit Type
	Cu start/final	H ₂ SO ₄ start/final	Co	Ni	Mn	Fe	
Ex-1	14/7	51/61	25	45	0.5	0.3	1
Ex-2	42/35	7/17	25	45	0.5	0.3	2
Ex-3	8/1	58/68	25	45	0.5	0.3	3

From these examples the following can be concluded.

- 5 Comparative Example 2: The final Cu concentration is too high (35 g/L) and therefore results in Type-2 deposition.

Comparative Example 3: The final Cu concentration is too low (1 g/L) and therefore results in Type-3 deposition.

10 Tests in large scale cells

Examples 4 to 12 were performed as continuous processes.

Large-scale Cu-EW tests were performed in a 13 L cell, connected to a circulation tank of 100 L.

Electrolyte was circulated at 20 L/h and heated with an oil bath to the desired temperature (40,

- 15 respectively 60 °C). In the cell, two anodes (PbCaSn, 89 x 7 cm²) and one cathode (Cu starter sheet, 94 x 8.5 cm²) are present. During the experiment, Cu is removed from the electrolyte and deposited on the cathode, while H₂SO₄ is produced. To keep the Cu and H₂SO₄ concentration constant (according to Table 3) during the experiment, the electrolyte in the circulation tank was fed with electrolyte with a high Cu concentration (40 to 45 g/L) and low H₂SO₄ concentration (2 to 3 g/L). The composition of the
- 20 electrolyte is indicated in Table 1. Sparging with air was applied underneath the cathode.

Table 3 – Overview of the experiments in large scale cells

	[Cu] (g/L)	[H ₂ SO ₄] (g/L)	Current density (A/m ²)	Temperature (°C)	Sparging flow (L/h)	Time (days)	Deposit type
Ex-4	5	58	140	60	10	10	1
Ex-5	20	30	140	60	10	7	2
Ex-6	5	57	225	60	10	3	3
Ex-7	5	59	185	60	10	10	1

	[Cu] (g/L)	[H ₂ SO ₄] (g/L)	Current density (A/m ²)	Temperature (°C)	Sparging flow (L/h)	Time (days)	Deposit type
Ex-8	5	60	140	40	10	2	3
Ex-9	5	58	140	60	20	10	1
Ex-10	5	57	140	60	0	7	3
Ex-11*	20	29	140	60	10	10	1
Ex-12*	5	56	140	60	10	10	3
*Additives used: guar (105 g/ton Cu) and gelatine (200 g/ton Cu)							

From these examples the following can be concluded.

Comparative Example 5: The Cu concentration is too high (20 g/L), which results in Type-2 deposition.

Comparative Example 6: The current density is too high (225 A/m²), which results in Type-3 deposition.

5 Comparative Example 8: The temperature is too low (40°C), which results in Type-3 deposition.

Comparative Example 10: No sparging is applied, which results in Type-3 deposition.

Comparative Example 11: The use of organic additives at high Cu-concentration results in Type-1 deposition.

Comparative Example 12: The use of organic additives at low Cu concentration results in Type-3

10 deposition.

Claims

1. Process for electrowinning of Cu from an aqueous sulfuric acid solution containing Cu and one or more of Ni and Co onto a cathode starting sheet, comprising the steps:
 - providing a copper electrowinning cell;
- 5 - electrowinning of Cu from an aqueous sulfuric acid solution at a temperature of 50 to 70 °C, wherein the concentration of sulfuric acid is 20 to 100 g/L, wherein the concentration of Cu is at least 2 g/L and at most 15 g/L, and wherein the aqueous acidic solution is free of organic additives;
- applying means for agitating the electrolyte; and,
- applying a current density of 100 to 210 A/m²,
- 10 thereby obtaining a Cu-deposit on the cathode starting sheet;
 wherein the aqueous sulfuric acid solution containing Cu and one or more of Ni and Co is obtained by leaching of starting materials comprising Li-ion batteries or their waste.
2. Process according to claim 1, wherein the cathode starting sheet is a copper starter sheet or a
- 15 stainless steel or titanium blank.
3. Process according to claim 1 or 2, wherein the current density is below 200 A/m², more preferably below 150 A/m², and even more preferably at 140 A/m² or less.
- 20 4. Process according to any one of claims 1 to 3, wherein the means for agitating comprise sparging with air or nitrogen, mechanical or ultrasonic agitation or forced circulation.
5. Process according to any one of claims 1 to 4, wherein the copper electrowinning cell is a parallel plate cell.
- 25 6. Process according to claims 1 to 5, wherein the aqueous sulfuric acid solution has a Ni concentration of at least 20 g/L.
7. Process according to claims 1 to 5, wherein the aqueous sulfuric acid solution has a Co concentration
- 30 of at least 5 g/L.