



**Sustainable processing of Europe's low-grade sulphidic and lateritic nickel/cobalt ores and tailings into battery-grade metals (eNiCoN)**

**D3.1**



Public

Authors:

Iryna Makarava, Aalto University

Kirsi Yliniemi, Aalto University

Benjamin P. Wilson, Aalto University

Mari Lundström, Aalto University

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## Executive Summary

This technical report is a **deliverable D3.1** of the eNiCoN project and reports **on the success of direct simultaneous anodic Co-oxide and cathodic Ni recovery in the HCl-route (cf. T3.1.1), determining the decision to select the processing strategy (T3.1.1 vs. T3.2.2) for further Co recovery validation.**

Renewable energy production and storage is highly mineral intensive, and especially it results in high demand for Co and Ni metals. The International Energy Association (IEA) estimated in 2022 substantial increase in Co demand in clean energy technologies from 2020 to 2040, if aiming at Sustainable Development Scenario of Paris agreement goals.

The research has concentrated on the following aspects:

- **The fundamentals of Co-oxidation, i.e. thermodynamic analysis and kinetics of different reactions involved.** This work contributes to both eNiCoN *Task 3.1.1. Direct cobalt recovery as oxide along cathodic nickel recovery from Co/Ni-rich solution* and *Task 3.1.2 Direct recovery Co-oxide product on anode from purified Co-solution.*
- **The effectiveness of an electrochemical route for Co oxide recovery on anode in multi-metal Co/Ni-rich solution in the presence of impurities.** Here, a two-step approach may be needed *i.e.* before the recovery step (Step 2), impurity removal step(s) may be conducted (Step 1). This work contributes to eNiCoN *Task 3.1.1. Direct cobalt recovery as oxide along cathodic nickel recovery from Co/Ni-rich solution.*

The original hypothesis of direct Co oxide recovery as a mixture of  $\text{Co}_3\text{O}_4$ ,  $\text{CoOOH}$ ,  $\text{Co}(\text{OH})_3$  was successfully proved both from impure and pure solutions. However, the process efficiency was low in both cases due to the passivation of the anode. Preventing the anode passivation is seen as the primary focus area for future work.

When using Co/Ni-rich solution with impurities a simultaneous deposition of Ni on cathode was not observed as was hypothesised in the original plan, and Mn impurity was competing with Co-oxidation on the anode. Despite of these drawbacks using impure solutions still shows a great promise as – unlike in typical, currently used Co and Ni separation processes – nickel does not compete with Co recovery, and therefore Co could be selectively recovered from such solutions by this approach. Also, by adding a separate Mn removal step prior to cobalt removal from impure multi-metal solutions solved the issue with Mn oxidation, and thus a processing route with two steps was created: Step 1 is Mn removal (either electrochemically or by using methods already in use in industry) and Step 2 is the Co recovery from impure but Mn-free solution, *i.e.* from Co-Ni solution having still other impurities (e.g. Zn, Al, and Si) present.

Therefore, it can be concluded that passivation of the anode during Co recovery is currently the challenge in the recovery of Co by anodic oxidation while most impurities and especially nickel do not impact on the selectivity. **The research is suggested to be continued with multi-metal solutions - after Mn and possibly Al removal either by electrochemical methods or methods currently used in industry - and focuses on Co-recovery step to overcome anode passivation.** This is a modified approach of T3.1.1 aiming at selective anodic cobalt recovery from impure multi-metal solutions (T3.1.1), however with features of T3.1.2 - with cathodic reaction of  $\text{H}_2$  formation. When thinking about the whole process holistically, this approach has potential for “high gain” vs. state-of-the-art processing as several of the costs in hydrometallurgical processing relate to separation of elements from multi-metal solutions. All in all, this route can also be considered as having the highest success rate, compatibility and novelty value.



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## 1. Introduction

Cobalt is a highly valuable metal that is in high demand due to its use in various industrial applications however, there is increasing pressure on resources due to its relative scarcity [1,2]. The global need for cobalt is rapidly increasing, particularly in the electric mobility sector where it forms a key component in lithium-ion batteries [3]. Nevertheless, the current primary global source of cobalt, the Democratic Republic of Congo (DRC), presents a supply chain concern due to widespread use of artisanal mining and related geopolitical issues [4]. Cobalt is typically recovered from sulfide and laterite ores using pyrometallurgical and hydrometallurgical techniques [5]. State-of-the-art refining processes include leaching, neutralization, precipitation, and solvent extraction/ion-exchange to remove impurities and separate cobalt from nickel that can be energy and chemical intensive in nature [6–8]. In contrast, electrochemical recovery methods may offer environmentally competitive and effective alternative routes for cobalt separation and/or recovery from the process solutions, especially if the electricity itself is from renewable energy sources. Moreover, cobalt is known to be oxidized at higher electrochemical potentials and therefore, precipitation of cobalt oxide compounds - that could potentially be directly used in battery applications - is thermodynamically possible via electro-oxidation methods [9]. Research and industrial operation of cathodic cobalt recovery is well known [10,11], however the understanding of anodic electro-oxidation of cobalt for metal recovery from primary and secondary resources is limited, as the existing literature mainly focuses solely on catalytic applications.

Nevertheless, the presence of impurities in industrial process solutions as well as competing reactions may challenge the feasibility of electrochemical anodic cobalt oxide recovery. Typically, the leachates of sulfide or laterite ores contain a wide variety of impurities such as Mg, Mn, Al, Zn, Si, Fe [12] and many of these can potentially interfere with cobalt oxidation and complicate the oxidation process [13]. On the other hand, some of the side reactions may be beneficial, either by lowering the cell voltage (by providing cathodic reaction with lower overpotential) or by creating compounds (e.g., hydrogen gas, H<sub>2</sub>) that could be potentially captured and further utilized within metallurgical processing operations.

As part of the eNiCoN project, the objective of this work is to investigate the feasibility of a direct anodic oxidation of Co as a Co-oxide recovery process unit operation: such a unit operation could be part of a flexible, next-generation HCl-based route for Co recovery. If successful, anodic oxidation could potentially offer an alternative unit process and/or recovery method to the current state-of-the-art processing routes for sulfidic ores (Pyrometallurgical) and laterite ores (Pyrometallurgical and High-Pressure Acid Leach, HPAL). In the current report, two the experimental findings of anodic cobalt recovery are evaluated as part of WP3: *Ni/Co ultrarefining to battery-grade Ni/Co precursors*.

### 1.1 Structure of the deliverable

This technical report relates to deliverable D3.1: *Direct simultaneous anodic Co-oxide and cathodic Ni recovery in the HCl-route*. Chapter 1 outlines the research approach of the eNiCoN project and its Tasks 3.1.1 and 3.1.2.

It is critical to understand the fundamentals of anodic oxidation of cobalt and thus, both thermodynamic analysis (Chapter 2.1) and kinetics of Co-oxidation are studied (Chapter 2.2): such a profound understanding contributes to both eNiCoN **Task 3.1.1. Direct cobalt recovery as oxide along cathodic nickel recovery from Co/Ni-rich solution** and **Task 3.1.2 Direct recovery Co-oxide product on anode from purified Co-solution**. This knowledge creates a solid background for the further studies on anodic oxidation of Co in solutions such as e.g. solutions simulating mixed-hydroxide precipitate (MHP) or other industrially relevant multi-metal solutions (Chapter 2.3): this work contributes mainly to **Task 3.1.1. Direct cobalt recovery as oxide along cathodic nickel recovery from Co/Ni-rich solution**.



In Discussion Chapter 3 the advantages and disadvantages of different recovery steps are presented, and finally, Conclusions (Chapter 4) proposes the decision for the next steps, to contribute for Co recovery validation in eNiCoN project WP3: *Ni/Co ultrarefining to battery-grade Ni/Co precursors*.

### 1.2 Link of this deliverable to eNiCoN Objectives

One of the primary eNiCoN project objectives is “*To develop a Direct Oxide Recovery process as downstream unit operation for the envisaged flexible, next-generation HCl-based route that can be used as an alternative for the state-of-the-art processing routes for sulphide ores (pyro) & laterite ores (pyro & HPAL). (Obj4 – Direct Oxide Recovery)*”.

### 1.3 Goal of the work

In order to try to reach this objective, different technology readiness routes have been investigated as a methodology for more efficient and sustainable cobalt and nickel recovery. Although it has been previously suggested that both cathodic cobalt recovery and anodic oxidative cobalt recovery are thermodynamically and technically possible from hydrometallurgical solutions, such processing routes - and possible, related side reactions - have not been investigated in detail within the metallurgical industry. Consequently, this approach was selected as a low technology readiness level (TRL) level route to be investigated as an alternative recovery route for cobalt that could be potentially further developed.

The goal of this deliverable is to study the electrochemical oxidation behaviour of cobalt to evaluate and ascertain research, which offer the most promise for future industrial-scale application: can impure solutions be utilised in the anodic cobalt oxidation: is the proposed route in T3.1.1 *Direct cobalt recovery as oxide along cathodic nickel recovery from Co/Ni-rich solution* possible or should anodic oxidation of cobalt be performed only from purified solutions as stated T3.1.2: *Direct recovery Co-oxide product on anode from purified Co-solution*). The research has concentrated on the following aspects:

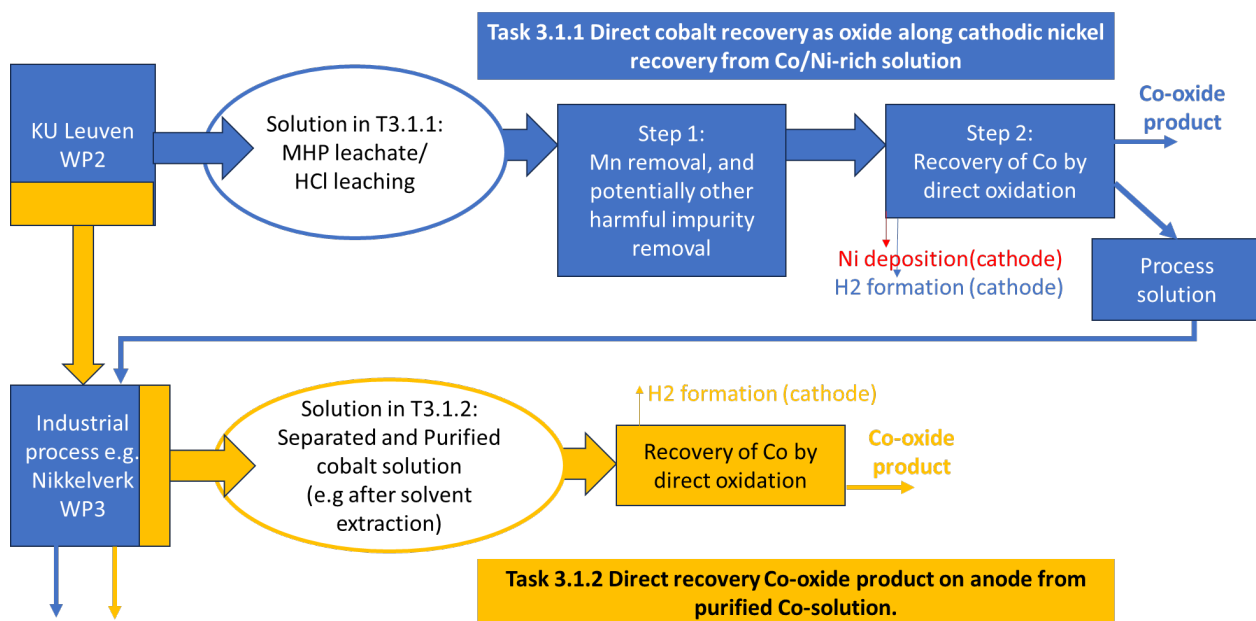
- **The fundamentals of Co-oxidation, i.e. thermodynamic analysis and kinetics of anodic oxidation of cobalt.** This work contributes to both eNiCoN *Task 3.1.1. Direct cobalt recovery as oxide along cathodic nickel recovery from Co/Ni-rich solution* and *Task 3.1.2 Direct recovery Co-oxide product on anode from purified Co-solution*.
- **The effectiveness of an electrochemical route for Co oxide recovery on anode from multi-metal Co/Ni-rich solution in the presence of impurities.** Here, a two-step approach may be needed *i.e.* before the recovery step (Step 2), impurity removal step(s) may be conducted (Step 1). This work contributes to eNiCoN *Task 3.1.1. Direct cobalt recovery as oxide along cathodic nickel recovery from Co/Ni-rich solution*.

This deliverable contributes to Objective 4 through evaluation of direct simultaneous anodic Co-oxide and cathodic Ni recovery in the HCl-route success (cf. T3.1.1) and by determining the decision to select the processing strategy (T3.1.1 vs. T3.2.2) for further Co recovery validation.

### 1.4 Presentation of two cobalt recovery strategies

Two strategies for cobalt recovery were evaluated. The schematic presentation of different steps of strategies, obtained products and used solutions are presented in the Fig.1.





**Fig. 1.** Outline of the research presented in this deliverable; blue relates to Task 3.1.1 and yellow to Task 3.1.2.

Task 3.1.1 (Fig. 1, blue) focuses on investigating selective electrochemical Co-recovery from (synthetic) hydrometallurgical solutions which contain impurities. In this case, the targeted cathodic reaction is direct Ni recovery due to the use of lower cell voltage *cf.* H<sub>2</sub> evolution. If successful, the solvent extraction stage typically required prior to Co recovery could be avoided, which could lead to reduced levels of required CapEx and OpEx as well as the associated environmental burden related to processing. In the research plan the potential co-precipitation of Ni-oxides or Mn-oxides were suggested to be addressed with pH and potential control when possible. Results showed that a common impurity element, manganese, competes strongly with cobalt anodic deposition thereby preventing selective cobalt recovery. Consequently, a separate electrochemical Mn removal step was instigated prior to cobalt removal, *i.e.* a two-step process was investigated as follows:

- **Step 1:** uses a Co-Ni solution with typical process impurities of Mn, Zn, Al, and Si (Step 1 in Fig. 1) to assess oxidative Mn removal. Two alternative electrochemical set-ups were used:
  - A one-chamber cell set-up and potentiostatic recovery or
  - A two-chamber cell set-up and galvanostatic recovery.
- **Step 2:** is conducted in Mn-free solution, *i.e.* Co-Ni solution with impurities of Zn, Al, and Si. This step relates to anodic cobalt recovery from solution: the selectivity and cathodic reactions are also investigated.

T3.1.2 (Fig. 1, yellow) addresses the direct electrochemical recovery of cobalt via oxidation from already purified cobalt solutions, with H<sub>2</sub> formation expected as the reciprocal cathode reaction. In the current work cobalt oxidation was undertaken by applying potentiostatic (electrical potential controlled) techniques in synthetic cobalt chloride solution simulating purified hydrometallurgical process solutions.

Along with the original hypothesis, cobalt oxide could be recovered selectively as a mixture of Co<sub>3</sub>O<sub>4</sub>, CoOOH, Co(OH)<sub>3</sub> on anode from multi-metal solutions that also contained nickel and some other impurities. The following chapters outline the key experimental results related to investigated processing strategies.





## 2. Recovery of cobalt on anode: kinetics of Co oxidation and effect of impurities

In order to make a new unit operation for a selective recovery of Co from multi-metal solutions, understanding of possible reaction pathways and kinetics is needed. Therefore, thermodynamic analysis and studies on kinetics of Co-oxidation were performed. Fundamental knowledge gained in these studies benefits both **Task 3.1.1. Direct cobalt recovery as oxide along cathodic nickel recovery from Co/Ni-rich solution** and **Task 3.1.2 Direct recovery Co-oxide product on anode from purified Co-solution**.

### 2.1 Thermodynamic Analysis

The solution used may contain multiple elements such as Co, Ni, Mn, Zn, Al and Si ions, of which Ni and Mn are considered providing most likely the competing reactions for Co-oxidation via anodic recovery. Therefore, thermodynamic analysis calculated by using HSC Chemistry software shows Pourbaix diagrams (Fig. 2) for cobalt, nickel, and manganese at 60 °C. The concentrations for Co, Ni and Mn used were 55 g/L, 30 g/L and ~2 g/L, respectively.

#### Cobalt

The diagram shows that dissolved cobalt, as complexed cobalt chloride, is likely to form  $\text{Co}_3\text{O}_4$  at potentials higher than 0.6 V vs. Ag/AgCl in a pH range 3-6. The formation of cobalt is possible within the stability area of water in solutions which are similar to eNiCoN process solutions. Increase in pH increases the likelihood and required potential for cobalt deposition. This finding is equally valid also in solutions where no impurities is present. From a thermodynamics point of view, when observing cobalt solution alone, the expected cathodic reaction is water decomposition *i.e.*  $\text{H}_2$  formation at the cathode. Similarly, the increase in pH is suggested to benefit the process.

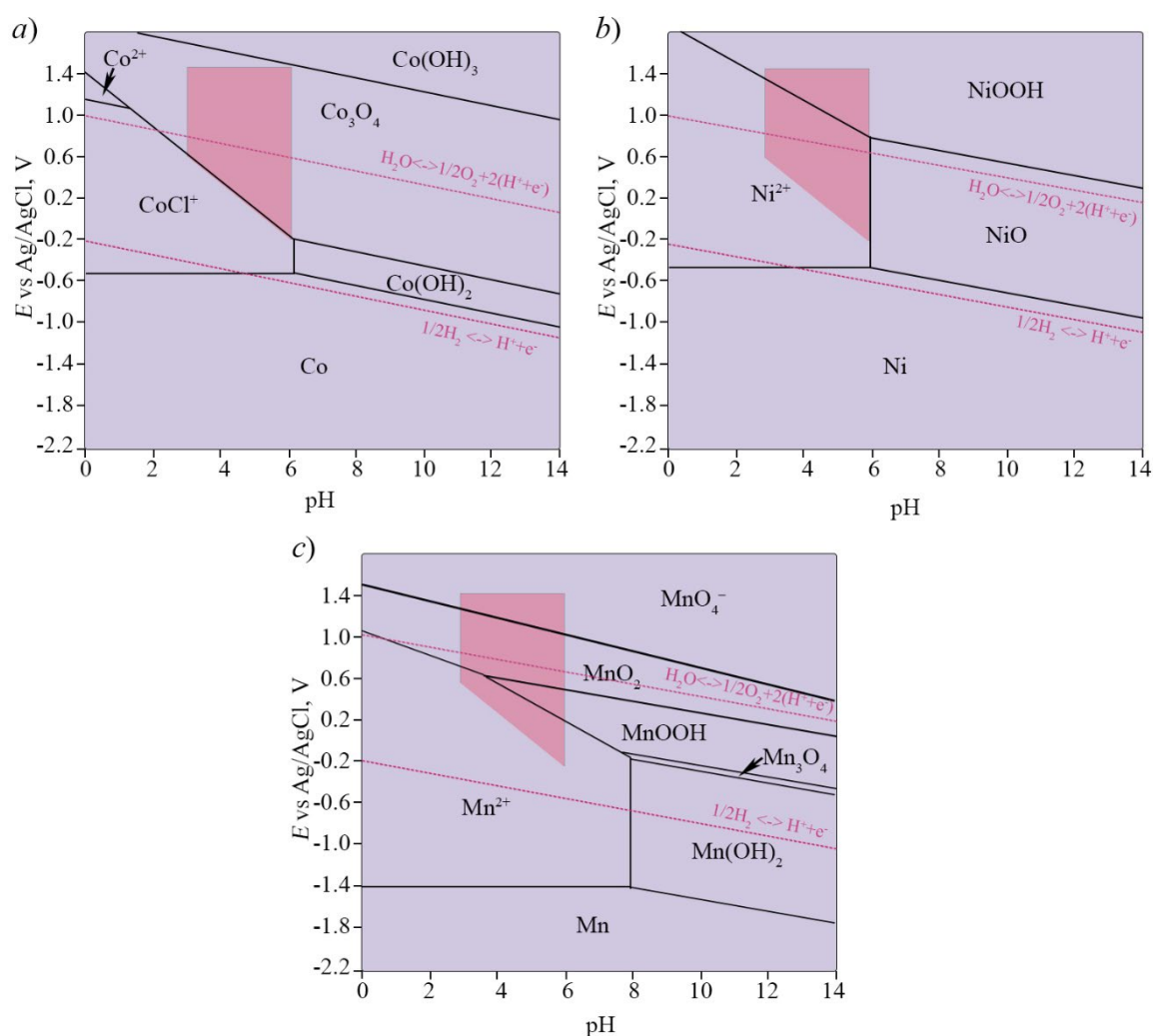
#### Nickel

In similar conditions, nickel oxidation ( $\text{NiOOH}$  formation) occurs at a potential range 0.9 – 1.4 V vs. Ag/AgCl. These values are above the stability area of water, therefore it is thermodynamically more likely that water starts to decompose *i.e.* oxygen formation occurs, when compared to nickel oxidation. This suggests that nickel present in the solution would not most likely compete with cobalt oxidation but would remain as soluble as  $\text{Ni}^{2+}$  in the solution.

#### Manganese

According to Pourbaix diagram, divalent manganese – even at low concentrations (2 g/L) has tendency to oxidize from  $\text{Mn}^{2+}$  to  $\text{MnO}_2$ . Thermodynamically cobalt oxidation is more likely; however, Mn oxidation is possible and this increases with a rise in pH. However, the pH-oxidation dependency is stronger for cobalt when compared to that of manganese.





**Fig. 2.** Pourbaix diagrams of (a) Co (55 g/L  $\text{Co}^{2+}$ ), (b) Ni ( $\sim 30$  g/L  $\text{Ni}^{2+}$ ), (c) Mn ( $\sim 2$  g/L  $\text{Mn}^{2+}$ ) at 60 °C chloride solution (CoOOH was neglected due to a lack of available data).

Pink area – preferred zone for cobalt oxide recovery.

In order to conclude the thermodynamical analysis; Fig. 2 suggests that in multi-metal solutions similar to eNiCoN process solutions, manganese indeed can compete with oxidative cobalt recovery. The experimental work conducted indeed confirmed this hypothesis as well as thermodynamical order, where dissolved nickel remains in the solution within the stability area of water and does not oxidize.

## 2.2 Kinetics of Co oxidation

The results in Chapter 2.2. are available in open access publication [18]: I. Makarava, J. Vänskä, A. Kramek, J. Ryl, B.P. Wilson, K. Yliniemi, M. Lundström “Electrochemical cobalt oxidation in chloride media”, *Minerals Engineering* **211** (2024) 108679. <https://doi.org/10.1016/j.mineng.2024.108679>.

Thermodynamical analysis (HSC Chemistry) of the most favourable process conditions was conducted (potential-pH-metal concentrations) to support selective electrochemical Co-oxide recovery). Higher pHs are linked to cobalt hydroxides and/or higher temperatures and anodic potentials to oxides: therefore the precipitation of cobalt can take place in any of  $\text{Co}_3\text{O}_4/\text{Co}(\text{OH})_2/\text{CoOOH}$  forms in the studied conditions.



### 2.2.1 Experimental conditions: Kinetics of Co-oxidation

A typical three-electrode cell (with a one-chamber set-up) was used in the recovery of Co-oxide: the cell comprises saturated silver/silver chloride (Ag/AgCl) as a reference electrode, platinum (Kultakeskus Oy, Finland) both as a counter electrode and as a working electrode. Electrochemical measurements were performed with IviumStat 24-bit CompactStat potentiostat (Ivium Technologies, Netherlands). Cobalt chloride was used for solution preparation and the solution composition mimics an industrial hydrometallurgical process electrolyte. Table 1 outlines the solutions used to investigate Co recovery.

**Table 1.** Solution composition (g/L) investigated in [18].

Solution	Co (g/L)	Cl (g/L)	Na (g/L)	T (°C)	pH
<i>Solution 1</i>	55	65	–	20–60	1–6
<i>Solution 2</i>	5.5	6.5	–	60	3
<i>Solution 3</i>	55	72.5–100.5	2.3–23	60	3

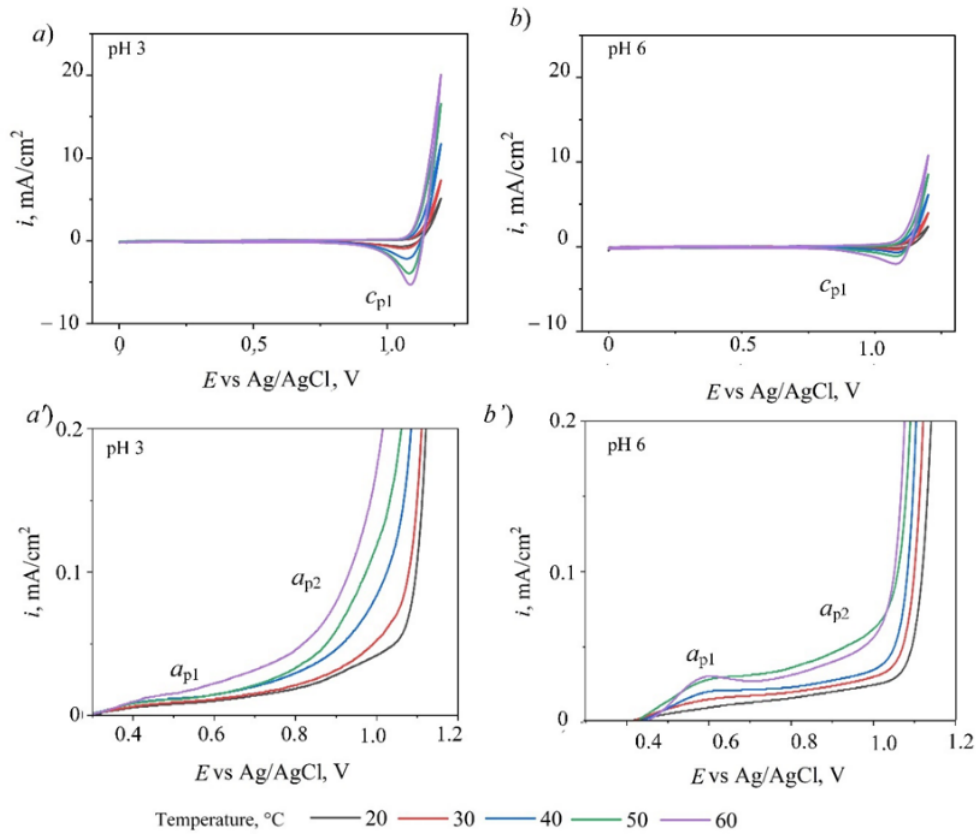
During the experiments, solution pH, cell voltage, and potentials of the electrodes as a function of time were measured. The pH of the solution was monitored using a pH meter (Seven Excellence, Mettler Toledo), and the temperature of the electrolyte was controlled by a thermostatic water bath (Isotemp, Fisher Scientific, U.S.A.). Products of anode reaction were analysed by chemical analysis (total leaching + ICP-OES (5900 SVDV, Agilent, US)), SEM (Mira<sup>2</sup> Tescan GM (Czech Republic)-EDS (Thermo Fisher Scientific, U.S.A.), XRD (Bruker D8 Advance, Germany), XPS (ThermoFisher Scientific, U.S.A.), TGA (Netzsch STA 449 F3 Jupiter & QMS 403 Aëolos Quadro, Germany), AFM (MultiMode 8, Bruker, U.S.A.) and weighing. Cyclic voltammetry was undertaken in all solutions to study the electrochemical oxidation of cobalt. The current efficiency for the anodic reaction was calculated.

### 2.2.2 Results: Kinetics of Co-oxidation

According to the indicative Pourbaix diagram calculations, Fig.2a, it was identified that the increase of pH, the concentration of cobalt, and temperature has a positive effect on the oxidation process, thus cyclic voltammetry was implemented to identify kinetics and mechanism of cobalt oxidation.

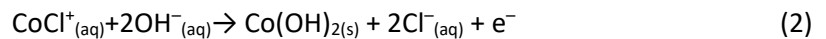
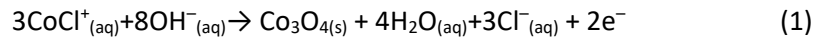
Cobalt oxidation reactions in *Solution 1* occur in 0.3 V-1.15 V vs. Ag/AgCl (Fig. 3) and the increase in temperature (from 20 to 60 °C) leads to changes in the anodic and cathodic current densities at both pH 3 and 6. Also, small shoulders (up to 0.15 mA/cm<sup>2</sup>) related to oxidation were detected in the voltammograms in the potential range from 0.9 to 1.15 V vs. Ag/AgCl while a more substantial and rapid current increase is clearly evident at potentials higher than 1.15 V vs. Ag/AgCl. These results can be explained by higher local pH at higher temperature [10], and higher selectivity of Cl<sub>2</sub> rather than O<sub>2</sub> formations [19–21], which all benefits cobalt oxide formation: the increase in solution pH slightly increases the size (current density) of the first oxidation peak ( $a_{p1}$  at  $E \sim 0.6$  V vs. Ag/AgCl). These results indicate that the stability of the oxide/oxyhydroxide layer [22], which can be predicted as the major cobalt product within this potential range, is increased with higher temperatures. Interestingly, the anodic current is very similar at temperatures 50 and 60 °C at pH 6, Fig. 3b, which indicates than something else than kinetics is affecting the deposition process. As Co<sub>3</sub>O<sub>4</sub>/Co(OH)<sub>2</sub>/CoOOH are more insulating in nature and such a behaviour may be a result of surface passivation due to the deposited Co oxides.



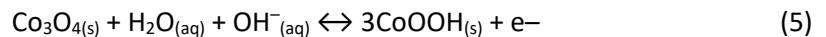
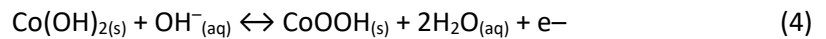
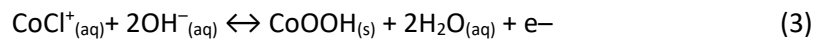


**Fig. 3.** (a, b) Cyclic voltammetry at pH 3 and pH 6 (scan rate of  $25 \text{ mV}\cdot\text{s}^{-1}$ ) with  $55 \text{ g/L Co}^{2+}$  and  $65 \text{ g/L Cl}^-$  at  $T = 20 - 60 \text{ }^\circ\text{C}$ . (a', b') magnified range potential range [18].

The anodic peaks  $a_p$  in the Fig. 3 around  $0.9 \text{ V vs. Ag/AgCl}$  are expected to be associated with  $\text{Co}_3\text{O}_4/\text{Co}(\text{OH})_2$  film formation by Eq. 1 and 2 [23]:



Equations 3 - 5 highlights the oxidation of  $\text{CoCl}^+/\text{Co}(\text{OH})_2$  or  $\text{Co}_3\text{O}_4$  into  $\text{CoOOH}$  [24], which is evident at oxidation potentials higher than  $1.15 \text{ V vs. Ag/AgCl}$ :

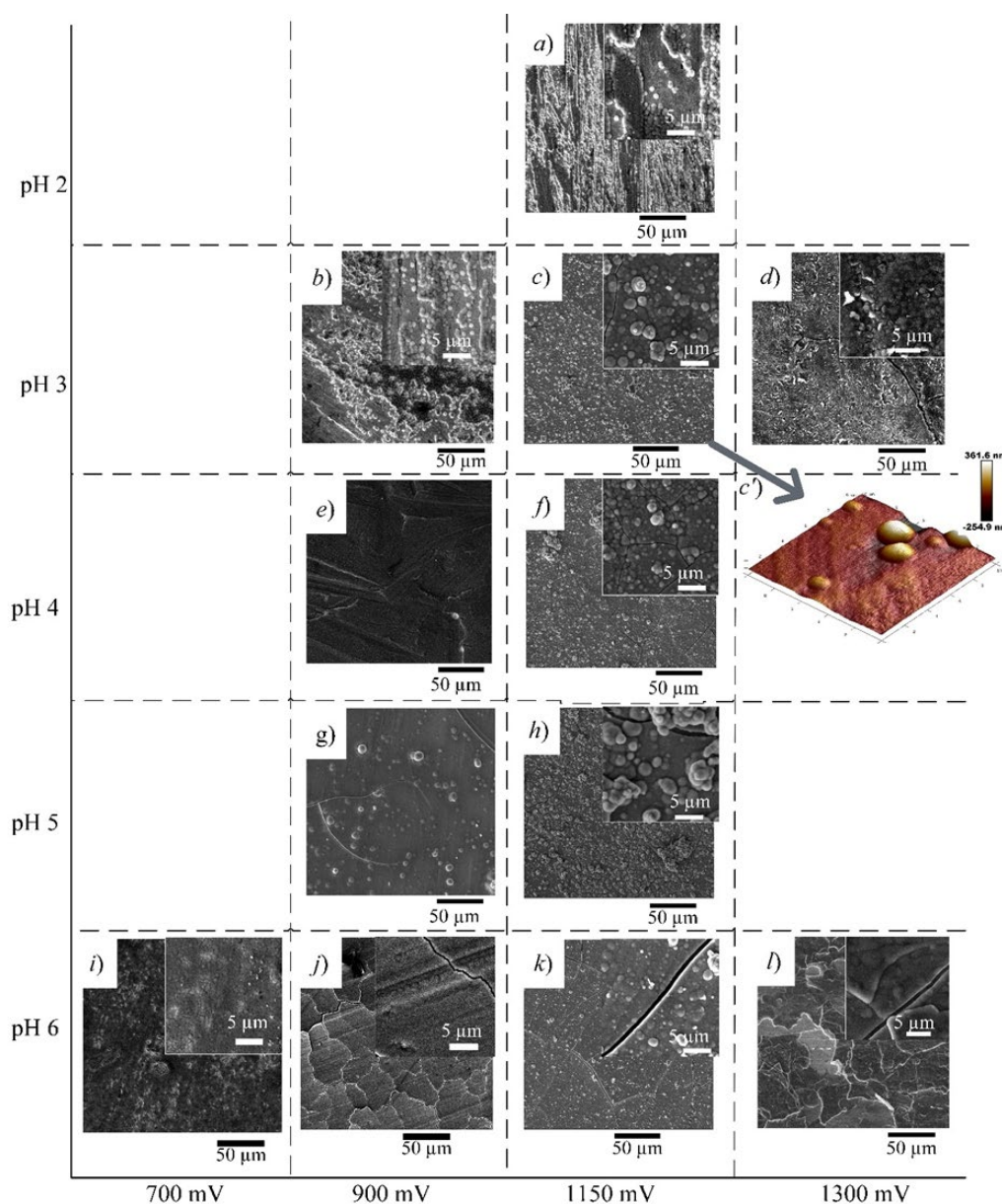


As Fig. 3 shows also a reduction peak  $c_{p,1}$ , the reactions 3-5 can take place to the reverse direction and  $\text{CoOOH}$  can be reduced to  $\text{CoCl}^+/\text{Co}(\text{OH})_2$ . Therefore it can be concluded that a mixed oxygen-based cobalt (most likely containing oxides and hydroxides) can precipitate on a Pt electrode surface by anodic potentiostatic deposition. However, the calculated efficiency in cobalt recovery was low ( $< 1\%$ ) and this also supports the idea that the anode is passivated during the deposition process.



Morphology of anodically deposited mixed cobalt oxide (deposited at 1150 mV vs. Ag/AgCl) was found to be relatively flat with cracks and did not show any noticeable pH dependence (SEM data in Fig. 4). The deposit was black in colour at  $pH = 3-6$  and at potential  $\geq 900$  mV vs. Ag/AgCl, whereas at lower potentials, no formation of deposits was observed.

EDS analysis indicates the presence of higher cobalt oxidation states [25] in  $pH = 2-6$  as the oxygen content in the cobalt precipitate increases from 60 to 80 %, and the stoichiometric ratio (Co:O) increases from 1:2 to 1:4 in this pH range due to increased level of oxygen in Co sites. Kouidri *et al.* [26] have also reported similar findings. In order to effectively utilise the electrons for cobalt oxide formation, rather than  $O_2$  formation, high Co concentration ( $\sim 55$  g/L) are preferred. Deeper analysis of potentiostatic results also indicated instantaneous oxide film growth at 1300 mV vs. Ag/AgCl [27], while XPS confirms that three forms of cobalt -  $Co_3O_4$ ,  $\alpha-Co(OH)_2$  and  $\gamma-CoOOH$  – are present rather than a single Co oxide form [28,29].



**Fig. 4.** (a–f) SEM of cobalt precipitate in 55g/L  $Co^{2+}$  solution  $T = 60$  °C at different potentials and pH; (c') AFM of cobalt precipitate in at 1150 mV, pH 3 [18].



## 2.3 Multi-metal solutions

In order to create a viable process for Co recovery by anode oxidation, the effect of impurities needs also to be studied. Therefore, the anodic oxidation of Co is studied also in solution compositions simulating mixed-hydroxide precipitate (MHP), *i.e.* in multi-metal solutions and this research contributes mainly to **Task 3.1.1. Direct cobalt recovery as oxide along cathodic nickel recovery from Co/Ni-rich solution.**

### 2.3.1 Experimental conditions: multi-metal solutions

The Co chloride solution was used as a base solution to which different impurity metals (Zn, Si, Mn, Al) and Ni were added. Co concentration was ~55 g/L and chloride concentration ~66 g/L, while pH of the solution was either 1, 3 or 6: these are very similar solution compositions that were used to study Co recovery. The concentration of Ni was kept below ~30 g/L, while concentration of other impurities (Mn, Al, Si) was ~2 g/L or less. Also, sodium (~66 g/L) and sulphate were present in the system.

A typical three-electrode cell with saturated Ag/AgCl as a reference electrode and two platinum electrodes (Kultakeskus Oy, Finland) as working and counter electrodes were used with IviumStat 24-bit CompactStat potentiostat (Ivium Technologies, Netherlands). Solution pH, cell voltage, potentials of the electrodes, and metal concentrations as a function of time were measured in all experiments. The pH of the solution was monitored using a pH meter (Seven Excellence, Mettler Toledo), and the temperature of the electrolyte was controlled by a thermostatic water bath (Isotemp, Fisher Scientific, U.S.A.). Anodic products were analysed by chemical analysis (total leaching + ICP-OES (5900 SVDV, Agilent, US)), SEM (Mira<sup>2</sup> Tescan GM (Czech Republic)-EDS (Thermo Fisher Scientific, U.S.A.), XRD (Bruker D8 Advance, Germany) and weighing, and the current efficiency for the anodic reaction was calculated. The final chemical compositions of the deposit (as atom percent) comprise of average EDS values from 10 point/area spectra. The leachate residues were quantified by ICP-OES. The samples of anodic deposits (0.1 g) prior ICP analysis were weighed and dissolved in a mixture of HCl and HNO<sub>3</sub> and filled with distilled water until 50 mL. The ICP measurement was performed in a mixture of 5% HNO<sub>3</sub> (Ultrapure, Merck). Blank samples were assayed and subtracted from the analysis of the sample. The value of the sample was considered zero in the case subtraction generates a negative number. The relative standard deviation of all ICP measurements was less than 3.6%. Cyclic voltammetry, potentiostatic deposition and galvanostatic deposition on the surface of Pt electrode were undertaken in all solutions to study the electrochemical manganese and cobalt oxidation.

Potentiostatic deposition was carried out in a one-chamber cell and galvanostatic electrolysis in a two-chamber cell. The anolyte in two-chamber cell was the simulated MHP leachate and the catholyte was sodium sulphate solution.

### 2.3.2 Results: multi-metal solutions

The thermodynamic analysis (Chapter 2) as well as the cyclic voltammetry studies in solutions containing impurities indicated that indeed the most problematic impurity in the solution is Mn. When Mn is added to Co solution, the anodic current density increases already at potentials <1.0 V vs. Ag/AgCl, showing that also Mn can be oxidised on the anodic process. This also confirms the hypothesis shown in Pourbaix diagrams and suggests that manganese not only thermodynamically but also kinetically competes with oxidative cobalt precipitation.

When the composition of the anode deposits obtained after potentiostatic anodic oxidation was studied with EDS, it was found out that Mn does not only compete with anodic Co deposition, but it dominates the process as Mn at% (10-25at%) is double when compared to Co at% (4-10 at%). Some Al and Ni was also observed in the anodic deposits but clearly at lower at% levels (<1 at%). However, cathode seems to be clear of the



deposits, suggesting that Ni reduction does not act as a cathodic counter (Fig. 1., red text), unlike originally postulated but instead, H<sub>2</sub> is formed.

The strong oxidation behaviour of Mn creates a clear challenge for anodic recovery of Co and leads to one of the main results in this task - impurity removal steps must be performed before Co-recovery. Therefore, a two-step process is postulated:

- **Step 1:** Impurity removal, targeting Mn removal
- **Step 2:** Anodic recovery of Co-oxides

### **Step 1 – Mn removal**

The manganese oxidation was found to be the dominating process in impure solution of **Co, Ni, Mn, Zn, Al and Si** and therefore manganese needs to be conducted prior cobalt recovery. An electrochemical route was tested for manganese oxide recovery from a solution simulating MHP leachate. Increase in temperature resulted in a corresponding increase in the rate of oxidation of manganese, when using the one-chamber set-up. Even if MnO<sub>2</sub> was recovered with high purity (close to 80 %, Co) the efficiency of the removal was only appr. 5 %. Therefore, also a two-chamber cell was investigated as an alternative cell set-up for manganese oxide recovery. A significant increase in the recovery of MnO<sub>2</sub> was found to take place in a two-chamber cell, reaching over 80 % MnO<sub>2</sub> recovery, but with a lower purity (<80 %). Alternatively, any state-of-the-art Mn removal route used in industry can be applied, e.g. based on chemical oxidation using SO<sub>2</sub>+O<sub>2</sub> in order to enable manganese to be removed efficiently prior subjecting solution for the targeted oxidative cobalt recovery.

### **Step 2 – Co recovery**

Electrochemical cobalt oxidation was studied in a synthetic, **impure but Mn-free solution** in Step 2 (**Co, Ni, Zn, Al and Si**). The cyclic voltammetry studies suggested that the increase of pH, concentration of cobalt and temperature can facilitate cobalt oxidation, which is in line with thermodynamical analysis. Similarly to pure Co solution (Task 3.1.2) anodic potentiostatic deposition showed that a mixed oxygen-based cobalt (Co<sub>3</sub>O<sub>4</sub>, α-Co(OH)<sub>2</sub> and γ-CoOOH) precipitate could be recovered on a Pt substrate surface, but also in this case efficiency of the process is low (<1%). This is believed to be due the anode passivation, which was also the limiting factor for Co-recovery from pure solutions. Moreover, no other metal deposition was observed in cathode which indicates that simultaneous Co recovery on anode and Ni recovery on cathode is not possible (Fig. 1, red text), and we postulate that the cathodic reaction is H<sub>2</sub> evolution.

Also, aluminium was detected in the anodic precipitate while the presence of other metals (Ni, Zn or Si) was not detected. This result is extremely interesting as in the typical separation processes, it is difficult to selectively recover Co without the presence of Ni in the deposits.

## **2.3 Summary of Research in T3.1.1 and T3.1.2**

Research presented here contributes to **Task 3.1.1 Direct cobalt recovery as oxide along cathodic nickel recovery from Co/Ni-rich solution (AALTO, Nikkelverk) | (M1-45)** and **Task 3.1.2 Direct recovery Co-oxide product on anode from purified Co-solution (AALTO) | (M13-45)**.

The results demonstrate a successful direct cobalt oxide recovery by anodic oxidation, in the form of a mixed cobalt oxides and hydroxides, namely Co<sub>3</sub>O<sub>4</sub>, α-Co(OH)<sub>2</sub> and γ-CoOOH. However, the efficiency of this approach was calculated to be only 1% or less, and as a result, the future research should focus on preventing the passivation of anode to enhance the efficiency. Furthermore, these results show that cobalt oxide recovery is successful in the solution free of Mn impurity but in the presence of other impurities, and there is also selectivity against nickel *i.e.* nickel oxide is not competing during anodic deposition. As a result, a two-



step process is necessary for successful anode oxidation of Co: Mn (and possibly Al) must be removed from the solution (Step 1) before anodic Co oxidation for cobalt recovery (Step 2). Mn removal can be addressed electrochemically either in a one-chamber cell or in a two-chamber cell, and the process can be driven potentiostatically or galvanostatically. Alternatively, any industrially used state-of-the-art method can be used for Mn removal. Also, Al removal e.g. via pH adjustment – as suggested in the original research plan – may facilitate higher purity Co-oxide recovery.

### 3. Discussion

Advantages and disadvantages of different steps (Fig.1), as well as metal species present in the experimental solutions used, final products composition, efficiency of recovery and purity of MnO<sub>2</sub> are shown in Table 2.

**Table 2.** Advantages and disadvantages of anodic Co-oxide recovery from multi-metal and pure solutions.

Task	Step	Solution	Advantages	Disadvantages	Final product
<b>Task 3.1.1</b>	<b>One cell configuration in Step 1:</b> Selective electrochemical removal of Mn in a form of MnO <sub>2</sub>	Co, Ni, Mn, Zn, Al and Si	Selective recovery of manganese	-Efficiency of Mn removal low (<5%). -Final product purity high (> 80%)	Anode: MnO <sub>2</sub> with impurities of Co, Al and Ni. Cathode: H <sub>2</sub>
	<b>Two-cell configuration in Step 1:</b> Selective electrochemical removal of Mn in a form of MnO <sub>2</sub>		Higher efficiency of manganese removal (> 80 %).	-Lower final product purity (<80 %)	Anode: MnO <sub>2</sub> with impurities of Co, Al and Ni. Cathode: H <sub>2</sub>
	<b>Step 2:</b> Selective electrochemical recovery of cobalt oxide product on anode from purified Mn-free MHP leachate	Co, Ni, Zn, Al and Si	Selective recovery of cobalt without metal loss as cathodic deposit.	- Low efficiency of electro-oxidation of cobalt (<1%) due to passivation of anode.	Anode: Mixture Co <sub>3</sub> O <sub>4</sub> , CoOOH, Co(OH) <sub>3</sub> with impurity of Al. Cathode: H <sub>2</sub>
<b>Task 3.1.2</b>	<b>Direct recovery</b> cobalt oxide product on anode from purified Co-solution	Co	Selective recovery of manganese	Low efficiency of electrooxidation of cobalt (<1%) due to passivation of anode.	Anode: Mixture Co <sub>3</sub> O <sub>4</sub> , CoOOH, Co(OH) <sub>3</sub> . Cathode: H <sub>2</sub>

Direct Co oxide recovery process (from impure T3.1.1 and pure T3.1.2 solutions) was studied, **and it was found out the mixture of Co<sub>3</sub>O<sub>4</sub>, CoOOH, Co(OH)<sub>3</sub> is the main product of cobalt oxidation process on the anode** while hydrogen evolution was found to be cathodic reaction. Due to passivation of anode a low efficiency of Co oxidation is observed, and thus the main focus of future research will be improvement of efficiency of Co oxidation by preventing anode passivation.





Two-step procedure needs to be implemented in impure solutions:

- 1) Mn removal either in a one-chamber or two-chamber set up (Step 1)
- 2) Recovery of cobalt (Step 2).

Step 1 of MnO<sub>2</sub> removal can be performed electrochemically (by potentiostatic and by galvanostatic deposition). In tested electrochemical removal of Mn, potentiostatic deposition of MnO<sub>2</sub> allowed to higher purity but clearly lower efficiency, while galvanostatic deposition reached over 80 % oxide recovery but <80 % purity. Any other industrially applicable Mn removal can be alternatively applied. Step 2 showed selectivity of Co oxide recovery in Mn-free solution along with H<sub>2</sub> evolution on cathode *i.e.* Ni deposition as cathodic reaction could not be realized. The low efficiency in Step 2 is related to the passivation of anode.

### 3.1 Selection of future research strategy

Along the experimental work conducted we have found the following focus areas for eNicoN Research in Task 3.1:

**1. Impurities.** The research presented in this deliverable shows that Mn is the most challenging impurities in the selective anodic recovery of Co. Also, Al may co-precipitate from impure solutions. However, there is a positive indication that anodic nickel deposition – which is the main challenge in a typical Co and Ni separation process - is not competing with anodic Co deposition. This gives a high promise that anodic Co-recovery may be selective also in multi-metal solutions, after Mn and possible Al removal either by electrochemical or by the methods already used in industry.

**2. Anode passivation occurs in both investigated processing strategies.** In this respect both impure (used in T3.1.1) and pure (used in T3.1.2) solutions have currently the same weakness. Our main future focus is to prevent the passivation of the electrodes. Therefore, a combination strategy is proposed for further research: the passivation of anode needs to be addressed before Co-recovery either from pure or impure solutions can be implemented.

**3. Cathode reaction is not selective nickel deposition as initially hypothesised.** In this respect both routes behave currently similarly, as no nickel deposition occurs at the cathode and there is no advantage over the impurities present in the system, but H<sub>2</sub> formation occurs instead in both systems. Therefore, it is suggested that cathodic reaction is not considered anymore as the decision point for the strategy selection.

The original application stated that this technical report would provide a clear decision between T3.1.1 (Co solutions with impurities but Ni reduction as cathode reaction) or T3.1.2 route (pure Co solution with H<sub>2</sub> evolutions as cathode reaction). **The current results, however, indicate that the best approach – when thinking about the holistic processing – is to study impure solutions (T3.1.1) but aiming at H<sub>2</sub> as cathodic reaction (like in T3.1.2). Strategy T3.1.1. further requires a two-step route, *i.e.* Mn and possibly Al removal (Step 1) before Co recovery (Step 2).** Here, typical impurity removal steps used in industrial operations for Mn or Al recovery may be also applied instead of the electrochemical recovery. Also, anodic Co recovery will be in focus, and especially, the prevention of anode passivation. This approach is selected because the main challenge with impure solutions does not seem to be other impurities than Mn and Al but rather, the passivation of the anode due to more insulating nature of Co<sub>3</sub>O<sub>4</sub>, CoOOH, Co(OH)<sub>3</sub>. Thus, by solving the issues related to the anode passivation e.g. via mechanical and electrochemical methods can increase the efficiency Co recovery by anodic oxidation both from impure and pure solutions and this is independent of cathodic reaction.



## 4. Conclusions

Fundamental aspects of the direct Co-oxide recovery process by anodic oxidation showed that recovery of mixed form Co oxides and hydroxides is possible with the anodic oxidation:  $\text{Co}_3\text{O}_4$ ,  $\text{CoOOH}$ , and  $\text{Co}(\text{OH})_3$  were the main products of cobalt oxidation. However, the recovery efficiency was low (<1%) due to the anode passivation by the Co oxide and hydroxide products.

When evaluating cobalt recovery from impure solutions, the primary finding was that  $\text{MnO}_2$  is the predominant product of the oxidation process when multi-metal solutions are treated. Therefore, a two-step process was suggested:

- Step 1: Impurity removal, with focus on Mn
- Step 2: Recovery of Co by anodic oxidation

Step 1 can be performed electrochemically (potentiostatically in a one-cell or galvanostatically in a two-cell configuration) or by any industrially used Mn recovery methods. In the tested electrochemical removal method, a two-cell configuration resulted in over 80 % Mn removal efficiency. In Step 2 Co-oxide recovery from Mn-free solutions revealed potential for selective Co-oxide recovery without nickel impurities on the cobalt product. However, aluminium was found to be incorporated into the oxide precipitate. Manganese and aluminium were identified as competing with cobalt anodic deposition, necessitating their removal before cobalt anodic recovery can proceed effectively.

Even though Co-oxidation step exhibited low efficiency due to the anode passivation, a selectivity of cobalt oxidation over nickel and other metal impurities was observed when performing recovery from impure solutions. **Therefore, the work is suggested to be continued with focus on multi-metal solutions (modified T3.1.1), ensuring on Mn and Al removal, and focusing on selective cobalt recovery and overcoming the passivation of anode during the process.** The mitigation strategy for passivation includes both mechanical and electrochemical methods that can prevent the full coverage of the electrode surface.  $\text{H}_2$  will be the main cathodic reaction which was initially aimed in T3.1.2 but is equally competitive in Strategy T3.1.1.



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