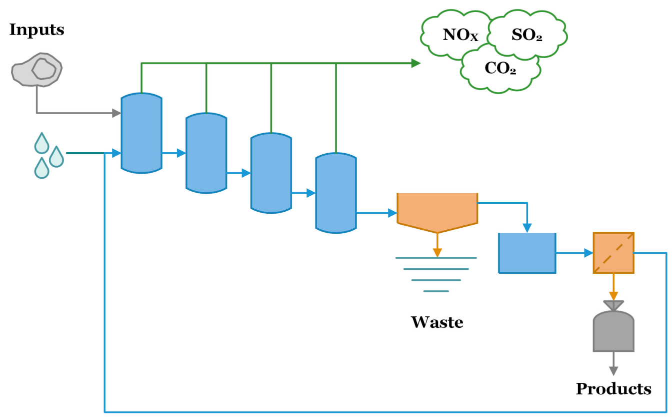
Department of Chemical and Metallurgical Engineering

Prospective life cycle assessment of hydrometallurgical cobalt processes for the battery value chain

Marja Rinne



Aalto University

DOCTORAL THESES

Aalto University publication series
DOCTORAL THESES 164/2024

Prospective life cycle assessment of hydrometallurgical cobalt processes for the battery value chain

Marja Rinne

A doctoral thesis completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Chemical Engineering, at a public examination held at the lecture hall Platinium of the school on 4 October at 12 o'clock.

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Hydrometallurgy and Corrosion

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Aalto University publication series
DOCTORAL THESES 164/2024

ISBN 978-952-64-1964-0 (printed)
ISBN 978-952-64-1965-7 (pdf)
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)
http://urn.fi/URN:ISBN:978-952-64-1965-7

Images: Marja Rinne

Unigrafia Oy
Helsinki 2024

Finland

Printed matter
4041-0619

Aalto University

Abstract

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Author
Marja Rinne

Name of the doctoral thesis
Prospective life cycle assessment of hydrometallurgical cobalt processes for the battery value chain

Publisher School of Chemical Engineering

Unit Department of Chemical and Metallurgical Engineering

Series Aalto University publication series DOCTORAL THESES 164/2024

Field of research Processing of Materials

Manuscript submitted 11 April 2024 **Date of the defence** 4 October 2024

Permission for public defence granted (date) 19 June 2024 **Language** English

☐ **Monograph** ☒ **Article thesis** ☐ **Essay thesis**

Abstract

The environmental impact of electrification has been debated due to the considerable increase in consumption of metals such as cobalt, nickel, manganese, and lithium. Although cobalt can be partly substituted in electric vehicle batteries with metals such as nickel, it remains a critical metal for energy transition and its demand is projected to increase. The sustainable supply of cobalt is dependent on the diversification of sources, including both mining and recycling. The goal of this study was to assess the impacts of emerging primary cobalt and lithium-ion battery recycling processes using a simulation-based life cycle assessment approach, which enables the modeling of prospective scenarios in high detail.

In this thesis, life cycle inventory data was obtained by simulating the selected flowsheets with HSC Sim software, and the impacts were calculated using GaBi. Scenario, contribution, and sensitivity analyses were used to aid interpretation of the results. Overall, six primary cobalt and four lithium-ion battery recycling scenarios were simulated based on several preliminary simulations that were used to guide flowsheet development. To be potentially industrially relevant, all scenarios utilize hydrometallurgical processing in sulfuric acid solutions.

According to the results, higher grade feeds result in lower impacts during hydrometallurgical processing, and optimizing the leaching conditions may effectively decrease the impacts. Although maximizing cobalt recovery is recommended for primary cobalt, it was observed for lithium-ion battery recycling processes that some valuable losses may be justifiable if this means that milder conditions can be applied. The results also suggest that solvent extraction chemicals may contribute more significantly to the environmental impacts than previously thought, and there is a critical need for primary life cycle inventory data from extractant manufacturers.

Simulation-based life cycle assessment was used to assess the impacts of the hydrometallurgical processing of cobalt-bearing raw materials in this research, but it is a suitable method for the evaluation of a wider array of raw materials and processes. The strength of the methodology lies in the ability to create high resolution inventories from limited experimental or literature data. However, it requires both metallurgical and life cycle assessment expertise to correctly justify assumptions and interpret the results for informed decision-making. This thesis presents the effect of some of the assumptions and process parameters in the impacts of hydrometallurgical processing and suggests improvements to further develop the studied processes.

Keywords simulation, environmental impacts, lithium-ion battery recycling, cobalt ores

ISBN (printed) 978-952-64-1964-0 **ISBN (pdf)** 978-952-64-1965-7

ISSN (printed) 1799-4934 **ISSN (pdf)** 1799-4942

Location of publisher Helsinki **Location of printing** Helsinki **Year** 2024

Pages 163 **urn** http://urn.fi/URN:ISBN:978-952-64-1965-7

A?
Aalto-yliopisto

Tiivistelmä

Aalto-yliopisto, PL 11000, 00076 Aalto www.aalto.fi

Tekijä
Marja Rinne

Väitöskirjan nimi
Koboltin hydrometallurgisten prosessien elinkaariarviointi akkujen arvoketjussa

Julkaisija Kemian tekniikan korkeakoulu

Yksikkö Kemian tekniikan ja metallurgian laitos

Sarja Aalto University publication series DOCTORAL THESES 164/2024

Tutkimusala Materiaalien prosessointi

Käsikirjoituksen pvm 11.04.2024 **Väitöspäivä** 04.10.2024

Väittelyluvan myöntämispäivä 19.06.2024 **Kieli** Englanti

☐ **Monografia** ☒ **Artikkeliväitöskirja** ☐ **Esseeväitöskirja**

Tiivistelmä

Sähköistymisen ympäristövaikutukset ovat herättäneet keskustelua, koska se kasvattaa metallien, kuten koboltin, nikkelin, mangaanin ja litiumin, kulutusta. Vaikka koboltti pystytään litium-ioniakuissa osittain korvaamaan muilla alkuaineilla kuten nikkelillä, se on edelleen kriittinen metalli energiasiirtymälle, ja sen kysyntä on kasvussa. Koboltin kestävä tuotanto riippuu lähteiden monipuolistamisesta sekä kaivostoiminnan että kierrätyksen saralla. Tämän tutkimuksen tavoitteena oli tarkastella kehittyvien koboltin primääri- ja litium-ioniakkujen kierrätysprosessien ympäristövaikutuksia käyttämällä simulaatioperusteista elinkaariarviointia, joka mahdollistaa kehittyvien prosessien yksityiskohtaisen mallintamisen.

Tässä väitöskirjassa elinkaariarvioinnin inventaarioanalyysi suoritettiin mallintamalla valitut prosessikaaviot HSC Sim-ohjelmalla, ja ympäristövaikutukset laskettiin GaBilla. Tulosten tulkinnassa hyödynnettiin skenaario-, kontribuutio-, ja herkkyysanalyysejä. Yhteensä kuusi primäärikoboltti- ja neljä litium-ioniakkujen kierrätysskenaariota mallinnettiin alustavien prosessisimulaatioiden perusteella. Kaikki skenaariot perustuivat hydrometallurgisiin prosesseihin rikkihappoliuoksissa, joten prosessit ovat mahdollisesti teollisuuteen soveltuvia.

Tulosten perusteella korkean arvoasteen raaka-aineet johtivat pienempiin ympäristövaikutuksiin hydrometallurgisissa prosesseissa, ja liuotusolosuhteiden optimointi saattaa laskea vaikutuksia tehokkaasti. Primäärikobolttiskenaarioiden perusteella koboltin saantoa kannattaa maksimoida, mutta toisaalta kierrätyskenaarioissa huomattiin, että arvometallien pienet häviöt voivat olla perusteltavissa, jos siten voidaan hyödyntää miedompia prosessiolosuhteita. Uuttokemikaalien vaikutusten prosessiin huomattiin olevan aiempaa luultua suurempia, ja olisikin kriittistä saada lisää primääri-inventaariodataa uuttokemikaalien valmistajilta.

Vaikka työssä hyödynnettiin simulaatioperusteista elinkaariarviointia arvioimaan kobolttia sisältävien raaka-aineiden hydrometallurgisen prosessoinnin vaikutuksia, metodologiaa voi hyödyntää laajemmin eri raaka-aineille ja prosesseille. Menetelmän vahvuus on, että sillä voidaan laskea korkean resoluution inventaariodataa vähälläkin kokeellisella tai kirjallisuusdatalla, mutta toisaalta menetelmä vaatii sekä metallurgian että elinkaariarvioinnin osaamista olettamusten perusteluun sekä tulosten tulkintaan. Tässä väitöskirjatutkimuksessa esitetään joidenkin olettamusten ja prosessiparametrien vaikutusta hydrometallurgisten prosessien ympäristövaikutuksiin ja tehdään ehdotuksia tutkittujen prosessien edelleen kehittämiseksi.

Avainsanat prosessimallinnus, ympäristövaikutukset, litiumioniakkujen kierrätys, kobolttimalmit

ISBN (painettu) 978-952-64-1964-0 **ISBN (pdf)** 978-952-64-1965-7

ISSN (painettu) 1799-4934 **ISSN (pdf)** 1799-4942

Julkaisupaikka Helsinki **Painopaikka** Helsinki **Vuosi** 2024

Sivumäärä 163 **urn** http://urn.fi/URN:ISBN:978-952-64-1965-7

Acknowledgements

The research work was carried out at the Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, the research group of Hydrometallurgy and Corrosion in 2020-2024. The work has been supported by Business Finland projects BATCircle (grant number 4853/31/2018), BATCircle2.0 (grant number 44887/31/2020), Aalto University's School of Chemical Engineering, and Walter Ahlström Foundation. EU Horizon-financed RESPECT project (grant agreement 101069865) and Academy of Finland's RawMatTERS Finland Infrastructure (RAMI) are also gratefully acknowledged.

I wish to start by thanking my supervisor, Prof. Mari Lundström, for turning a fledgling metallurgist into an expert. I appreciate the freedom and encouragement I have received to pursue my own research interests, which has enabled me to grow both as a researcher and a person. I express my deepest gratitude to my advisor, Dr. Heini Elomaa, for introducing me to the world of simulation and life cycle assessment, and for setting the foundation for my research topic.

I am grateful to Prof. Emer. Olof Forsen, Dr. Jari Aromaa, and Dr. Benjamin Wilson for passing down their field-related expertise, usually over coffee, which has been invaluable. I owe special thanks to Dr. Antti Porvali, Riina Aromaa-Stubb, Heikki Lappalainen, Diana Arellano, and Tianxiang Nan for discussing HSC modeling and life cycle assessment with me. Conquering such a broad area would not have been possible without all your special skills.

The journey from a bright-eyed student to a researcher would not have been the same without a space to freely experiment and make mistakes. Therefore, I also need to thank the many colleagues who have provided joy to my mornings and afternoons, including but not limited to Dr. Petteri Halli, Dr. Sipi Seisko, Dr. Zulin Wang, Dr. Linfan Cui, Dr. Saeed Rahimpour, Jere Partinen, Mika Sahlman, Sugam Shukla, Anssi Karppinen, Reima Herrala, and Henri Palomäki.

I express my deepest gratitude to my ever-witty friends for sharing this journey with me, and I thank my family for their ceaseless support despite the hardships these years have thrown at me. My final thanks go to my father (b. 1959, d. 2016), who I hope would be proud of my accomplishments despite passing some years before I even started considering doctoral studies.

Espoo, June 3rd, 2024
Marja Elina Rinne

Contents

List of Publications

I. **Rinne, Marja;** Elomaa, Heini; Lundström, Mari. 2021. Life cycle assessment and process simulation of prospective battery-grade cobalt sulfate production from Co-Au ores in Finland. The International Journal of Life Cycle Assessment, 26, 2127-2142. doi: 10.1007/s11367-021-01965-3

II. **Rinne, Marja;** Elomaa, Heini, Lundström, Mari. 2023. Flowsheet design and environmental impacts of cobalt co-product recovery from complex Au-Co ores. Minerals Engineering, 204, 108444. doi: 10.1016/j.mineng.2023.108444

III. **Rinne, Marja;** Elomaa, Heini; Porvali, Antti; Lundström, Mari. 2021. Simulation-based life cycle assessment for hydrometallurgical recycling of mixed LIB and NiMH waste. Resources, Conservation and Recycling, 170, 105586. doi: 10.1016/j.resconrec.2021.105586

IV. **Rinne, Marja;** Aromaa-Stubb, Riina; Elomaa, Heini; Porvali, Antti; Lundström, Mari. 2024. Evaluation of hydrometallurgical black mass recycling with simulation-based life cycle assessment. The International Journal of Life Cycle Assessment. doi: 10.1007/s11367-024-02304

Author’s Contributions

Publication I: Life cycle assessment and process simulation of prospective battery-grade cobalt sulfate production from Co-Au ores in Finland

MR conducted the process simulations and the life cycle assessment with the guidance of HE, performed data analysis and visualizations, and wrote the manuscript. The work was reviewed by HE and ML.

Publication II: Flowsheet design and environmental impacts of cobalt co-product recovery from complex Au-Co ores

MR was aided by HE in the conceptualization and formulation of the scenarios. The simulations were conducted by MR, who also performed data analysis and visualization, and wrote the manuscript. HE and ML evaluated the work and provided remarks.

Publication III: Simulation-based life cycle assessment for hydrometallurgical recycling of mixed LIB and NiMH waste

MR, AP, and HE conducted the process simulations. MR performed life cycle assessment, data analysis, and visualization. The manuscript was written by MR and reviewed by AP, HE, and ML. The work was supervised by ML.

Publication IV: Evaluation of hydrometallurgical black mass recycling with simulation-based life cycle assessment

The study was conceptualized by MR, HE, and AP. The simulations and life cycle assessment were performed by MR, and the sensitivity analysis by RA-S. The visualizations were made by MR, who also wrote the first draft. The work was reviewed by HE and ML.

List of abbreviations and symbols

Abbreviations

ADPe	Abiotic depletion potential, elements
ADPf	Abiotic depletion potential, fossil fuels
AP	Acidification potential
CIL, CIP	Carbon-in-leach, carbon-in-pulp
DON	Direct Outokumpu Nickel
DRC	Democratic Republic of Congo
EoL	End of life
EP	Eutrophication potential
EV	Electric vehicle
EW	Electrowinning
GHG	Greenhouse gas
GWP	Global warming potential
FAETP	Freshwater aqueous ecosystem toxicity potential
HTP	Human toxicity potential
LCA	Life cycle assessment
LCC	Life cycle costing
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
LCO	Lithium cobalt oxide
LFP	Lithium iron phosphate
Li-ion	Lithium-ion
LMO	Lithium manganese oxide
NCA	Lithium nickel cobalt aluminum oxide
NiMH	Nickel metal hydride
NMC	Lithium nickel manganese cobalt oxide
ODP	Ozone depletion potential
PGM	Platinum group metal (Pd, Pt, Ir, Rh, and Os)
PLS	Pregnant leach solution
POCP	Photochemical oxidant creation potential
S/L	Solid-to-liquid ratio (mass to volume)

SLCA	Social life cycle assessment
SX	Solvent extraction

Symbols

$[H_2SO_4]$	Sulfuric acid concentration (g/L)
$[Co^{2+}]$	Dissolved cobalt concentration (g/L)
$[Ni^{2+}]$	Dissolved nickel concentration (g/L)
T	Temperature, °C
M	Concentration (mol/L)
m.-%	Percentage by weight
vol.-%	Percentage by volume

1. Introduction

The Paris Agreement seeks to limit the global average temperature increase to 1.5 °C above pre-industrial limits (United Nations, 2015), which requires urgent actions from the 196 parties to curb their greenhouse gas (GHG) emissions. The EU, for instance, has the ambitious goal of reaching net carbon neutrality by 2050 (COM/2919/640 final, 2019). Transport is the EU's only major sector that has not seen a decline in GHG emissions since 1990. It follows that the decarbonization of road transport is currently at the forefront of the EU's climate policy (EEA, 2022), and the number of electric vehicles (EVs) is rapidly increasing. In response to the electrification efforts, questions have justifiably been raised by academics and the public alike: can the raw materials for EV batteries be produced sustainably? Are there enough raw materials for the batteries to begin with?

The fastest-growing end consumer of cobalt is the EV battery sector (Cobalt Institute, 2022). The demand for cobalt and other battery metals, such as nickel, manganese, and lithium, is expected to continue to soar, and raw materials could become a bottleneck for electrification even in the short to medium term (Ballinger et al., 2019; Junne et al., 2020; Valero et al., 2018; Zeng et al., 2022). Closed-loop recycling of batteries can partially mitigate the dependency on virgin raw materials, but the long life of EV batteries limits this option; it is projected that a maximum of 30% of cobalt demand can be met by recycling alone in 2030, and increasing the mine supply remains critical (Alves Dias et al., 2018). Cathode metal extraction causes a significant share of the environmental impacts of EVs (Kim et al., 2016), so it follows that it is also vital to find opportunities to maximize the benefits of recycling and mitigate the burdens from the raw material processing of these materials. The goal of this thesis is to investigate the technical and environmental aspects of novel processes for cobalt-rich raw materials using digital tools to inform further process development.

1.1. Background

Although cobalt was first recognized as a distinct element by the Swedish chemist Georg Brandt in 1735, the first applications of the metal and its salts date back to the prehistoric era, in the form of brilliant blue pigments used in glass and ceramics (Bernhardt, 2019). The elusive metal has, for much of history, been treated more as a curse than a blessing, and it remains a challenging element to recover and separate even today. Indeed, the word *cobalt* is supposedly derived either from the Greek word *kobalos* (mine), or from the German word *kobold* (goblin or evil spirit), which may refer to a malicious mountain-dwelling spirit in German folklore (Gauthier & Deliens, 1999). According to the stories, late medieval German silver miners attempted to process a particularly challenging ore, which upon heating released toxic fumes that caused the workers to fall ill, and no silver was recovered (Morral, 1957). Without a better explanation, the miners reasoned that a vicious mine spirit was to blame for spoiling the silver and making the workers ill.

A modern metallurgist might conclude that the mystery mineral causing the miners' troubles was not, in fact, silver, but possibly cobaltite ($CoAsS$), smaltite ($CoAs_2$), safflorite ($CoAs_2$), or skutterudite ($CoAs_3$), which release arsenic fumes when heated. The troubles of German miners were far from over, however, as later accounts suggest that the workers at Schneeberg mine-associated cobalt-nickel smelters had an extremely high prevalence of lung cancer that is possibly due to arsenic trioxide exposure (Lee & Fraumeni, 1969). Although neither cobalt nor silver are mined in Germany today, deposits that contain the same minerals are found around the world, including the United States (Bookstrom et al., 2016), Canada (Trinder, 2018), and European Fennoscandia (Horn et al., 2021). Some of these countries have also historically utilized such deposits, for example the closed Blackbird and Skuterud mines (Bookstrom et al., 2016; Grorud et al., 1997). For a long time, the Moroccan Bou Azzer mine has remained the only operating mine where cobalt is not the by-product of copper or nickel (Eljechtimi, 2022), at least until the nearly finished Idaho Cobalt Operations mine is commissioned by Jervois (Sletten et al., 2021). In these mines, cobalt occurs predominantly as arsenides and sulfoarsenides, such as cobaltite, skutterudite, smaltite, safflorite, erythrite ($Co_3(AsO_4)_2 \cdot 8H_2O$), or rare sulfides such as linnaeite (Co_3S_4). Other valuable metals, such as silver, gold, copper, and nickel, are usually present in these deposits (Cook, 2007; Slack et al., 2017).

Cobalt's by-product dependency creates a situation where the supply of cobalt cannot increase without a continued demand for nickel and copper (Campbell, 2020). Cobalt is also notorious for historical price volatility (Manley et al., 2022), the latest example being how the rapid ramp-up of Indonesian cobalt production in 2021 has led to oversupply and sharply declining prices (Cobalt Institute, 2023). Nevertheless, there are indications that cobalt supply shortages may be inevitable even with technology substitution, and cobalt will remain a key metal for energy transition even if its importance decreases (Zeng et al., 2022). Although unconventional raw materials, such as the arsenide and sulfoarsenide ores mentioned above, are not globally significant, they could provide local security and mitigate the by-product dependency.

The recycling of batteries is not sufficient to satisfy the growing metal demand either, but its role in the sustainability of EVs cannot be overstated. The extraction of cathode metals constitutes a large share of the environmental burden of Li-ion batteries (Mohr et al., 2021; Peters & Weil, 2018; Winjobi et al., 2022), which can be mitigated by recycling (Arshad et al., 2022). Traditionally, Li-ion batteries have been recycled in non-tailored processes that usually focus on the recovery of the most valuable elements in the cells: nickel, cobalt, and copper. The recycling of lithium has also become a priority in recent years: it has been considered a critical raw material by the EU since 2020, and the new EU regulatory framework is looking to impose element-specific recovery targets for lithium, copper, cobalt, and nickel starting from 2025 in addition to the previous generic mass recovery mandate (COM(2020)798 final, 2020). Nevertheless, this still leaves graphite, other anode materials, electrolyte, aluminum, and other cathode metals without a reclamation mandate in a rapidly changing field.

The primary challenge in the recycling of EV batteries is the heterogeneity of the waste in both physical design and chemistry, which complicates dismantling, mechanical pre-treatment, and chemical material separation alike. Although EV manufacturers have no interest in the oldest commercial cathode chemistry, lithium cobalt oxide (LCO, $LiCoO_2$), it is still used especially in portable and consumer electronics, which also have a growing market (Cobalt Institute, 2023). The gradual substitution of cobalt with other elements has led to the development of increasingly nickel-rich chemistries, including various stoichiometries of lithium nickel manganese cobalt oxide (NMC, $LiNi_xMn_yCo_zO_2$), and lithium nickel cobalt aluminum oxide (NCA, $LiNi_{0.84}Co_{0.12}Al_{0.04}O_2$). NCA is best known for being used in Tesla vehicles, while NMC dominates in EVs (Camargos et al., 2022). Lithium iron phosphate (LFP, $LiFePO_4$) is the only commercial cobalt-free cathode to find application in EVs. So far, LFP has mainly been used in China in EVs and e-buses (Hao et al., 2020), although vehicle manufacturers in the USA and Europe have shown interest in it in recent years (Walvekar et al., 2022). Research on manganese-rich chemistries could also be expected to grow due to their low cost, although lithium manganese oxide (LMO, $LiMn_2O_4$) has so far been mainly used in power tools (Li et al., 2021). It may be concluded that, while the share of cobalt decreases in batteries, it is difficult to eliminate, and recycling processes need to be developed to tolerate, recover, and treat a multitude of chemistries economically.

The woes experienced by medieval German miners highlight the importance of safety and environmental impacts as performance indicators in process design. Life cycle assessment (LCA) has been increasingly conducted alongside traditional techno-economic assessment in chemical and metallurgical industry projects (Adnan & Kibria, 2020; Davidson et al., 2021; Patel et al., 2016; Salkuyeh et al., 2018). The complexity of metallurgical processes, however, also complicates LCA, since aggregated or technology-specific data obtained from the literature or databases is almost never suitable for assessing any specific case. For instance, life cycle inventory (LCI) data for cobalt recovery from ores from the Democratic Republic of the Congo (DRC) is not applicable to nickel ores, and one hydrometallurgical process may not have the same impacts as another hydrometallurgical process even when it uses the same raw material (Eckelman, 2010; Farjana et al., 2019; Mohr et al., 2021; Zhang et al., 2021). The issue of using secondary data is recognized among LCA practitioners (Parvatker & Eckelman, 2019), but facility-level data of emerging processes does not exist, so alternative methods to collect input/output data from these processes are needed.

Process simulation has been a widely applied tool for generating LCI data for the *ex-ante* assessment of biorefinery and chemical plant concepts (Lu et al., 2021; Sutar et al., 2023; Tsalidis and Korevaar, 2022; Tsoy et al., 2023). Segura-Salazar et al. (2019) have encouraged the adoption of the methodology in the mineral and metallurgical industry too, where it has been used to evaluate some early mining projects or non-commercial processes (Aromaa et al., 2022; Cairncross & Tadie, 2022; Elomaa et al., 2020; Pell et al., 2019). Despite the demonstrated and argued benefits, many of the data quality issues faced by "typical" LCA practitioners are transferred to the simulation stage when they are used for LCI compilation. Lack of experimental data, extrapolation from similar processes, incomplete flowsheets, and so forth, affect the resolution and reliability of the results.

Villares et al. (2017) have argued that the outcome of a prospective study should not be regarded as the final result due to the unavoidable uncertainties, which makes *ex-ante* LCA an entirely different type of tool than conventional LCA. The value of the early application of the methodology is, instead, in informing further process development in a systematic fashion (Villares et al., 2016). Future-oriented studies have the added uncertainty of the background processes, which are typically presumed to be static. Changes in technology or energy mix can, however, also have a drastic impact on the background, so it would be essential for the temporal scopes of foreground and background to match (van der Giesen et al., 2020; Buyle et al., 2019). Interestingly, Arvidsson et al. (2017) propose that prospective studies should only include the foreground impacts. This goes against the convention of LCA, which is why other authors recommend other ways, such as scenario analysis, to avoid temporal mismatch (Buyle et al., 2019; Thonemann et al., 2020, van der Giesen et al., 2020).

Despite the many challenges and uncertainties with future-oriented and *ex-ante* life cycle assessment, the methodology may have significant value in the sustainable development of metallurgical processes provided that these uncertainties are properly addressed. Process simulation can aid with this by providing the necessary engineering dimension to formulate detailed scenarios for evaluation. This was also applied in this thesis on both primary and secondary cobalt processes.

1.2. Objectives and scope

Nickel and cobalt production are recognized as one of the key hotspots in the cradle-to-grave impacts of EV batteries, yet many of the existing studies are reliant on outdated or incomplete secondary data for Li-ion batteries. The LCI reported by Shafique and Luo (2022), for instance, had an inflow only for cobalt metal, and the battery chemistry was not reported at all. The same issue is evident for the end-of-life stage of the battery, as the processes are usually not reported transparently. This thesis focuses solely on the extraction of cobalt and other metals from cobalt-bearing ores and pre-treated Li-ion active material mixture, known as black mass, to contribute to the existing knowledge on the impacts of battery metals and their recycling.

The specific objectives of this research were as follows:

1) Investigate the cradle-to-gate impacts of producing cobalt sulfate heptahydrate (CSHH), which is used for the synthesis of NMC precursor materials, from Finnish Au-Co ores through simulation-based LCA [Publications I, II]

2) Study the grave-to-gate impacts of hydrometallurgical recycling of high and low cobalt content black mass with simulation-based LCA, with and without nickel metal hydride (NiMH) battery waste [Publications III, IV, compendium]

3) Identify problem areas in each of the scenarios and suggest the most effective ways to increase their sustainability, while also identifying the probable technical or environmental trade-offs from said decisions [Publications I-IV]

4) Evaluate the role of data gaps, modeling approaches, system boundaries and assumptions of the results, and find some appropriate measures to improve data quality in prospective LCA [Publications I-IV, compendium]

The structure of this thesis is presented in **Figure 1**, which also shows the raw materials that relate to Objective *1* (initial and updated composition of Au-Co ores), and Objective *2* (high and low cobalt content Li-ion black mass, crushed NiMH batteries), and the main products from the processes investigated in the work. Objectives *3* and *4* relate to all the thesis parts, but Objective *3* especially to the publications, and Objective *4* more to the compendium.

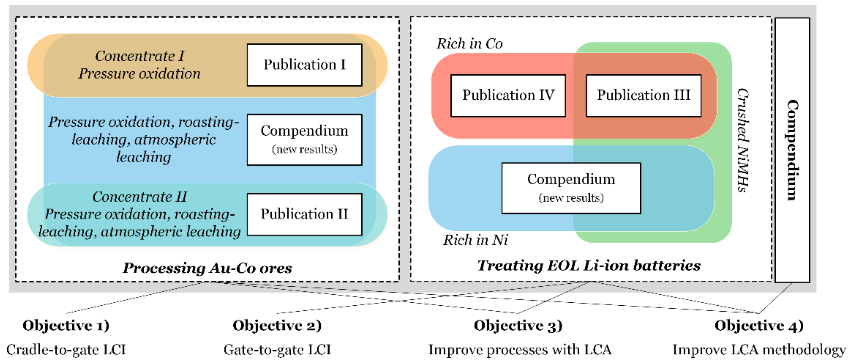


Figure 1. Structure of the thesis with respect to the objective statements.

The methodology used in the studies follows the LCA framework defined in ISO 14040, which consists of four stages, with the aid of process engineering tools at appropriate points. This methodology was adapted from Elomaa (2020). Metallurgical know-how and literature analysis were used to draw the flowsheets and scenarios, which aided in the goal and scope definition and process simulation. The processes were simulated with the SIM module of HSC Chemistry software (Metso, 2023), and the mass and energy balances were modified into LCI. Life cycle impact assessment (LCIA), where all substances and resources entering or exiting the technical boundary are classified and the impacts are characterized, was performed with Sphera's GaBi software using the Ecoinvent 3.8 database for secondary data, and various methods were used in the interpretation of the results. The process is iterative, and the LCA model is refined as the study progresses. **Figure 2** shows how the framework was used in combination with metallurgical engineering and process simulations. The software, databases, and LCIA methods used are also shown in the figure.

Total life cycle assessment, or life cycle sustainability assessment, would comprise all three dimensions of sustainability, and the adoption of social life cycle assessment (SLCA) and life cycle costing (LCC) methods would enable provision of a more holistic understanding of the processes. However, this study explicitly refers to environmental life cycle assessment, and complementary methods for the assessment of social and economic impacts are beyond the scope of this thesis.

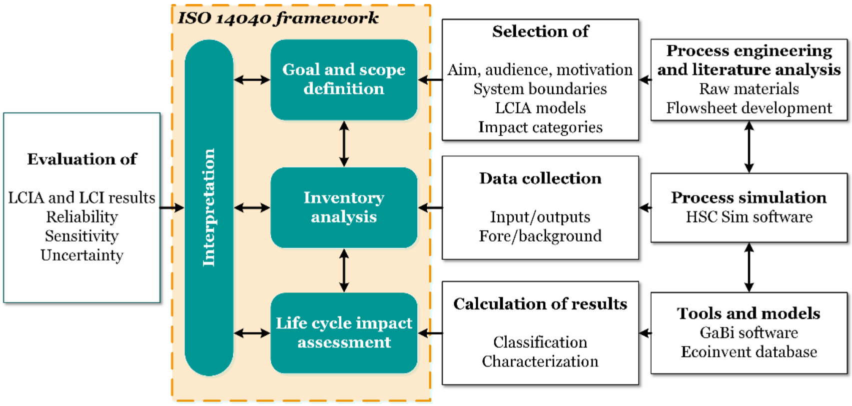


Figure 2. Research methods and tools used in this thesis in relation to the LCA framework (ISO 14040:2006, 2006).

1.3. New scientific contribution

This study contributes to the existing knowledge of the treatment of cobalt-bearing raw materials both from process engineering and life cycle perspectives using a combination of literature analysis, process simulation, and life cycle assessment. The flowsheets studied in the compendium were selected by scoping the scenarios in the Publications. The following case studies and observations are believed to be original:

Publication I: Pressure oxidation of Au-Co ores was investigated for the first time with process simulation and LCA. The effects of concentrate grade on the impacts of the hydrometallurgical process were analyzed. Sensitivity analysis was performed for selected process parameters and the allocation method.

Publication II: Pressure oxidation, atmospheric reactor leaching, and roasting-leaching of Au-Co ores was studied by simulation and LCA with three intermediate products: impure cobalt hydroxide, cobalt sulfide, and aqueous solution. Sensitivity analysis was performed for the value of gold and cobalt in the future with respect to the allocation method.

Publication III: Synergistic processing of Li-ion and NiMH black masses were investigated. Three ways of precipitating rare earth elements were assessed: 1) virgin sodium sulfate, 2) crystallization and re-use of Glauber salt from the process, and 3) circulation of sodium sulfate-bearing solution in the process. Sensitivity analysis was performed for the system boundaries and electricity mix.

Publication IV: Internally reducing H_2SO_4-Fe-Cu leaching system and downstream process were studied. Manganese recovery was studied in three scenarios: 1) synergistic solvent extraction of manganese, iron, and aluminum, 2) removal of iron and aluminum prior to manganese solvent extraction, and 3) direct precipitation of manganese without solvent extraction. The impacts of low-acid leaching were also investigated, and the sensitivity of the system to NMC feeds was assessed.

Compendium: The environmentally most feasible scenarios based on the publications were selected for further analysis. The environmental impacts of organic chemicals used in solvent extraction were further investigated by sensitivity analysis.

1.4. Thesis structure

This thesis consists of four scientific journal publications [**I, II, III, IV**] and the compendium section. The publications are included with the thesis as appendices.

The structure of the compendium section is as follows. Chapter 2 discusses the theoretical background necessary in the research: the LCA methodology and its usefulness in the chemical industry, how cobalt is recovered from a variety of primary resources, the state of lithium-ion battery recycling processes with the focus on cobalt, and the current knowledge of the environmental impacts of cobalt production. This knowledge is used in Section 2.5 to justify the selection of processes for simulation. Chapter 3 presents the framework used in the simulation and LCA in Publications I-IV, and the results of the technical and environmental evaluations are provided in Chapter 4. The results are critically discussed in Chapter 5, and the concluding remarks are presented in the final Chapter 6.

2. Theoretical background

The literature review for this thesis is described in this section. The analysis starts from the key concepts that are necessary to understand life cycle assessment: what it is, what it is not, and what additional considerations should be included in the assessment of emerging processes. The current state of cobalt ore processing and battery recycling is outlined in Sections 2.2 Cobalt extraction from ores: 2.2.1 copper-cobalt, 2.2.2 nickel sulfide, 2.2.3 nickel laterite, 2.2.4 arsenical cobalt ores, and 2.3 battery recycling, while focusing on the effect of the raw material composition on the process routes and their efficiency. The literature on battery recycling and primary cobalt LCA is also reviewed in Sections 2.2.5 and 2.3.3.

Information from the literature was used in two ways: in formulating the modeled flowsheets, and in building the process simulations in HSC Sim. The mass and energy balance modeling of the flowsheets requires knowledge of chemical reactions and their extent, process conditions, and phase distributions. Since the models were used as the basis of the LCA, an accurate view of the processes was needed to obtain high quality LCI data.

2.1. Environmental life cycle assessment

LCA is a systematic way to assess the impacts of products from raw material extraction to end-of-life. The method is relative, and the results are always scaled to a mathematically defined functional unit, e.g., 1 kg produced cobalt, or 100 km driving distance. This enables the comparison of different products with the same function, or different production routes for the same product, which makes LCA a particularly useful comparative tool.

2.1.1. Description of the framework

LCA has its roots in the energy accounting studies conducted in the early 1970s on different packaging alternatives, meant for internal use within companies (Bjørn et al., 2017). The approaches varied significantly until the need for harmonization was recognized in the 1980s. Approximately a decade of rapid development and standardization culminated in the establishment of ISO 14040/44 (2006) (Guinée et al., 2010). The standards, however, do not provide detailed instructions on how to perform an LCA study, and leave several details up for debate (Weidema, 2014). More detailed guidelines, such as the ILCD Handbook (ERC-JRC-IES, 2010) and Product Environmental Footprint (PEF) (Zampori & Pant, 2018) aim to further harmonize the methodology, and they are largely ISO compliant but may deviate in some details. The ILCD Handbook (ERC-JRC-IES, 2010), for instance, emphasizes iteration far more than the standard.

As stated in Section 1.2 and **Figure 2**, LCA is comprised of four phases, which are as follows: 1) goal and scope definition, 2) inventory analysis, 3) impact assessment, and 4) interpretation. The impact assessment phase is omitted in LCI studies, which operate otherwise on a similar principle. As LCA is an iterative approach, each of the phases is repeated and finetuned as many times as it takes to reach the stated goals. The ILCD Handbook (2010a) specifies that two to four revisions are typical, but the ISO 14040:2006 standard does not define a number for iterations.

1) Goal and scope definition. The first step is to define the goal, which states the intended application, reasons for conducting the study, intended audience, and if comparative assertions will be disclosed to the public. The scope is defined so that the goals may be achieved, and addresses the following: the investigated product system(s) and its/their functions, the functional unit, system boundaries, cut-off rules, relevant impact categories and LCIA methods, data requirements, assumptions, LCI modeling methods, allocation procedures, whether the study will be reviewed critically, and how the study is reported. The system boundaries include temporal, spatial, and technical boundaries. A “technical boundary” refers to life cycle stages, such as end-of-life, as well as individual unit processes and services, such as transport or infrastructure.

Although climate change and energy are the most commonly assessed impact categories, selection should be done carefully, especially in comparative studies to avoid impact transfer. Novel energy saving and electrified technologies, for instance, require more technical and rare metals, which may lead to increased toxicity and mineral depletion impacts depending on the battery chemistry (Oliveira et al., 2015; Arshad et al., 2022). Santero and Hendry (2016) recommended the inclusion of global warming, acidification, eutrophication, smog (stratospheric ozone) creation, and ozone depletion potential, as well as the reporting of primary energy demand, net water consumption, and waste generation. Santero and Hendry (2016) discouraged the use of resource depletion, toxicity, land use change, and water scarcity categories due to the lower reliability of the current environmental models behind them, although it can also be argued that not including these categories runs the risk of leading to biased conclusions. While it is necessary to acknowledge the shortcomings of some of the environmental categories, including human toxicity and material scarcities, the guidelines for alternatively fuelled vehicles, and powertrain metals by extension, recommend including them (Del Duce et al., 2013; Hill et al., 2020).

The LCI modeling method refers to whether the study depicts the environmental impacts of a system (attributional LCA), or the *consequences* that a decision has on the impacts of the system (consequential LCA). Consequential modeling also gauges market responses, supply, and demand, which makes it better at measuring the effects of policy (Plevin et al., 2013). Average or market data is typically used to model attributional LCA, while consequential LCA requires marginal data from suppliers and is therefore time-intensive when performed in detail (Plevin et al., 2013). The selection between attributional or consequential also affects the appropriate allocation procedures (Schrijvers et al., 2016), and therefore it is important to understand the distinction. Most published studies, as well as the studies in this thesis, are attributional (Finnveden et al., 2009; ERC-JRC-IES, 2010), and although consequential LCA is acknowledged, it is not further discussed here.

Multifunctional systems perform more than one function, i.e., they produce multiple different products, treat different kinds of feeds, or treat waste and produce products, or a combination of them. This problem is addressed through allocation, for which there are multiple approaches, and therefore it remains a contested issue in LCA (Schrivjers et al., 2016). The ISO 14044:2006 (2006) states that partitioning should, when possible, be avoided through sub-division or system boundary expansion. If partitioning is done, it should preferably be based on physical relationships between the flows, such as mass, energy, or exergy, while economic allocation is discouraged since prices change over time. Value allocation is, however, justified when the unit prices of the co-products are vastly different, and much of the revenue comes from low-volume products. A classic example from the metal industry is precious metal-bearing base metal ores (Santero and Hendry, 2010), but also rare earth ores as reported by Vahidi and Zhao (2018).

2) Inventory analysis. The inventory analysis phase consists of foreground data collection, validation, and relating the inputs and outputs to the functional unit. The data may be obtained through on-site measurements, mass balances, extrapolation from similar processes, or databases. (Bjørn et al., 2017) The background is usually modeled using databases. Attributional LCA typically uses geographical and technological market averages to model the background (Plevin et al., 2013).

3) Impact assessment. In short, the impact assessment phase refers to the calculation of the impact category indicators using the LCI, and it comprises two mandatory steps: classification and characterization, and two optional steps: normalization and weighting. In the classification phase, the elementary flows in the LCI (i.e., natural gas in, carbon dioxide to air, sulfur dioxide to air) are grouped based on their potential effects: natural gas consumption, for instance, affects resource depletion, while carbon dioxide contributes to global warming, and sulfur dioxide affects acidification and human health. The characterization phase quantifies the classified flows and converts them into a category indicator result. These two steps are, in practice, done automatically with LCA software. The optional normalization step aims to examine the magnitude of the results with respect to a reference system, while weighting similarly compares the importance of each impact category with respect to the others. In grouping, the impact categories are either sorted or ranked into different categories based on characteristics or hierarchy.

One of the weaknesses of LCA, according to the ILCD Handbook, is the diversity of LCIA methods with different sets of impact categories and models behind them, which is one of the obvious reasons why the results of different published LCA results should not be compared directly without taking proper care (ERC-JRC-IES, 2010). Some commonly used LCIA methods include but are not limited to ReCiPe (Huijbregts et al., 2017), CML (CML, 2016), TRACI (Bare, 2012), and USEtox (Fantke et al., 2017). A harmonized methodology would make it simpler to compare results, but it is also noteworthy that some of the models correspond better to certain geographical areas than others, and certain environments are more sensitive to some types of emissions than others – compromises, therefore, need to be made between simplicity and the level of detail.

Some of the methodologies, such as TRACI and ReCiPe, contain both endpoint and midpoint categories. An endpoint category represents the final area of protection, like resources, human health, and ecosystem quality, while midpoint categories describe the impacts between the emission itself and the endpoint. The way midpoint categories, and therefore individual emissions, relate to endpoints can be highly complex and uncertain: ozone depletion, for instance, affects both ecosystem quality and human health through several pathways that are not even properly known, and endpoint categories are consequently not recommended by the ILCD at present (ERC-JRC-IES, 2010). Examples of impact categories and which substances affect each category are provided in **Table 1** for CML2001 methodology, which has no endpoints (CML-IA, 2016).

Table 1. LCIA terminology and impact categories in the CML-IA methodology, corresponding impact indicator, and examples of contributing substances. (Rosenbaum, 2017; JRC-IES, 2010b; CML-IA, 2016)

Impact category	**Impact indicator**	**Key substances**	**Unit**
Climate change, 100 years	Global warming potential (GWP100)	CO_2, CH_4, N_2O, SF_6	CO_2-eq
Acidification	Acidification potential (AP)	SO_2, NO_x, NH_3	SO_2-eq
Eutrophication, marine and freshwater	Eutrophication potential (EP)	PO_4^{3-}, NO_3^-, N compounds, chemical oxygen demand	PO_4^{3-}-eq
Ozone depletion	Ozone depletion potential (ODP)	Halocarbons	R11-eq
Photochemical ozone formation	Photochemical ozone creation potential (POC)	NO_x, CO, volatile organic compounds	C_2H_6-eq
Human toxicity	Human toxicity potential (HTP inf)	>800 substances, incl. pesticides, heavy metals	1,4-DCB-eq
Freshwater ecotoxicity	Freshwater aquatic ecotoxicity potential (FAETP inf)	>800 substances	1,4-DCB-eq
Marine ecotoxicity	Marine aquatic ecotoxicity potential (MAETP inf)	>800 substances	1,4-DCB-eq
Terrestrial ecotoxicity	Terrestrial ecotoxicity potential (TETP inf)	>800 substances	1,4-DCB-eq
Mineral depletion	Abiotic depletion potential, elements (ADPe)	Elements	Sb-eq
Fossil depletion	Abiotic depletion potential, fossil (ADPf)	Fossil carbon	MJ

The characterization is performed relative to a reference substance – for climate change, the reference is carbon dioxide, which has a GWP of 1 kg CO_2-eq/kg regardless of the LCIA method. Different time horizons (20, 100, 500 years) are used to measure the strength of GHGs due to their different lifespans in the atmosphere, although GWP100 is almost always used due to the convention set by the IPCC (Thoughton et al., 1990). The other category indicators are characterized similarly for different substances, with or without a temporal scope.

4) Interpretation. Interpretation is the last phase in LCA, which involves the identification of significant issues in the LCI and LCIA, assessing data quality for sensitivity, consistency, and completeness, making conclusions and recommendations, and reporting the limitations of the study. The goals of the study inform the interpretation, and the consequences of methodological choices are also evaluated at this stage.

The framework is flexibly applicable to any kind of products or product systems, but the ambiguity has resulted in non-uniform practices and numerous efforts to harmonize the methodology and details (Santero & Hendry, 2016; Segura-Salazar et al., 2019). Weidema (2013) argued that the ISO standards have failed their purpose for this reason, and it does appear challenging for practitioners to follow best practice with the rapid developments in the field. Seemingly the best way to address these issues would be to amend the ISO standards that clarify the most contested issues, including multifunctionality, and attributional and consequential modeling. Regardless of this, however, it is even more vital for LCA practitioners to report the scope, assumptions, LCI, and uncertainty *transparently* so that the reviewer or expert reader may evaluate any assertions for themselves.

2.1.2. Assessment of emerging technologies

The use of LCA in early-stage processes is rationalized to enable hotspot identification, optimization, scenario analysis, and to assess whether the new technology can replace the incumbent one. It worth noting that some studies provide different meanings for "prospective" and "ex-ante" LCA, and that consequential LCA is sometimes referred to as "prospective LCA" (Buyle et al., 2019). This text, however, uses the words interchangeably to refer to *LCA of technologies not yet industrially applied in the investigated form*.

While most LCA studies have been retrospective, LCA is a decision-making tool, and especially nowadays is frequently used to assess emerging technologies. The challenges associated with performing LCA of non-mature processes are partly the same as with *ex-post* assessment: data quality, uncertainty, and even temporal inconsistency between foreground and background with the use of outdated databases (Thonemann et al., 2020; van der Giesen et al., 2010). The product systems are, however, not nearly as well known in prospective studies, and the uncertainty is therefore more pronounced.

The methods for obtaining LCI data on the foreground system include laboratory- or pilot-scale experiments, patents, literature, and simulation and modeling (Parvatker & Eckelman, 2019). The scale-up of lab-scale processes is crucial for data quality, especially in comparative studies – the direct extrapolation of laboratory and even pilot data to LCI overestimates the impacts compared to industrial scale, as demonstrated in several studies (Arvidsson & Molander, 2016; Röder et al., 2022; Sun et al., 2023; Tsalidis & Korevaar, 2022). Thonemann and Schulte (2019) suggested a four-step approach for scaling and implementing the findings of LCA in process design, and Picinno et al. (2016) provided useful estimates for chemical processes and equipment. Process simulation is also an accepted tool for scale-up, and can provide very similar results to commercial processes (Tsalidis & Korevaar, 2022). The accuracy of simulation, however, depends on the simulation setup, and how well the parameters and variables correspond to industrial scale.

Scope-related problems with prospective studies include function, as well as spatial and temporal dimensions. "Function" is relevant if the novel technology has different properties or performs alternative functions from the existing solution, and it should be considered which technology or technologies should be compared to the prospective one(s). Temporal inconsistency has to do with the fact that the foreground product system is usually modeled in a future state, but the background is static and modeled with current or outdated data. A change in energy production affects both the background and the foreground, but entirely new technologies that affect the background may also be implemented, such as carbon capture and storage (Mendoza Beltran et al., 2018). If the study is comparative, the incumbent technology should also be modeled in a future state for a fair comparison. The exclusion of background systems, or reporting them separately, avoids many of these issues (Arvidsson et al., 2017). Shared scenarios and databases have been presented as a solution (Mendoza Beltran et al., 2018; Steubing & de Koning, 2021).

Scenario analysis is almost invariably used in prospective LCA, but the scenarios themselves focus on different aspects depending on the goal of the study. For instance, Tsalidis and Korevaar (2022), Thonemann and Schulte (2019), and Sun et al. (2023) studied processes at different scales, while Elomaa et al. (2020), Tsoy et al. (2023), and Schulze et al. (2018) evaluated possible process conditions, configurations, and variables instead. The background system, spatial or temporal, has also been the subject of scenario analyses, although often limited to the electricity mix (Arvidsson and Molander, 2016; Manda et al., 2014; Pini et al., 2017).

2.2. Cobalt extraction from ores

Cobalt occurs alone extremely rarely in extractable quantities, and almost all of it is mined as the by-product of copper and nickel. The above-mentioned Bou Azzer mine, which supplies approx. 1% of the world's cobalt mine production, is an exception, although others have been utilized historically and are likely to be used again in the future. The mine production of 2022 and identified reserves (USGS, 2023) are provided in **Figure 3**. Recycled cobalt supplies approximately 24% of the demand, but differences in the recycling rates and processes between different products – e.g., EV or portable batteries, cemented carbides, alloys – are large (USGS, 2023; Godoy Léon et al., 2020). Another interesting fact in the value chain of cobalt is that the top countries producing refined cobalt are China (76% global refinery capacity in 2022) and Finland (10% in 2022), despite only accounting for ca. 1-2% of mine output (Cobalt Institute, 2023; USGS, 2023). Both countries rely on imports of impure precipitate from the DRC, which has very little refining capacity of its own despite its immense resources (Cobalt Institute, 2023).

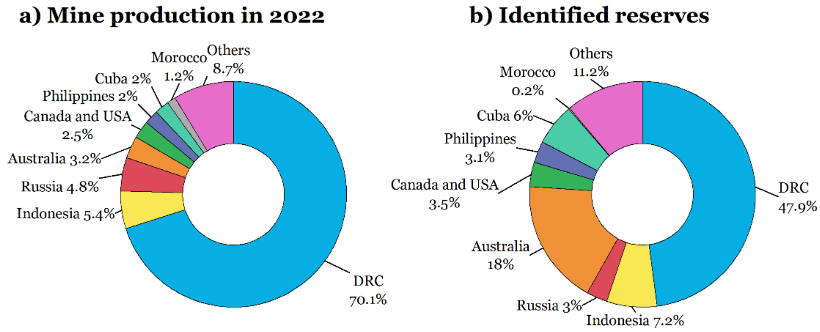


Figure 3. a) Cobalt mine production estimates in 2022 (% total), and **b)** identified cobalt reserves (% total). (USGS, 2023). "Others" include China, Turkey, Papua New Guinea, New Caledonia, South Africa, and Finland.

Copper-cobalt ores occur mainly in the DRC, which controls approximately half of the world's known resources, as well as in the neighboring African countries, e.g., Zambia (Fisher, 2011). Although laterites hold the majority of the remaining cobalt, nickel sulfides are simpler to process and have therefore been the chief source of nickel and nickel-associated cobalt (Schmidt et al., 2016). Australia, for instance, has vast underutilized laterite deposits, which undoubtedly explains the gap between the existing production capacity and known deposits shown in **Figures 3 a)** and **b)** (Mudd, 2010). Notably, Indonesia only emerged as a major cobalt producer in 2021 due to technology development (Cobalt Institute, 2023). Cobalt-bearing nickel sulfides are mostly mined in Russia, Canada, Australia, South Africa, and Finland, whereas laterite mining occurs by a rule closer to the equator: in Cuba, Philippines, Madagascar, Oceania, and Indonesia (Dulfer et al., 2016; USGS, 2023; Cobalt Institute, 2023).

2.2.1. African copper-cobalt ores

Approximately half of the world's currently known cobalt and 8% of copper reserves occur in the Central African zone known as the Copperbelt, which stretches across the border of Zambia and the DRC (USGS, 2023). This leaves cobalt supply vulnerable to geopolitics, corruption, dismal socioeconomic conditions, and armed conflicts in the region. Traditionally, there have been two cobalt products produced in the Copperbelt: crude cobalt hydroxide and electrowon cobalt cathode, but nowadays very little cobalt metal is produced in the region, and most of the metal is exported overseas, primarily to China and Finland, as a crude intermediate (Crundwell et al., 2020). Future projects in the region appear to concern higher purity upgraded products with changes in the legislative landscape (Sole et al., 2018).

The Copperbelt is not homogeneous in mineral composition, and the mineralogy varies between different areas of the zone. The Congolese deposits tend to be more weathered and richer in cobalt than the Zambian deposits, which are characteristically more sulfidic and have lower Cu/Co ratios

(Crundwell et al., 2020). The cobalt grade in the largest Congolese deposits varies between 0.2% and 0.5%, and the Cu/Co ratio varies from 7 to 50 (Dehaine et al., 2021; Peek et al., 2009). The deposits consist of a weathered oxide layer and a deeper sulfide layer. The main minerals of interest in the oxide zone are heterogenite ($CoO(OH)$), chrysocolla ($CuO{\cdot}SiO_2{\cdot}2H_2O$), and malachite ($CuCO_3{\cdot}Cu(OH)_2$), with quartz and dolomite as the gangue minerals. The principal sulfides are carrollite ($CuCo_2S_4$) and chalcocite (Cu_2S). In both ore types, the impurities that affect the metallurgical processing and flowsheet selection are Fe, Al, Mn, Zn, and Ni from the ores, and Mg and Ca from process chemicals (Crundwell et al., 2020; Sole et al., 2018).

Oxide ores are easier to process than sulfides and thus more cost-effective to treat, so they are prioritized over the deeper-lying sulfides. Oxides are not amenable to froth flotation by conventional means, so ores are typically crushed, milled, and leached in sulfuric acid media. Leaching is performed continuously in acidic media usually in series of tanks or heaps (Crundwell et al., 2020; Sole et al., 2018). In some configurations, copper and cobalt may be separated as early as in the leaching step by first dissolving copper and then extracting cobalt from the leach residues (Sole et al., 2018). This is possible since the trivalent cobalt in heterogenite is not stable in solution and is treated with reducing agents, unlike the copper minerals. Either sulfur dioxide or sodium metabisulfite is used to reduce cobalt to stable Co^{2+} (Crundwell et al., 2011). The leaching reactions for heterogenite, chrysocolla, and malachite are given by **Reactions 1-3**:

$$2\mathrm{CoOOH} + \mathrm{H_2SO_4}(aq) + \mathrm{SO_2}(g) \rightarrow 2\mathrm{CoSO_4}(aq) + 2\mathrm{H_2O} \quad \textbf{(1)}$$
$$\mathrm{CuCO_3} \cdot \mathrm{Cu(OH)_2} + 2\mathrm{H_2SO_4}(aq) \rightarrow 2\mathrm{CuSO_4}(aq) + \mathrm{CO_2}(g) + 3\mathrm{H_2O} \quad \textbf{(2)}$$
$$\mathrm{CuO} \cdot \mathrm{SiO_2} \cdot 2\mathrm{H_2O} + \mathrm{H_2SO_4}(aq) \rightarrow \mathrm{CuSO_4}(aq) + \mathrm{SiO_2} + 3\mathrm{H_2O} \quad \textbf{(3)}$$

The deeper-lying sulfides are treated differently from the oxides, and are pre-concentrated by flotation to produce either a single copper-cobalt concentrate or separate concentrates. There are two routes for sulfides: matte smelting and roasting-leaching, of which smelting has been used mainly for copper-rich, low-cobalt concentrates since cobalt is oxidized in the slag (Crundwell, 2020). The reduction of copper smelting slag with carbon results in a cobalt-bearing “white alloy”, which consists of metallic cobalt, copper, and iron (Crundwell et al., 2020). The same process is also suited for the reclamation of cobalt from discarded slags (Jones & Pawlik, 2019), but the option is unlikely to be viable for concentrates with significant cobalt values, and they are instead treated by the roasting-leaching route, which leads to better recovery.

As stated above, sulfides do not readily dissolve in atmospheric sulfuric acid media, so the typical approach is to pre-treat them by sulfating roasting at ~700 °C in air, which converts sulfides to soluble sulfates. **Reactions 4** and **5** represent the stepwise sulfation of carrollite. The released sulfur dioxide may be used for sulfuric acid production to avoid environmental problems.

$$CuCo_2S_4 + \frac{11}{2}O_2(g) \rightarrow CuO + 2CoO + 4SO_2(g) \quad \textbf{(4)}$$

$$CuO + 2CoO + \frac{3}{2}O_2(g) + 3SO_2(g) \rightarrow CuSO_4 + 2CoSO_4 \quad \textbf{(5)}$$

After leaching and solid-liquid separation by counter current decantation (CCD), the purification of the pregnant leaching solution (PLS) is the same for sulfide and oxide ores, **Figure 4**. Copper is separated from the PLS and recovered by the highly conventional solvent extraction (SX) and EW route, and the SX raffinate is purified from the impurities. Typical extractants used in Cu SX are oximes like LIX 984N or ACORGA M5640 (Crundwell et al., 2011). Iron, aluminum, and most of the manganese is always removed before cobalt is precipitated, and zinc and residual copper may be removed at this stage – if not, they are incorporated in the cobalt product and managed by the refinery. It appears that Zn and Cu removal prior to cobalt recovery has been practiced at plants that produce cobalt metal on-site (Sole et al., 2018).

The precipitation of iron and manganese requires that ferrous iron is oxidized to ferric and divalent manganese Mn^{2+} to quadrivalent Mn^{4+} state with an air/SO_2 gas mixture. Increasing the pH to 3.5 causes Fe, Al, and Mn to precipitate as hydroxides, which are separated from the solution and discarded (Crundwell et al., 2020). Cobalt metal producing operations in the region have opted to remove copper by hydroxide precipitation with lime at pH 5.5-6, and the copper cake is recycled back to leaching. Zinc (and nickel) cannot be selectively removed by hydroxide precipitation, and SX with D2EHPA has typically been used for zinc (Crundwell et al., 2020). Residual zinc, nickel, manganese, and copper are controlled at the refinery by ion exchange or SX depending on the specifications (Sole et al., 2018).

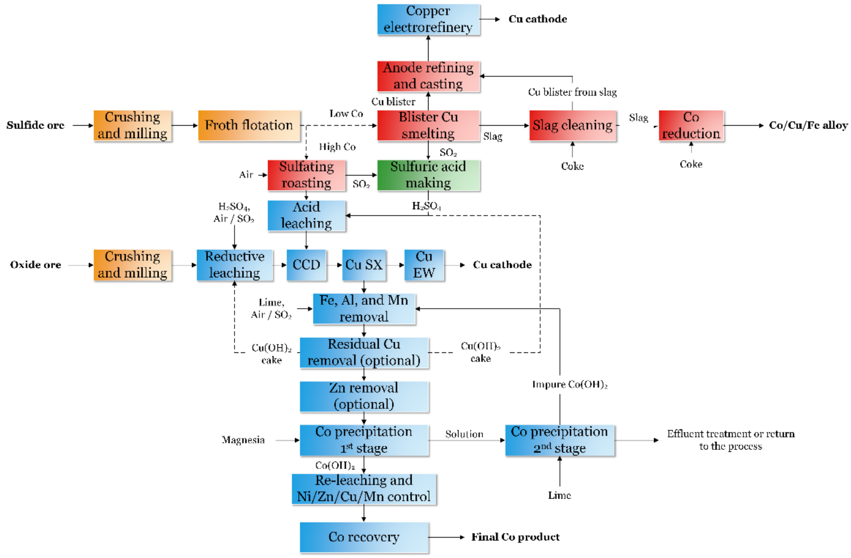


Figure 4. Schematic for cobalt hydroxide and copper production from sulfide and oxide ores in the DRC and Zambia, not including all flows or steps (Crundwell et al., 2014; Crundwell et al., 2020; Sole et al., 2018; Schmidt et al., 2019).

Cobalt hydroxide precipitation has been the practice even at plants which refine cobalt locally by EW. Cobalt hydroxide precipitation is commonly performed in two stages to reach an overall Co recovery of >99%. In the first step, magnesia is used to neutralize the solution to pH 7.5, and the pH is adjusted to 8.5 with lime in the second stage. The precipitate from the second stage is contaminated with gypsum, so it is returned to the leaching step (Sole et al., 2018). The hydroxide cake is re-leached and purified from the incorporated impurities, such as nickel, zinc, and any remaining manganese and copper, usually by ion exchange (Sole et al., 2018). The actual flowsheet for the refining of cobalt hydroxide precipitates depends on the desired cobalt products. Many refineries, such as the Kokkola refinery in Finland, produce several products specifically for different applications (Alves Dias et al., 2018). CSHH ($CoSO_4 \cdot 7H_2O$) has the fastest growing market owing to its use in NMC cathode manufacturing (Cobalt Institute, 2023).

2.2.2. Nickel sulfide ores

Nickel sulfide ores have, at least traditionally, been the second largest source for cobalt after Cu-Co ores, although laterite processing has grown in importance (Cobalt Institute, 2023; Faris et al., 2022). Sulfide deposits are found in almost every continent, but the most significant ones are in Russia, Australia, Canada, and South Africa, with smaller deposits in Zimbabwe, China, Finland, and the United States (USGS, 2023). Many of the deposits also contain other valuable metals in addition to nickel and cobalt, including gold, silver, copper, and notably platinum group metals (PGM). Nickel and cobalt are virtually always present as pentlandite, $(Ni,Fe,Co)_9S_8$, or nickel-cobalt-bearing pyrrhotite or pyrite, copper as chalcopyrite $CuFeS_2$, and the main sulfide minerals present in the ores are usually pyrrhotite, $Fe_{1-x}S$, and/or pyrite, FeS_2 (Crundwell et al., 2011).

Nickel sulfide ores are predominantly treated by flotation and matte smelting. It was previously speculated that the hydrometallurgical pressure oxidation (POX) process would become more widely used in the processing of sulfide ores (Mäkinen & Taskinen, 2008), but only a few hydrometallurgical plants process concentrates in the present day. The Sherritt process based on ammoniacal pressure leaching has been used to process concentrates in the past, but the operation has changed to matte refining over time (Crundwell et al., 2011; Faris et al., 2022). The Long Harbour refinery recovers base metals from Voisey's Bay mine concentrates by chlorine pre-leaching and pressure oxygen-sulfuric acid leaching (Faris et al., 2022). The prevailing pyrometallurgical process routes and the typical cobalt grades at each stage are shown in **Figure 5**, along with a schematic diagram of the industrially operated hydrometallurgical Long Harbour plant process for comparison.

Despite the problems, hydrometallurgical processes have potential for the treatment of ores that are not amenable to flotation or are not otherwise within the operating window of smelting. Heap bioleaching has, for instance, been successfully implemented in Finland to treat black shale-hosted Ni-Zn-Cu-Co ores that do not respond to flotation, which is a pre-requisite for smelting and most hydrometallurgical operations (Crundwell et al., 2011). The impure heap leaching solution is treated by stepwise sulfide precipitation to recover copper and zinc sulfides suitable for their respective smelters, and mixed nickel-cobalt sulfide (MSP) for hydrometallurgical refining to sulfates.

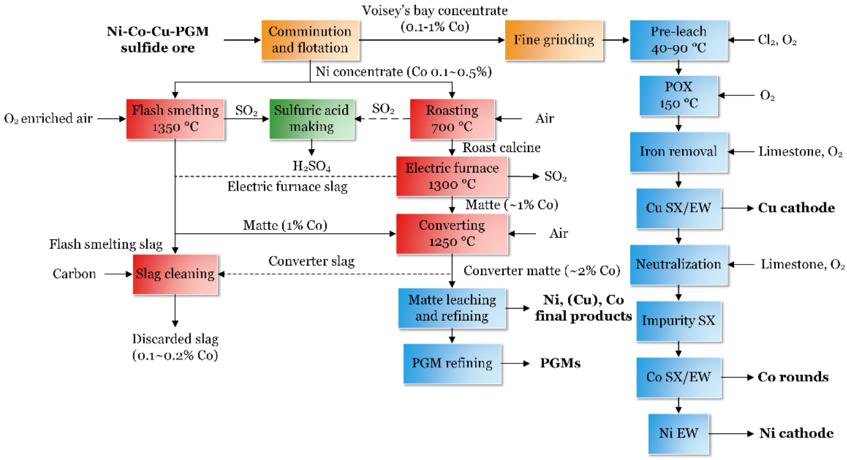


Figure 5. Generic matte smelting flowsheets via flash smelting and electric furnace smelting routes – converting is conducted at the flash smelting stage in the Direct Outokumpu Nickel (DON) process, and a simplified schematic of the hydrometallurgical Long Harbour refinery process. Co grades (m.%) are provided for beneficiation and pyrometallurgical units. Compiled from Crundwell et al. (2011); Faris et al. (2022); Warner et al., (2007).

The goal of smelting and converting is to increase the nickel (and cobalt) grade in the material through the oxidation of sulfur and iron, and to form a molten Ni-Co matte, a mixture of base metals, sulfur, and iron, with 40~70% Ni and a molten iron oxide-silica slag, in which the gangue minerals are dissolved. The pyrometallurgical process consists of three stages: roasting, melting, and converting. These steps are carried out separately in electric furnace smelting, which starts with fluidized bed roasting followed by melting in an electric furnace, and converting in conventional Peirce-Smith converters, whereas flash smelting combines roasting and melting in a single vessel and the matte is converted separately. The DON process, currently known as Metso's Direct Nickel flash smelting process, combines all three into a single stage (Mäkinen & Taskinen, 2008). The final converter matte composition is approximately 40~70% Ni, 1~5% Fe, 20~25% S, and 1~2% Co depending on the feed (Crundwell et al., 2011; Warner et al., 2007).

The operating principles and reactions are largely the same in all options, but the Direct Nickel and flash smelting processes are more energy efficient. The goal of roasting is to oxidize 40-70% of the sulfur in pentlandite, pyrrhotite, and other sulfide minerals by controlling the air flow to the furnace. The roasting reactions (**Reaction 5** for pentlandite) generate heat, which powers the furnace. In the subsequent melting stage (1300-1350 °C), the roast calcine melts together with silica flux and separates into immiscible Ni-Fe-Co-(Cu)-S matte and siliceous slag phases. Upon descending through the slag layer on top, unreacted iron sulfide in the calcine reacts with oxidized nickel, which is then recovered in the matte layer (**Reaction 6**) (Crundwell et al., 2011). In flash smelting, the oxidation (**Reaction 5**) occurs in the reaction shaft of the furnace, and the molten droplets descend to the furnace settler, where the two phases separate. The heat from sulfur and iron oxidation may be enough to sustain the process, which makes flash smelting energy efficient (Crundwell et al., 2011). The sulfur dioxide from the roasting reaction is, at most plants, used for producing sulfuric acid. The sulfur dioxide from the electric furnace is usually too dilute for sulfuric acid plants, so the gas is released into the atmosphere.

$$\mathrm{Ni_{4.5}Fe_{4.5}S_8} + 12.5\mathrm{O_2}(g) \rightarrow 4.5\mathrm{NiO} + 4.5\mathrm{FeO} + 8\mathrm{SO_2}(g) \quad \textbf{(5)}$$
$$\mathrm{NiO}(slag) + \mathrm{FeS}(l) \rightarrow \mathrm{NiS}(l) + \mathrm{FeO}(slag) \quad \textbf{(6)}$$

The matte from electric furnace or flash smelting contains 30-50% iron, which is decreased to 1-5% in the converting stage. Oxidized iron further reacts with silica flux to form fayalite, **Reaction 7**, and like roasting, the reaction is highly exothermal, which is a benefit of the Direct Nickel process. Iron oxidizes preferentially to sulfur. Unlike in copper converting, the goal of nickel converting is usually not to eliminate sulfur from the matte, so the converting step is performed in only one stage where iron is removed. The oxidation of nickel, copper, PGMs, silver, and gold is not thermodynamically favorable under converting conditions, and they are recovered in the matte phase. Cobalt, which thermodynamically behaves similarly to iron, reports both to the matte and the slag, and the final recovery of cobalt varies between 50% and 70% between smelters (Crundwell et al., 2011; Mäkinen & Taskinen, 2008). Electric furnaces have better control over nickel and cobalt oxidation, so slag cleaning is not usually necessary, but separate slag cleaning furnaces are used by all flash smelters and Direct Nickel smelters.

$$\mathrm{Fe}(matte) + \mathrm{O_2}(g) + \mathrm{SiO_2}(flux) \rightarrow \mathrm{Fe_2SiO_4}(slag) \quad \textbf{(7)}$$

Regarding by-products – cobalt, copper, PGMs, gold, and silver – matte smelting is highly efficient in recovering all of them apart from cobalt. Precious metals do not chemically dissolve in slags, so they can be recovered from mattes in the subsequent refining stages (Crundwell et al., 2011). Cobalt, however, oxidizes more readily than nickel, but slightly less readily than iron (Crundwell et al., 2011). Considering that the economic importance of cobalt to the nickel industry has increased further in recent years, it is likely that nickel smelters have aimed to optimize their cobalt recoveries in the process further. This is not an easy task, considering the aim of the converting process is to oxidize iron (Crundwell et al., 2011). Cobalt may be recovered in highly reducing conditions albeit at the cost of also retaining more iron in the matte (Avarmaa et al., 2020).

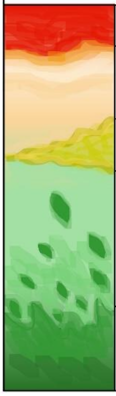
Granulated nickel-cobalt mattes, or mixed nickel-cobalt precipitates, are purified hydrometallurgically. The most commonly used processes start with base metal leaching in air-ammonia, oxygen-sulfuric acid, or chloride-sulfate media (Crundwell et al., 2011). Iron and the gangue oxides have already been removed from the matte so the PGMs are enriched in the residues significantly more efficiently than in direct concentrate leaching (Mpinga et al., 2015). The solution purification stage is no different from the purification of copper-cobalt and the Long Harbour (**Figure 5**) process solutions. Residual iron is removed by precipitation, and copper, cobalt, and nickel are separated by stepwise SX, and recovered in the desired form from the purified solutions either by EW, hydrogen reduction, precipitation, or crystallization.

2.2.3. Nickel laterite ores

Primary nickel is generally divided into two product classes: Class I, >99.8% nickel, which comprises pure products like cathode, nickel chemicals, briquettes, and powders; and Class II, which contains nickel pig iron and ferronickel. Whereas nickel sulfides are processed into Class I products, laterite ores are processed for both (Schmidt et al., 2019). This has a relevance for cobalt as it is only recovered as the by-product of Class I nickel. Significant laterite deposits are found and mined in New Caledonia, Australia, Philippines, Indonesia, and Cuba. The geographic distribution between the tropics is no coincidence, as laterites form through weathering in humid tropical conditions (Elias, 2002). Nevertheless, laterite deposits are also found in Turkey and across the Balkans, and there is at present some mining in Albania and ferronickel production in Greece (Horn et al., 2021; Stanković et al, 2020). The Turkish Gördes mine is currently the region’s only verified cobalt-producing laterite deposit (Horn et al., 2021).

Laterites are formed through the intense weathering of rocks, usually peridotite, where the main component is olivine, $(Mg,Fe)_2SiO_4$. The dissolution and re-deposition of elements in the rocks (Ni, Co, Fe, Mg, Si, Al, Mn, etc.) at different depths forms layered laterite profiles, as presented in an ideal form in **Figure 6**. The recognizable zones are an iron crust known as ferricrete, limonite, sometimes smectite, and saprolite on top of the bedrock. Since laterites form through a delicate process that is affected by factors such as climate, water circulation in the soil, and topography, laterites are highly heterogeneous ores with variable compositions (Elias, 2002). This complicates the processing of the ores, and the treatment varies between laterite types.

Laterites are not amenable to conventional flotation strategies, and no effective and universal methods to substantially increase the valuable metal content has yet been found (Quast et al., 2015). The physical upgrading of the ores is usually limited to comminution and particle size classification, which can only increase the nickel grade in the materials slightly (Quast et al., 2015). The high processing costs and price volatility of nickel appear to make laterite mine projects particularly prone to prolonged holds. The *industrially* applied processes and approximate cobalt recoveries are also included in **Figure 6**. The high pressure acid leaching (HPAL) process is highlighted as the most significant limonite process by far.



Laterite profile	Composition (%)				Minerals	Industrial processing	Co recovered?
	Fe	Ni	Co	Mg			
Ferricrete	>50	<0.8	<0.02	<0.3	Iron oxide	N/A	N/A
Limonite	40-50	0.8-1.5	0.1-0.2	0.3-3	Goethite, Mn oxide	Hydromet: HPAL, Caron, tank/heap	HPAL >95%, Caron ~50% Heap <80%
Smectite	10-30	0.6-2	0.02-0.1	3-10	Nontronite, other clays		
Saprolite	10-25	1.5-3	0.02-0.1	10-20	Garnierite, serpentine, talc, smectite...	Pyromet: usually FeNi smelting	No
Bedrock	<10	~0.3	<0.02	>20	Unweathered peridotite	N/A	N/A

Figure 6. Idealized laterite profile, characteristic mineralogy of each zone, typical processing pathways, and whether cobalt is recovered from the ore. Compiled from Crundwell et al. (2011), Elias et al. (2002), Gabb (2018), and Stanković et al. (2020).

There are different approaches for the processing of different ore compositions – high-iron limonites, intermediate clays, and high-magnesia saprolites – as shown in **Figure 6**. The Fe:Mg ratios and nickel grades largely explain the different processing routes. Ferronickel smelting requires a sufficiently high (>1.8%) nickel grade, which excludes most limonite ores, while the HPAL process does not tolerate the high magnesia content of saprolites for reasons of acid consumption (Gabb, 2018). In contrast, atmospheric processes are more mineralogy dependent and less effective in the treatment of limonite ores (McDonald & Whittington, 2008), and certain process plants, such as Ravensthorpe in Australia, have integrated atmospheric saprolite leaching with limonite HPAL (Crundwell et al., 2011; Quantum Minerals, 2022). Limonite and some smectite ores are treated hydrometallurgically by HPAL, where leaching is conducted at 240-270 °C (4,000-5,600 kPa) in sulfuric acid media (Gabb, 2018). The Caron process, where limonite ore is reduction roasted before leaching in ammoniacal solutions, results in poor nickel (~75%) and cobalt (~50%) recoveries even with its high energy consumption and is highly unlikely to be applied in new projects (Crundwell et al., 2011). Matte smelting by a modified electric furnace route is also practiced by a handful of processing plants. The matte is produced by spraying molten sulfur onto the ore during pre-treatment and the sulfur-ore mixture is then melted in an electric furnace (Crundwell et al., 2011).

The dominant hydrometallurgical HPAL process is complex, and many projects have either struggled or failed to reach the design capacities even after long ramp-up periods (Gabb, 2018). The Moa Bay plant in Cuba, Coral Bay in the Philippines, and the newly operating Indonesian plants are among the few to succeed on the first attempt (Durrant, 2023; Gabb, 2018). In addition to the high capital expenditure needed for the autoclave, the process also suffers from technical challenges and high operating costs (Gabb, 2018; McDonald & Whittington, 2008). Nevertheless, the benefits of HPAL are high nickel and cobalt recoveries and rapid processing time (90 min) in comparison to 10-12 hours in atmospheric sulfate media, and up to hundreds of days in heap leaching (Stanković et al., 2020).

Another advantage of HPAL is that dissolved iron is rejected as stable iron oxides, preferably hematite, already in-situ, whereas atmospherically produced residues such as iron hydroxide and jarosite contain more impurities and are more voluminous (Miettinen et al., 2019). The chemistry of iron in a high-temperature sulfuric acid system is presented by **Reactions 8-10**, where **Reaction 10** describes jarosite formation. Nickel and cobalt remain in solution. Sulfuric acid is continuously fed to the autoclave to reach 30 g/L H_2SO_4 in the exit solution, with typical acid consumption varying between 300 kg/t_{ore} and 500 kg/t_{ore} (Gabb, 2018). The acid consumption, in addition to the feed grade, sets the HPAL process apart from commercial sulfide (i.e., refractory gold) POX, where the oxidation of sulfide to sulfate generates acid and heat.

$$2(\mathrm{Fe,Ni})\mathrm{OOH} + 5\mathrm{H_2SO_4} \rightarrow 2\mathrm{NiSO_4}(aq) + \mathrm{Fe_2(SO_4)_3}(aq) + 6\mathrm{H_2O} \quad \textbf{(8)}$$
$$\mathrm{Fe_2(SO_4)_3} + 3\mathrm{H_2O} \rightarrow \mathrm{Fe_2O_3} + 3\mathrm{H_2SO_4} \quad \textbf{(9)}$$
$$3\mathrm{Fe_2(SO_4)_3} + \mathrm{Na_2SO_4} + 12\mathrm{H_2O} \rightarrow 2\mathrm{NaFe_3(SO_4)_2(OH)_6} + 6\mathrm{H_2SO_4} \quad \textbf{(10)}$$

The HPAL exit slurry is de-pressurized in a series of flash tanks, limestone is added to pre-neutralize the slurry and precipitate gypsum, and the solids are separated and washed in a CCD circuit (Crundwell et al., 2011). The impurity load of laterite leaching solution is such that, as in the copper-cobalt treatment and Talvivaara operation in Finland, nickel and cobalt are recovered from the solution as solid intermediates. Direct SX has been attempted industrially, albeit with major difficulties (Donegan, 2006), and it follows that MSP or MHP precipitation is currently the preferred route until direct SX is developed further. Residual iron, manganese, copper, and zinc are removed before nickel and cobalt are precipitated together and sent for refining (Crundwell, 2011).

While atmospheric processes avoid the autoclave, reactor and heap processes still have several issues to address, i.e., slow kinetics, acid consumption, and iron control. Tank leaching in acidic sulfate, for instance, consumes more acid than HPAL, in the range of 500-700 kg/t_{ore}, or as much as 1600 kg/t_{ore} for some saprolite ores (Stanković et al., 2020). Miettinen et al. (2019) suggested simultaneous laterite leaching and iron removal as sodium jarosite, which reduces acid consumption since the precipitation reaction generates sulfuric acid, **Reaction 10**. Atmospheric laterite leaching is integrated into the Ravensthorpe HPAL plant, although there are no standalone operations to the author's knowledge.

Other mineral acids, such as nitric acid in the Direct Nickel process (not to be confused with Metso's Direct Nickel flash smelting), and hydrochloric acid in the Neomet process, have been demonstrated to be able to also treat saprolite ores more flexibly than HPAL with shorter residence times than sulfuric acid.

However, the process chemistry is more complex, and the processes are not in industrial operation (Harris & White, 2011; Robinson et al., 2017). Both the Neomet and Direct Nickel processes precipitate hematite atmospherically at elevated temperatures and regenerate the respective mineral acids – HCl in Neomet, and HNO_3 in Direct Nickel (Stanković et al., 2020). Neither is proven industrially, and the scalability of the processes remains to be seen.

Heap leaching is the simplest and least capital-intensive option, and therefore it has attracted considerable research attention. The disadvantages are relatively poor nickel and cobalt extraction (~70-80%) and extremely slow kinetics (McDonald & Whittington, 2008; Stanković et al., 2020). Solution percolation issues may be a concern particularly with clay-rich ores, although this can be overcome by heap engineering and agglomeration (Oxley et al., 2016). Heap leaching has been successfully piloted at several sites, including the Çaldağ project in Turkey (McDonald & Whittington, 2008), and it is integrated at the operating Murrin Murrin HPAL plant, and on a small scale in China (Oxley et al., 2016). It does, however, appear that atmospheric processes in their current form are operated to increase the flexibility of the existing HPAL plants.

2.2.4. Arsenical cobalt ores

In this thesis, the term "arsenical cobalt ores" is used to describe orebodies with similar features that bear no clear similarities to copper-cobalt and nickel ores. This mainly includes Co-Cu-Au and polymetallic deposits, where cobalt is present in cobaltite, arsenides, arsenates, and to a lesser degree as linnaeite, cobaltian pyrite, and cobalt pyrrhotite. The examples include but are not limited to the Bou Azzer (1.50% average Co grade), which is in operation, as well as Idaho Cobalt Operations (0.55%), Blackbird (0.74%), NICO (0.12%), Rompas-Rajapalot (0.04%) (Dehaine et al., 2021 a), Juomasuo-Hangaslampi (~0.25%) (Törmänen & Tuomela, 2021), and Mt Isa (~0.14%) (Kangari Consulting Ltd., 2019) deposits. The Broken Hill project in Southern Australia is a unique mineralization, where cobalt occurs primarily in pyrite rather than arsenical minerals (Cobalt Blue, 2021). In most of these deposits, cobalt occurs as the main product in only a few instances, and it is accompanied by other valuable metals - mainly gold, silver, and copper.

The presence of arsenic in late Medieval and Renaissance smalt (potassium glass pigment containing cobalt) has been associated with European arsenide minerals particularly from the German Erzgebirge region, where the ores were initially only exploited for silver (Giannini et al., 2017). Cobalt arsenide ores were roasted to remove most of the sulfur and arsenic, and a mixture of silica sand and cobalt oxide was molten with potash and other fluxes to obtain blue glass, that was then ground as pigments (Molera et al., 2021). It therefore stands to reason that the silver miners in Germany that were mentioned in the Introduction were left with only a cobalt oxide-bearing slag and arsenic vapor instead of silver upon melting the diabolical ores, and this part of the story may well be true. The early pyrometallurgical processing was clearly suitable for producing cobalt glass pigments, but modern hydrometallurgical methods are necessary for the recovery of pure cobalt salts from ores.

Cobalt arsenides and arsenical sulfosalts, i.e., cobaltite, can be separated by physical methods, such as gravity separation and flotation. The mineralogy of the Bou Azzer mine appears to be a complex mixture of arsenides, sulfides, and secondary minerals like heterogenite (CoOOH) and erythrite ($Co_3(AsO_4)_2 \cdot 8H_2O$), and the specifics of the flowsheet are unclear. It appears that the ores are concentrated by gravity separation and flotation, roasted, and leached (Dehaine et al., 2021 a). The Bou Azzer refinery produces cobalt metal by SX/EW (Dehaine et al., 2021 a), but details about arsenic management at the plant are not mentioned in the accessible literature.

Flowsheets and operational details have been better recorded for the Co-Cu-Au type deposits of the Idaho Cobalt Belt, which encompasses many prospects and deposits, including Idaho Cobalt Operations and the inactive Blackbird mine. The main minerals of metallurgical relevance are cobaltite, chalcopyrite, pyrite, native gold, and other sulfides. The Blackbird mine, closed in 1968, is the best-known example, with a few patents and research papers dedicated to the processing of concentrates (Abdollahi et al., 2021; Johnson et al., 2020; Stanley et al., 1982; Taylor & Vanderloop, 1980; Wang et al., 1995). Calera Mining Company processed the concentrates by acidic pressure oxidation from 1952 to 1960 as one of the very first acidic POX plants in the world, although design problems and severe corrosion ultimately led to the refinery's failure (Fassel, 1962). The ores were intermittently blended with low-arsenic concentrates and smelted until the closure of the mine (Taylor & Vanderloop, 1980).

Despite past failures and the operational and economic challenges, POX has become widely used in the processing of refractory gold concentrates and certain base metal concentrates (Dreisinger, 2005). In comparison to HPAL, POX is simpler to operate since it can be run in milder conditions (<200 °C), and the exothermal oxidation of sulfur to sulfuric acid can solve both heat and acid consumption issues (Dannenberg et al., 1987). The main leaching reactions are given by **Reactions 11-13** (Dannenberg et al., 1987). Iron sulfate typically hydrolyses to hematite (**Reaction 9**), but basic ferric sulfate (**Reaction 14**) or jarosite (**Reaction 10**) are also possible. A high iron to arsenic ratio in the solution (~8 mol/mol) facilitates arsenic precipitation (**Reaction 15**) (Fleming, 2010).

$$4CoAsS + 13O_2(g) + H_2O \rightarrow CoSO_4 + 3H_3AsO_4 \quad \textbf{(11)}$$

$$4CuFeS_2 + 17O_2(g) + 2H_2SO_4 \rightarrow 2CuSO_4 + Fe_2(SO_4)_3 + H_2O \quad \textbf{(12)}$$

$$4FeS_2 + 13O_2(g) + H_2O \rightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4 \quad \textbf{(13)}$$

$$Fe_2(SO_4)_3 + 2H_2O \rightarrow Fe(OH)SO_4 + 3H_2SO_4 \quad \textbf{(14)}$$

$$2H_3AsO_4 + Fe_2(SO_4)_3 \rightarrow 2FeAsO_4 + 3H_2SO_4 \quad \textbf{(15)}$$

Atmospheric oxidative leaching processes utilizing acidic ferric sulfate media for cobaltite and arsenide ores have been investigated by Abdollahi et al. (2021), Giebner et al. (2019), Johnson et al. (2020), Hourn et al. (1999), and Taylor and

Vanderloop (1980), using different strategies to enhance the kinetics or decrease chemical consumption. The patent for the industrial Albion process claims that ultra-finely ground (d80 10-12 µm) cobaltite concentrates can be atmospherically leached in ferric sulfate media with sufficient efficiency (Hourn et al., 1999), and further optimization may lead to better results. In ferric leaching, ferric iron may facilitate oxidation (**Reaction 16**, assuming complete oxidation of arsenic) and the oxygen feed restores the oxidant, **Reaction 17**.

$$\mathrm{CoAsS} + \frac{13}{2}\mathrm{Fe_2(SO_4)_3} + 8\mathrm{H_2O} \rightarrow \mathrm{H_3AsO_4} + \mathrm{CoSO_4} + \mathrm{FeSO_4} + \frac{13}{2}\mathrm{H_2SO_4} \quad \textbf{(16)}$$

$$4\mathrm{FeSO_4} + \mathrm{O_2(g)} + 2\mathrm{H_2SO_4} \rightarrow 2\mathrm{Fe_2(SO_4)_3} + 2\mathrm{H_2O} \quad \textbf{(17)}$$

The Albion process is industrially applied for refractory gold and some copper ores. Taylor and Vanderloop (1980) studied ferric leaching in sulfuric acid, but the kinetics were slow even at high ferric concentrations (>150 g/L) despite oxygen purging. The bioleaching of cobaltite and arsenide ores has been proven successful on laboratory scale (Abdollahi et al., 2021; Giebner et al., 2019; Johnson et al., 2020), and Johnson et al. (2020) showed that arsenic can also be immobilized as stable scorodite even during leaching.

In addition to direct leaching or smelting, the pre-treatment of sulfide concentrates by roasting before hydrometallurgical treatment is an established method in the base metals and gold industry (Marsden & House, 2006; Shelton et al., 1948). The goal of the process is to convert the base metal sulfides to water-soluble sulfates and acid-soluble oxides, iron to insoluble hematite (Fe_2O_3), and preferably to volatilize arsenic to form a clean calcine that can be selectively leached to extract the base metals. In similar zinc and copper processes, evaporated arsenic compounds are condensed from the off-gas and stabilized hydrometallurgically (Adham et al., 2019).

Wang et al. (1995) showed that achieving the goals in the same conditions is challenging, however. In oxidizing atmospheres, sulfur can be easily eliminated as sulfur dioxide at 650 °C, but arsenic remains trapped in the structure up to elevated temperatures (950 °C), where the process is disrupted by the formation of refractory cobalt ferrite ($CoO \cdot Fe_2O_3$). The formation of cobalt arsenates appears to hinder arsenic oxidation from the structure (Wang et al., 1995). This has not been confirmed for cobaltite, but the formation of ferric arsenate ($FeAsO_4$) from arsenopyrite can be minimized by controlling the conditions (Chakraborti & Lynch, 1983), which indicates that further work on cobaltite oxidation is warranted.

2.2.5. Environmental impacts of primary cobalt production

The by-product nature of cobalt and its scattered value chain makes the comparison of different LCA studies challenging. Refineries produce a multitude of different cobalt products for different purposes, such as cathode, powder, hydroxide, and sulfate, and allocation between products may be needed at several points (Dai et al., 2018). Most battery manufacturing LCA studies are reliant on average datasets that aim to be both technologically and geographically representative of the cobalt market. The most frequently used datasets have been published by the Cobalt Institute and Ecoinvent (Cobalt Institute, 2021; Ecoinvent, 2023); however, it must be stressed that the complexity of global cobalt flows makes this extremely challenging. It was noted by Šimaitis et al. (2021) that the global warming impact factors for cobalt sulfate are significantly lower according to the Cobalt Institute compared to Ecoinvent 3.8, for instance.

Farjana et al. (2019) studied the impacts of cobalt extraction and found that blasting and energy consumption are the largest individual contributors. Their study is not without severe problems, however – the data appears outdated and the LCI data is taken directly from Ecoinvent (Arvidsson et al., 2020). The geographical boundary is stated to be "global", and since the data does not differentiate between refining and mining stages, not to mention whether the cobalt is the co-product or copper or nickel, the findings are not particularly useful. The LCI developed for the GREET model is reported far more transparently, and was gathered using primary data on mining in the DRC and refining in China (Dai et al., 2018). The caveat, however, is that the GREET model only assesses a limited set of transportation-critical resources and pollutants (Wang, 2020), so while useful for energy technologies, it is less informative for the mining industry.

Cobalt is rarely addressed in nickel studies separately, although by-product allocation is sometimes mentioned (Eckelman, 2010). The study by Zhang et al. (2021) is an exception, as they focus on cobalt sulfate heptahydrate (CSHH) recovery from low-grade nickel-copper-cobalt ores in China. Nevertheless, a share of nickel production impacts can be presumed to be justifiably allocated to cobalt in sulfide smelting and hydrometallurgical laterite processes, where cobalt follows nickel to the refinery. Overall, the processing of laterites is far more environmentally intensive than sulfides due to its considerable energy and chemical consumption (Eckelman, 2010; Mistry et al., 2016; Norgate et al., 2007). Mining and beneficiation dominate the impacts of sulfide processing (Bai et al., 2022; Zhang et al., 2021), while energy and chemical consumption are a clear challenge for laterite processing (Fukuzawa, 2012; Khoo et al., 2017). The Direct Nickel laterite process has been evaluated by Khoo et al. (2017), and this route has much lower impacts than the predominant processes. Norgate and Jahanshahi (2011) identified that neutralizing agents lead to excessive emissions in hydrometallurgical laterite processes. The use of the saprolite fraction for the post-autoclave neutralization process, like at Ravensthorpe, provides one solution (Crundwell et al., 2011).

In general terms, mining is an energy intensive and diverse industry that faces global pressure to curb its environmental impacts and carbon footprint. This is further exacerbated by the growing demand and ever-plummeting ore grades, which further increases the energy intensity, and the solutions to the problem are likely to be site-specific (Issa et al., 2023). The future impacts of mining are therefore difficult to predict, yet van der Meide et al. (2021) forecasted the impacts of the cobalt industry up to 2050 using the following variables: ore grade, shares of primary and secondary markets, and energy transition. The total impacts were predicted to increase as a response to increased consumption. Although the climate impacts can be offset by "sustainable development", i.e., mainly decarbonization efforts, the increased demand for metal is also seen as an increase in the toxicity categories in the model.

2.3. Recycling of cobalt and other metals from spent Li-ion batteries

The methods for lithium-ion battery recycling can be loosely divided into hydrometallurgical, pyro-hydrometallurgical, and direct recycling. Direct cathode recycling refers to the regeneration of the cathode without first disintegrating it, whereas pyrometallurgical and hydrometallurgical processes decompose the lithium metal oxide structure and separate the metals.

2.3.1. Overview of metallurgical processes

The current industrial processes use a combination of mechanical, pyrometallurgical, and hydrometallurgical technologies to separate and purify the metals in the battery. Mechanical pre-treatment is a pre-requisite for hydrometallurgical processes and direct recycling that treat black mass. Some pyrometallurgical processes, like Umicore in Belgium, accept entire modules and cells with only minimal pre-processing, but others (e.g., Accurec in Germany, Fortum Batteries in Finland) also include pre-treatment (Sommerville et al., 2021). Several recycling plants only conduct the mechanical pre-treatment stages and sell the black mass to refineries, which exemplifies the difficulty of making broadly accurate generalizations. A schematic of the main treatment routes for spent Li-ion batteries is provided in **Figure 7**, which also shows which elements are recovered and which are not.

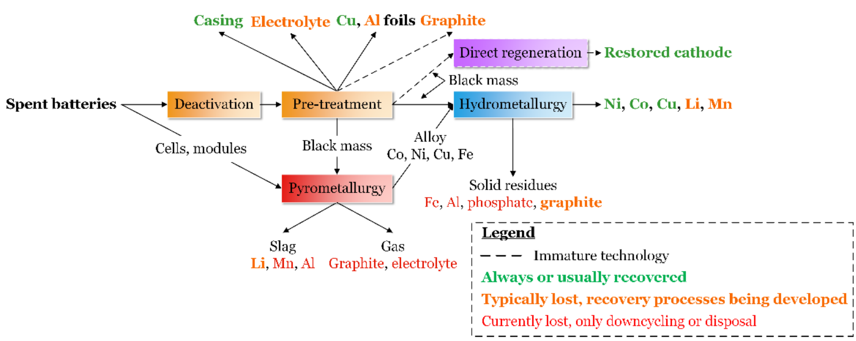


Figure 7. Treatment routes for batteries and status of the processes, specifically in Europe, Japan, and North America.

The technologies and flowsheets for the pre-treatment stage are as diverse as the plants themselves, and the selection of units affects the composition of the black mass. Spent batteries must be deactivated or stabilized before or during shredding to prevent explosions and fires, which can be done either by using an inert atmosphere or discharging (Kim et al., 2021). The battery pack, which consists of modules, which in turn is comprised of connected cells (**Figure 8**), is dismantled to cell or module level before comminution. The variety of pack design and the use of adhesives makes the automation of disassembly a key challenge for recyclers (Thompson et al., 2020).

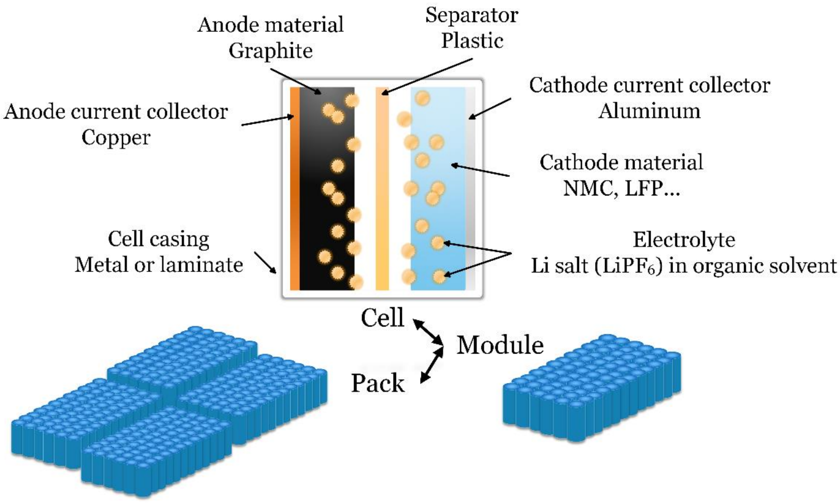


Figure 8. Simplified structure of battery packs, modules, and cells without the electronic and cooling components.

After shredding, ferrous metals may be removed by magnetic separation, and binder and remaining organic components are sometimes pyrolyzed. Simple size classification, e.g., sieving, can be used to separate some of the larger aluminum and copper foils from the fine active material powders, although with limited selectivity (Yu et al., 2021). The electrolyte, which is typically a mixture of $LiPF_6$ dissolved in cyclic and chain carbonate solvents, is volatile and evaporates. The electrolyte is arguably the most hazardous and toxic component in the cells, and while currently not recycled, its recovery has been considered by methods such as supercritical CO_2 extraction (Wu et al., 2022). Aluminum is typically not separated from copper foils, although there are physical and chemical ways to achieve this (Kim et al., 2021).

The current industrial pyrometallurgical processes, like the previously mentioned Umicore process, use high temperatures (1450~1500 °C) to form two immiscible melts. Perhaps the largest advantage of pyrometallurgical processing is the need for minimal pre-processing, given the difficulties of battery pack disassembly (Thompson et al., 2020), followed by the fact that organic materials decompose without the need for challenging waste treatment. The sulfating and reducing treatment of black mass at roasting temperatures (500-1000 °C) to improve leaching efficiency and selectivity in milder conditions is, so far, an experimental technique (Biswas et al., 2023). High temperature processes can tolerate a variety of other nickel- and cobalt-containing feeds in addition to spent Li-ion batteries, such as NiMH batteries or primary raw materials (Pinegar & Smith, 2019), which has been particularly attractive when the volumes of spent batteries have been limited.

The metals that reduce more easily with carbon than iron and cobalt, i.e., nickel and copper, form a molten mixed metal alloy, which is refined hydrometallurgically. Lithium, manganese, and aluminum dissolve in the slag, which is used as an aggregate material (Makuza et al., 2019). Slag leaching for lithium and manganese has been the subject of much discussion, overlooking the fact that both metals are bound to refractory aluminosilicates, which do not dissolve readily into aqueous solutions without intense pre-treatments (Xiao et al., 2017). Changes in the legislation and the skyrocketing price of lithium have, however, incentivized process development, and pyrometallurgical volatilization with suitable fluxes appears a promising method to selectively separate lithium from discarded slags or directly in the melting furnace (Holzer et al., 2021; Qu et al., 2022).

Even assuming that lithium can be recovered, some challenges remain with pyrometallurgical processes. First, the formation of toxic and corrosive fluorine-bearing gases in the burning of electrolyte and binder materials necessitates robust gas cleaning systems. Furthermore, the process requires a carbon source to reduce the mixed metal oxides. If present, graphite (and possibly metallic aluminum) act as auxiliary reducing agents in the process, and neither is recovered (Makuza et al., 2019). The loss of graphite may be avoidable by separating it from the black mass in pre-treatment.

The hydrometallurgical treatment of black mass is relatively new and only emerging on industrial scale. Nevertheless, the processes consist of three stages, which may partially overlap: leaching, solution purification, and metal recovery. There are numerous options for each stage, but sulfuric acid is the most widely accepted leaching agent, and solution purification usually involves precipitation of the impurities, solvent extraction, and sometimes ion exchange. The cathode metals are crystallized or precipitated as compounds. Graphite is inert in aqueous solutions, and the potential for leach residue valorization either as new anodes or other functional carbon materials has been demonstrated on laboratory scale (Sommerville et al., 2023; Wu et al., 2022).

2.3.2. Black mass recycling in acidic sulfate media

Black mass leaching has been investigated in a variety of media, ranging from the commonly used mineral acids (H_2SO_4, HCl) to organic acids and bioleaching, many of them interesting mainly from an academic perspective. Sulfuric acid is industrially the most widely accepted leaching reagent and therefore this work only considers process chemistry in sulfate solutions.

Lithium metal oxides can technically be dissolved in sulfuric acid without additives (**Reaction 18**) (Nan et al., 2005). The dissolution of pure LCO and NMC materials in sulfuric acid solutions alone, however, results in poor leaching efficiencies (70-90% Li, <50% Ni, Co, Mn) due to the need for an external reducing agent to destabilize the oxide structure (Vieceli et al., 2018; Vieceli et al., 2023). Hydrogen peroxide (H_2O_2) is considered to be an advantageous reductant since it introduces no new cations and anions to the solutions, but it is also consumed in side reactions with metallic impurities (Cu, Fe, Al). The dissolution of LCO in acid is represented by **Reaction** 16, and the reducing reaction with hydrogen peroxide by **Reaction 19**.

$$4LiCoO_2 + 6H_2SO_4 \rightarrow 2Li_2SO_4 + 4CoSO_4 + 6H_2O + O_2(g) \quad \textbf{(18)}$$
$$2LiCoO_2 + 3H_2SO_4 + H_2O_2 \rightarrow Li_2SO_4 + 2CoSO_4 + 4H_2O + O_2(g) \quad \textbf{(19)}$$

In the absence of an oxidant (i.e., H_2O_2) that would dissolve them, the cathode materials can be reduced by solid copper and aluminum. Just as ferric iron can facilitate the oxidation of sulfides (**Reactions 16** and **17**), the same mechanism can be used in reverse to mediate reduction (**Reaction 20**). It has been observed by Chernyaev et al. (2021) that the dissolution of active material oxides occurs more rapidly with dissolved iron present than with only copper or aluminum. Ferric iron is regenerated to ferrous when it oxidizes the current collector metals, which is represented for copper by **Reaction 21**. The kinetics and detailed chemistry of the system have been reviewed in detail by Porvali et al. (2021) and Chernyaev et al. (2021, 2022).

$$2LiCoO_2 + 4H_2SO_4 + 2FeSO_4 \rightarrow Li_2SO_4 + 2CoSO_4 + Fe_2(SO_4)_3 + 4H_2O \quad \textbf{(20)}$$
$$Fe_2(SO_4)_3 + Cu \rightarrow CuSO_4 + 2FeSO_4 \quad \textbf{(21)}$$

The most important point to observe from a process perspective is that industrial black mass, which contains the mentioned impurities, may not require a reducing agent at all. Guimarães et al. (2022), for instance, observed this by leaching NMC 811 type black mass with a staggering 13.6% Cu and 6.3% Al in sulfuric acid, concluding erroneously that no reducing agent is needed: the material itself is highly self-reducing due to the high Cu and Al. Another factor to keep in mind is that the high impurity content affects downstream processing. Ferrous iron is beneficial at low levels since it can be regenerated, but solid copper and aluminum are consumed as they dissolve. It is relatively simple to separate and valorize copper, but iron and aluminum are hardly ever recovered as products from hydrometallurgical circuits. Nevertheless, the optimization of leaching and purification stages should be preferably done jointly to achieve both high leaching extraction without excessively burdening the impurity removal.

Although the methods themselves may vary, the order of where each of the components is reclaimed or removed typically follows the one shown in **Figure 9**. Lithium is typically recovered as the last metal (blue route) (Davis & Demopoulos, 2023), but it can alternatively be recovered *first* by treating the black mass at roasting temperatures and selectively leaching and recovering lithium (teal route), which avoids lithium losses to other streams (Makuza et al., 2021; Zhang et al., 2023). Cathode active material is typically produced by calcining lithium hydroxide and the Ni-Co-Mn bearing precursor material, also known as pCAM, which is usually a co-precipitated hydroxide (Malik et al., 2022). Lithium hydroxide cannot be directly crystallized from sulfate solutions, so lithium carbonate must be converted to hydroxide by lime if required by the process.

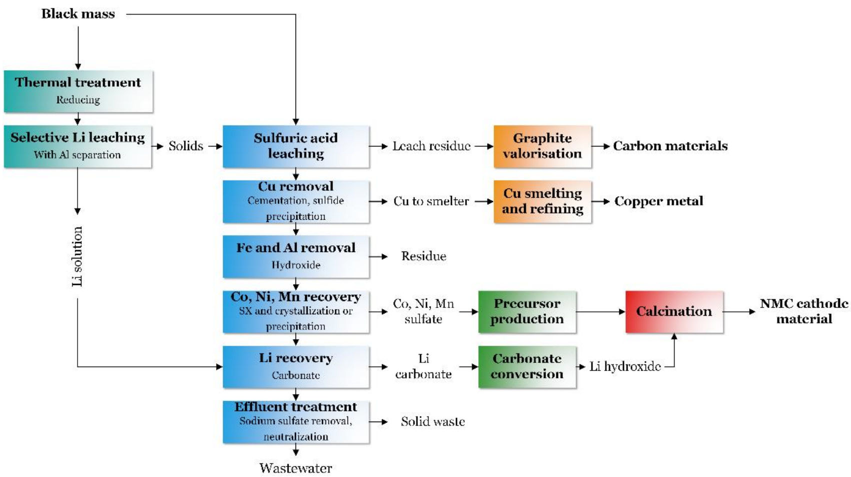


Figure 9. Process schematic for different options to recover cathode metals from black mass in sulfate media to synthetize new active materials.

NMC pCAM materials are synthetized by dissolving nickel, manganese, and cobalt sulfate salts in the desired ratio and precipitating the mixed hydroxide in controlled conditions (Malik et al., 2022). Transition metal sulfates are extremely water soluble and need to be produced from pure, preferably concentrated solutions to avoid excessive water evaporation. Stepwise solvent extraction using acidic extractants (e.g., D2EHPA, Cyanex-type reagents) is typical (Davis & Demopoulos, 2023), but the use of intermediate precipitates like manganese oxide and mixed Ni-Co precipitates might be applied as well. Ion exchange has also received some attention despite being a rare process in the recycling industry, and Fortum is looking to apply it industrially in the separation of cathode metals (Kivelä et al., 2022).

The discussion about battery leach solution effluent treatment has focused on two components: sodium sulfate and fluoride. Either crystallized sodium sulfate or sodium sulfate-bearing effluents are produced due to the use of sodium hydroxide for pH control, a problem that is shared by pCAM production (Tuovinen et al., 2021). Sodium sulfate is not expressly toxic and its disposal in the sea has been practiced despite disruption to marine ecosystems (Aqua Metals, 2023). A better solution would be to convert the sodium sulfate to useful chemicals, like sulfuric acid and sodium hydroxide, with methods like electrodialysis (Kuldeep et al., 2021). Fluoride is another tricky impurity due to its corrosiveness and the potential for generating hydrogen fluoride, but its behavior in hydrometallurgical circuits appears poorly understood and under-researched in the current literature (Xu et al., 2023). Fluoride volatilizes at elevated temperatures, so thermal treatment or other pre-treatments are likely to have a major role in the solution, but this remains to be seen.

2.3.3. Environmental impacts of Li-ion battery recycling

The environmental tradeoffs from the wider substitution of ICEVs with EVs are quite well established. In broad terms, the weight of the total cradle-to-grave burden shifts from fuel to the manufacturing phase, and – assuming clean electricity – the climate and air quality effects of fossil fuels are largely substituted by mineral resource scarcity and mining-related impacts. In LCA, the recycling of spent batteries has traditionally been modeled with a "black box" approach, where the LCI and assumptions are not presented in a transparent manner, if at all (Raugei & Winfield, 2019). In recent times, however, several published studies have been more detailed and process-centric (Blömeke et al., 2022; Cao et al., 2023; Kallitsis et al., 2022; Rajaeifar et al., 2021; Rey et al., 2021; Zhou et al., 2021). This is most likely to do with the fact that the industry is slowly maturing, and the broader view is becoming clearer.

There are many ways to address the EOL phase in LCA literature, many of which are more suitable for cradle-to-grave, or cradle-to-cradle, studies. In waste treatment-oriented studies, it is almost unequivocally assumed that the battery carries no environmental burdens from its manufacturing and use phase, and material recovery is assigned credits that represent the avoided burdens from primary raw material production. Negative impacts indicate that the recycling of materials has benefits, whereas positive impacts mean added burdens. The risk of double counting and other features of the modeling methods have been further discussed by Nordelöf et al. (2020). Closed-loop recycling methods may be applicable to direct recycling, but this is only true if the cathode quality remains the same as a newly synthetized one.

There is no single answer to whether recycling mitigates the lifetime impacts of batteries. Pyro- and hydrometallurgical approaches appear suitable for NMC, LCO, and NCA chemistries (Ciez & Whitacre, 2019), and a large share of the benefit more accurately comes from pre-treatment (Blömeke et al., 2022). Direct recycling appears to have the largest impact reductions across the board (Ciez & Whitacre, 2019; Wu et al., 2022; Xu et al., 2020), apart from the study of Quan et al. (2022), where hydrometallurgical processing is comparably better than direct regeneration. As direct recycling is a low maturity technology, the results are obviously only indicative at this stage, but the route could become particularly advantageous for challenging cathodes like LFP (Xu et al., 2020). It is also worth observing that pyrometallurgical processing has foreground (scope 1) carbon emissions due to the use of a carbonaceous reducing agent, whereas hydrometallurgical and direct recycling rely more on chemicals and electricity that result in indirect (scope 2 and 3) emissions.

The material recovery benefits of treating NMC or cobalt-rich feeds derive from nickel and cobalt, which are both heavier elements and more intensive to produce than, for instance, lithium (Mohr et al., 2021; Quan et al., 2022; Dunn et al., 2012). The recovery of both copper and aluminum is an effective measure to bring benefits, as current collectors occupy a considerable share of cell mass (Blömeke et al., 2022; Dunn et al., 2012; Kallitsis et al., 2022; Rajaeifar et al., 2021). The recycling of anodes has not been studied much, but Engels et al. (2022) reflected that the current *primary* datasets on graphite mining and refining underestimate its impacts and that its recycling might also be environmentally critical. The analysis of Castro et al. (2022) includes anode recycling, and a very wide global warming potential range (0.53-9.76 kg CO_2-eq/kg graphite) is presented in Rey et al. (2021) for recovered graphite as one of the early studies on the topic.

Some interesting points have been raised about the methodology and interpretation of results. Cao et al. (2021) demonstrated that the recovery of co-products, such as sodium sulfate, can add more burdens to the process than what is "avoided" by their reclamation. It should, however, be observed that *not recovering* the co- and by-products also has impacts, e.g., if sodium sulfate and lithium are not recovered, they either accumulate in the process or are released into the environment. Some battery metals are also interdependent, as in a pure nickel product recovery is difficult without first separating cobalt and copper, and aiming for a pure lithium carbonate salt may necessitate the removal of certain elements from the effluents.

In cradle-to-grave studies, the temporal boundary is also critical, as pointed out by Šimaitis et al. (2022). EV batteries have a long lifespan (5-10 years by estimate), and it is likely that the energy mix used at the time of their recycling will be significantly greener than during their manufacture. Decarbonization is projected to decrease the impacts from energy-intensive mining substantially, and it follows that the recycling credits are likely to be smaller than the original raw materials. Regulation (EU) 2023/1542 on batteries also dictates a set content of recycled materials in new batteries, which must be considered in future cradle-to-grave LCA studies.

3. Materials and methods

The same computational simulation and LCA tools were used in all of the scenarios: HSC Sim 10, GaBi, and Ecoinvent v.3.7 and 3.8. The specifics of the processes and the simulations are provided in the publications.

3.1 Flowsheet design

The feed materials and the flowsheets for both Au-Co materials (roasting-leaching, pressure leaching, and atmospheric reactor leaching, **Publications I-II**) and black mass (synergistic processing with NiMH battery waste, **Publication III**, and internally reducing processing, **Publication IV**) are discussed in the following two sections. Some scoping of the process flowsheets, such as the potential for sodium sulfate crystallization (**Publication III**) and the recommendation for sulfide intermediate precipitation (**Publication II**) has been done in the publications in detail and this is not further discussed in the compendium.

3.1.1. Processing of gold-cobalt ores

The raw material in **Publications I** and **II** is from a prospective mine in Finland, and information on its probable composition was obtained by physical and chemical characterizations as well as a literature survey. The material is a gold ore containing significant quantities of cobalt as a co-product. It was observed that cobalt occurs primarily in the form of cobaltite and linnaeite, copper as chalcopyrite, and iron mostly as pyrrhotite, making the raw material quite similar to Blackbird ore (Bookstrom et al., 2016). Linnaeite occurs mainly with pyrrhotite, which can be separated magnetically, while cobaltite is amenable to froth flotation (Dehaine et al., 2021).

The process modeling research was conducted with two concentrate blends. The first, CI, is a high-grade concentrate, and in **Publication I** the composition (**Table 2**) was varied by changing both the cobalt grade (0.5-10%, baseline 1.35%) and the mineral species (cobaltite or linnaeite as main cobalt mineral). The second raw material, CII, is an optimized blend of flotation and magnetic concentrates. The mineral compositions were calculated using the chemical composition, which was fitted stoichiometrically to a blend of minerals that are either confirmed or probably present in the feed. This enables an accurate representation of the reactions.

Table 2. Compositions of the concentrates (wt.%, Au in ppm), **Publications I-II.**

	Au (ppm)	CoAsS	Co_3S_4	$CuFeS_2$	$Fe_{1-x}S$	FeS_2	Silicates
CI	23.10	3.65	0.06	1.27	36.43	3.23	55.36
CII	12.90	0.27	0.16	0.31	27.36	0.65	71.25

Although few hydrometallurgical experiments have been conducted on these raw materials, some processing characteristics have been confirmed experimentally. First, the gold is free-milling and amenable to cyanidation without pre-treatment, and there is no indication of preg-robbing behavior (SRK Consulting Oy, 2022). Second, the main impurities are iron and arsenic, but other elements such as calcium and magnesium are also present in the silicate minerals (Mawson Gold Ltd, 2022). The dissolution and recovery of cobalt are therefore uncertain, but flowsheets were designed based on the similarities with Blackbird concentrates. Smelting was not considered due to the high arsenic content in the feed as well as the low grades and cobalt behavior in copper and nickel sulfide smelting.

An overview of the options for processing cobaltite ores was provided in the theoretical background section of the thesis. Pressure oxidation (POX) has the benefit of exothermally dissolving the sulfides at high temperatures while also hydrolyzing iron and arsenic as stable hematite and ferric arsenate precipitates already in the autoclave. The method is proven for both refractory gold and Blackbird ores but has high capital costs and is challenging to operate. Atmospheric leaching of sulfides is slow in oxygen-sulfuric acid media, although ultra-fine grinding has been shown to improve the kinetics; however, this is not proven for cobaltite ores. Roasting-leaching is another well-known process that is industrially implemented for many kinds of sulfide ores, although there is an indication that cobaltite roasting is challenging (Wang et al., 1995).

The solid leach residues are treated by cyanidation, carbon adsorption, and electrowinning. Another processing option could be cyanide leaching of gold followed by sulfide flotation and the hydrometallurgical processing of cobalt (SRK Consulting Oy, 2022), but this was beyond the scope of this thesis.

After leaching and impurity removal, cobalt is precipitated as cobalt sulfide intermediate, which is transported 500 km to a refinery, where it is re-leached and refined. Cobalt hydroxide and direct SX were also studied as options in **Publication IV**, but it was found that cobalt sulfide has both technical and environmental benefits due to its lower hygroscopicity and higher purity. The disadvantage is that both precipitation and re-dissolution are more complex and require special equipment. There are different options for the chemical used in sulfide precipitation: hydrogen sulfide (H_2S) gas, sodium hydrosulfide (NaHS), or sodium sulfide (Na_2S), the first being the most typical in the industry.

There is no actual laboratory scale data of the raw material in the studied processes, and therefore the process models were constructed as "best case scenarios", where the processes are assumed to perform as they are designed. The model parameters were estimated from a combination of industrial, laboratory, and pilot data on similar minerals and gold processes. The processes and the materials are presented in detail in **Publications I-II**.

3.1.2. Spent batteries

The different compositions for the feed materials are provided in **Table 3**. The assumptions and chemical analyses for cobalt-rich (RCo) and NiMH batteries are presented in **Publications III** and **IV**, but the chemical analyses were converted to species to represent the leaching chemistry more accurately. The nickel-rich composition was calculated by stoichiometrically converting the $LiMeO_2$ to NMC811 chemistry: 8 mol $LiNiO_2$ and 1 mol $LiMnO_2$ and $LiCoO_2$ for 10 moles of $LiMeO_2$.

The structure of NiMH batteries is briefly as follows: the cathode consists of nickel oxyhydroxide, the electrolyte a mixture of aqueous alkali (KOH and NaOH), and the anode is a hydrogen-adsorbing metal alloy. The alloy is typically AB5-type, where A is a rare earth element (REE), e.g., lanthanum, praseodymium, or cerium, and B is typically nickel, cobalt, or manganese. The composition in **Table 3** has been further modified from **Publication III** to be more representative. The RCo material is presumed to originate from portable batteries, given the high $LiCoO_2$ content.

Table 3. Battery compositions (wt.%), **Publications III-IV** and compendium. Chemical analyses for RCo and NiMH are obtained from Liu et al. (2019). RNi is calculated to have an equimolar amount of cathode material as RCo.

	$LiCoO_2$	**$LiNiO_2$**	**$LiMnO_2$**	**Cu**	**Fe**	**Al**	**C**
RCo	31.21	4.97	2.65	0.40	0.37	0.54	59.86
RNi	3.90	31.09	3.74	0.40	0.37	0.54	59.97
	$LaNi_5$	**$Ni(OH)_2$**	**KOH**	**NaOH**	**Fe**	**$LaCo_5$**	**$LaMn_5$**
NiMH	55.37	39.15	2.75	0.98	1.52	0.15	0.08

Both Li-ion and NiMH black masses contain nickel, cobalt, and manganese as valuable metals, and iron as an impurity. The differences are that NiMHs contain no lithium or graphite, whereas Li-ion batteries have no REEs. Some pyrometallurgical processes, i.e., Umicore, can therefore accept both battery types, but there are also benefits for hydrometallurgical processing. The hydrogen-adsorbing NiMH anode is reducing, i.e., requires an oxidant, whereas lithium metal oxides ($LiMeO_2$) are oxidizing and therefore require a reductant. The cycling reaction of NiMH batteries is based on the redox reaction, where $NiO(OH)$ reduces to $Ni(OH)_2$ during discharging while the anode oxidizes. The batteries in **Table 3** were assumed to be discharged, so the cathode is represented by nickel hydroxide that does not consume reducing agent.

The process for the synergistic hydrometallurgical treatment of Li-ion and NiMH black mass is presented by Liu et al. (2019) and modeled in **Publication III** using three flowsheets. The anode alloy in NiMHs acts as the reductant and lithium metal oxides as the oxidant in the leaching system. With the minimum NiMH to Li-ion mass ratio of 0.75 to 1, no other reducing agent is needed. The challenge is that the real volume of NiMH black mass in the market will be much lower than that of Li-ion black mass in the future: NiMHs have traditionally powered Toyota's hybrid electric vehicles (HEVs) in particular, but HEV manufacturers have also replaced NiMHs with more powerful Li-ion batteries. Leaching **Reactions 22** and **23** show that the dissolution of NiMH materials is highly acid-consuming.

$$2LaNi_5 + 13H_2SO_4 \rightarrow La_2(SO_4)_3(aq) + 10NiSO_4(aq) + 13H_2(g) \qquad \textbf{(22)}$$
$$Ni(OH)_2 + H_2SO_4 \rightarrow NiSO_4(aq) + H_2O \qquad \textbf{(23)}$$

At NiMH to Li-ion ratios lower than 0.75:1, additional reductants are needed, and the chemistry becomes more complicated. It is safe to presume that hydrogen peroxide would simply oxidize NiMH anodes and reduce Li-ion cathodes, rendering the system redundant, but copper and aluminum together with iron could be worth further investigation. The recovered metals are largely the same, aside from rare earths and lithium. Rare earths can be selectively separated as a double sulfate precipitate ($Na_2REE_2(SO_4)_4$) (Porvali et al., 2018), so the flowsheet in **Figure 9** only requires one additional step after leaching.

The internally reducing (INT) flowsheet utilizes copper as the reducing agent and small amounts of dissolved iron as a catalyst, as discussed in detail in Section 2.3.2 as part of the literature analysis. The process was modeled in **Publication IV** assuming copper cementation with iron, iron and aluminum hydrolysis, and three different scenarios for manganese recovery: SX of manganese with iron and aluminum scrubbing from the organic, iron and aluminum hydrolysis followed by SX, and no SX at all. Iron and aluminum removal followed by manganese SX was technically the most viable, leading to the lowest cobalt and nickel losses despite no SX at all being the lowest in environmental impacts, so manganese SX was selected for the harmonized flowsheets.

The downstream flowsheets, while similar, were harmonized and their industrial representativeness was improved. The process sequence is the same as in **Figure 9** with the addition of the previously discussed REE sulfate precipitation. In **Publication III** manganese dioxide was precipitated using potassium permanganate, and in **Publication IV** using sulfur dioxide/oxygen gas mixtures. In the harmonized flowsheets, manganese was crystallized from SX solution as sulfate monohydrate, which can be directly used in NMC pCAM synthesis without further processing. Lithium can also be reclaimed as less soluble lithium phosphate (Liu et al., 2019), but lithium carbonate was selected for the harmonized flowsheets as a more marketable product. The harmonized process parameters up to manganese recovery are presented in **Table 4**.

Table 4. Harmonized process controls for studied battery recycling flowsheets, Synergistic (SYN) and Internally reducing (INT) scenarios. The rest of the process, starting from cobalt SX, was modeled with the parameters provided in Publication IV.

	SYN	INT	References
Leaching parameters			
NiMH : Li-ion (wt)	0.75 : 1	-	Liu et al. (2019)
Cu : 2 LiMeO2 (wt)	-	1.20	Porvali et al. (2020a)
Fe : $LiMeO_2$ (wt)	-	0.11	Porvali et al. (2020a)
Solid concentration (g/L)	100	100	Selected
[H_2SO_4], baseline (M)	1.0	1.0	Selected
Copper cementation			
Iron feed	Stoich.	-	
Rare earth double sulfate precipitation			
Na_2SO_4 feed	4 x stoich.	-	Liu et al. (2019)
pH	1.4	-	Liu et al. (2019)
Iron and aluminum hydrolysis			
pH	3.5	3.5	Chernyaev et al. (2023)
Manganese SX			
Equilibrium pH in extraction	3.2	3.2	Peng et al. (2020)
A/O in extraction	1:2	1:2	Peng et al. (2020)
D2EHPA in diluent (M)	0.4	0.4	Peng et al. (2020)
A/O in scrubbing	10	10	Peng et al. (2020)
[Mn] in scrubbing (g/L)	4	4	Peng et al. (2020)
O/A in stripping	1:1	1:1	Peng et al. (2020)
[H_2SO_4] in pure solution (M)	20	20	Peng et al. (2020)
Manganese sulfate crystallization			
$MnSO_4$ solubility (mol/kg)	~0.3	~0.3	Kobylin & Taskinen (2012)
Temperature (°C)	~70	~70	Kobylin & Taskinen (2012)

The process sequence is as follows: leaching, S/L separation to obtain a graphite-rich residue, copper cementation (**Publication IV**, harmonized), REE double sulfate precipitation (**Publication III**, harmonized for SYN), iron and aluminum hydrolysis, manganese SX (**Publication IV**) and crystallization (harmonized), cobalt SX and crystallization, nickel SX and crystallization, lithium carbonate recovery, sodium sulfate crystallization, and final effluent treatment, such as in **Figure 9**. Manganese, cobalt, and nickel were recovered as soluble sulfates from pure SX solutions, and lithium as carbonate. Graphite, iron, and aluminum were considered lost, although graphite valorization from leach residues is a possible way to expand future studies. The effluent treatment includes sodium sulfate crystallization, as recommended in **Publication III**.

As can be established from the parameters and their references, the models for the black mass processes are based on laboratory scale data, and the processes are not commercially established. The uncertainties are therefore different from those of Au-Co processes, where the processes themselves have been industrially proven scalable, but their performance with the specific raw material has not. In contrast, the chemistry and residues of black mass processes are relatively well known on laboratory scale, but the processes themselves have not been operated industrially on full scale.

3.2. Goal and scope definition

As stated in the literature survey, the definition of goal and scope consists of defining the specific research question, intended audience, reasons for conducting the study, investigated product system and its function(s), functional unit, all system boundaries, impact categories, LCIA method, data requirements, assumptions, how LCI is modeled, allocation procedures, and reporting of the study.

3.2.1. Summary of goals and scope

The reason for conducting the study was to widen the understanding of how process selection and parameters affect the impacts of cobalt production and recycling at high levels of uncertainty. The specific goals for each publication were as follows:

- **I.** Study the impacts of cobalt sulfate heptahydrate (CSHH) production from arsenical and non-arsenical Au-Co-Cu ores by POX.
- **II.** Update the mineralogy of Publication I, compare the impacts between not recovering cobalt, POX, roasting-leaching, and the Albion-type atmospheric leaching process.
- **III.** Study the impacts of hydrometallurgical black mass treatment by synergistic processing of Li-ion and NiMH batteries and compare them to virgin metal impacts.
- **IV.** Study the impacts of hydrometallurgical treatment of Li-ion black mass in the Fe-Cu system, find ways to recover manganese, and compare to virgin metal impacts.

A fair comparison of the individual studies required harmonization of functional units, allocation procedures, and boundaries in some cases. In addition to the objectives stated in Section 1.2, the harmonized goals of the thesis were to:

- Summarize the findings for CSHH production from Au-Co ores.
- Compare the impacts of Li-ion black mass recycling in Fe-Cu and synergistic leaching systems.

The intended audience is metallurgical experts, chemical engineers, and LCA practitioners. The studies are intended to reach a wide audience by being published with open access in journals, and the compendium is an open thesis for Aalto University. The studies and compendium are reviewed both internally by the co-authors and externally by peer-review or the university's pre-examination procedures. The scope of the journal is summarized in **Table 5**. "Harmonized" refers to the methods used in the compendium to enable sound comparisons and conclusions.

Table 5. Scope of the work, I-IV referring to thesis publications and "harmonized" to new research in the compendium.

LCI modeling	
I-IV, harmonized	Primarily metallurgical flowsheet modeling. Mining model for I-II adapted from literature proxy. Electricity consumption calculated from estimated equipment dimensions.
Allocation procedures	
I	None or physical or economic allocation between Co, Au, and Cu
II	Economic allocation between Co and Au; unit subdivision; by-product credits for sulfuric acid
III-IV	Waste allocation, avoided burden method for REEs, Co, Ni, Mn, and Li
Harmonized	Details in Section 3.2.4
Functional unit	
I	Output-based, 1 kg CSHH
II	Output-based, 1 kg gold
III	Input-based, 1 kg mixed black mass
IV	Input-based, 1 kg black mass
Harmonized	Primary: output-based, 1 kg CSHH Secondary: input-based, 1 kg Li-ion black mass
Technical boundaries	
I-IV, harmonized	Cradle-to-gate or gate-to-gate, see Section 3.2.3 for details
Spatial boundary	
I-II	Finland
III-IV	Europe
Temporal boundary	
I-IV, harmonized	2030 onwards
Impact modeling	
All	CML v.4.8 (2016), see Section 3.2.4 for impact categories

3.2.2. Functional unit and multifunctionality

A functional unit is defined by the ISO standard as "the quantified performance of a product system for use as a reference unit", and quantity is a reference flow. This is particularly important when making or attempting to make comparative assertions of systems that have the same function, e.g., producing a metal or recycling wastes. While simple in theory, a poorly defined functional unit may easily lead to misleading results and unfair comparisons, which is why the functional units should be given comprehensive deliberation.

In **Publication I**, the functional unit was "1 kg CSHH" and the effects of allocating between gold, copper, and cobalt were considered as part of the sensitivity analysis. In **Publication II**, the functional unit was defined it as "1 kg gold that is produced", the impacts were allocated by value between gold and cobalt (copper was found to be insignificant in **Publication I**), and the process units were subdivided between the two metals as far as possible. The harmonized functional unit is, "1 kg CSHH produced in the processes," since the comparisons in **Publication II** suggest that cobalt recovery has benefits over several impact categories, and the "no cobalt recovery" scenario is excluded from further consideration in the *harmonized* analysis. The handling of co- and by-products was modeled after **Publication II**, consisting of unit sub-division, economic allocation between gold and cobalt, and system expansion (substitution) for sulfuric acid. The market values of cobalt and gold were averaged over a 10-year period, 2010-2020, as recommended (Santero and Hendry, 2016).

The functional unit of black mass processes was "the recycling of 1 kg of *lithium-ion* black mass", to enable comparison of treating a unit of black mass with similar composition. The product credits from the systems: manganese, cobalt, and nickel sulfate, lithium carbonate, and REE double sulfates, were calculated by substitution or the method otherwise known as "avoided burden".

3.2.3. System boundaries and scenarios

Temporal and geographical boundaries mainly affect the uncertainties and the modeling of the electricity mix. The studies were all placed in 2030 onwards, and the spatial boundary was either Finland or Europe: the ore in **Publications I** and **II** is mined and it was assumed to be processed in Finland, whereas Europe was thought to be a wide enough market for battery recycling.

The technical boundary of the primary processes was cradle-to-gate and included mining, beneficiation, sulfide dissolution, gold cyanidation, transport of cobalt-bearing intermediates for 500 km (**Publication II**), and CSHH recovery from re-dissolved intermediates. It was determined in **Publication II** that cobalt sulfide is both environmentally and technically the most superior intermediate over cobalt hydroxide and direct solvent extraction, and the precipitate is transported 500 km for refining to crystallized CSHH. An onsite oxygen plant is required for atmospheric (ATM) and pressure leaching (POX), whereas the roasting-leaching (RLP) process uses air only but requires a sulfuric acid plant to treat the sulfur dioxide-bearing roaster gases. The boundaries are shown in **Figure 10**.

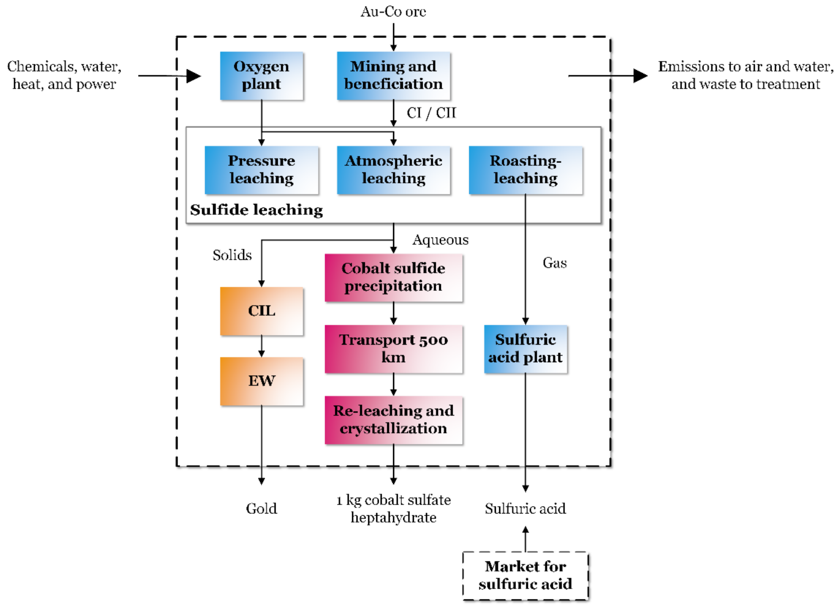


Figure 10. Technical boundary for Au-Co ore treatment in three sulfuric acid-based sulfide leaching scenarios (**Publications I-II**). Blue units are allocated between gold and cobalt, pink units are subdivided to cobalt alone, and orange units to gold.

Unit subdivision, where the impacts of units that treat gold or cobalt alone are only calculated towards the metal concerned, was used as the primary method for dividing the impacts between metals. Economic allocation (~90% value to gold) (World Gold Council, 2023; Cobalt Institute, 2021) was performed at the mining and beneficiation and sulfide leaching stages. While sulfide leaching is not required for gold separation and could therefore also be subdivided to cobalt, it was seen that sulfide destruction also benefits gold processing in **Publication II**, and consequently the point of allocation was after cobalt dissolution. Both concentrates CI and CII were modeled with each of the three processes and the concentrate cobalt content was varied to see whether further composition optimization benefits one of the processes more than others. The scenarios are summarized in **Table 6**.

For battery recycling, the pre-treatment stages were excluded to focus on the hydrometallurgical process alone, given that there are a multitude of methods for producing black mass of highly heterogeneous composition. The stages in the hydrometallurgical process were leaching, solution purification, and the step-wise SX and crystallization of manganese sulfate monohydrate, cobalt sulfate heptahydrate, and nickel sulfate hexahydrate, followed by lithium carbonate recovery and effluent treatment, see **Figure 11**.

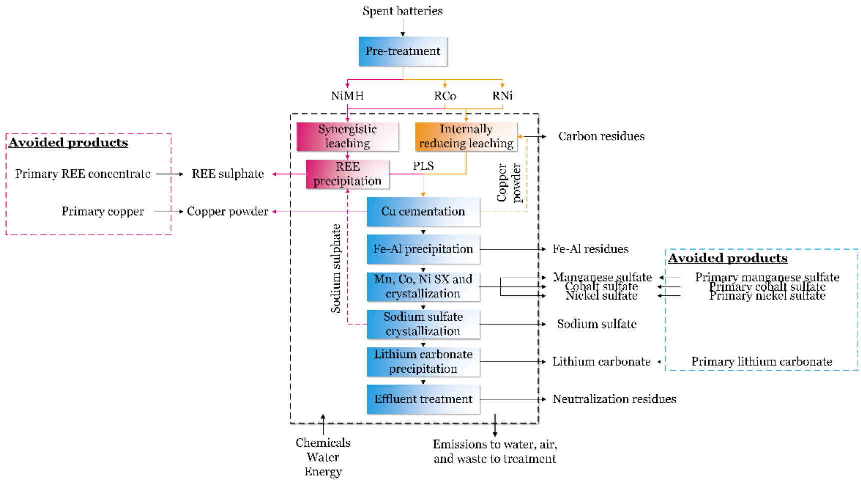


Figure 11. System boundary for recycling systems, synergistic-specific highlighted in pink and internally reducing (Fe/Cu) system-specific in orange. Shared units and avoided burdens are highlighted in blue.

A summary of all the studied scenarios is provided in **Table 11**. It can be observed that some products are specific to one scenario: only roasting-leaching (RLP) produces sulfuric acid, and only the synergistic systems have an outflow for copper, since the internally reducing Fe/Cu system re-uses the copper powder as a reducing agent in leaching. REE double sulfate is likewise not produced in the Li-ion black mass process. A total of ten scenarios were modeled between primary and secondary processes in the compendium in addition to the flowsheet scoping scenarios in the Publications.

Table 6. Summary of the scenarios for gold-cobalt and spent battery recycling processes

Gold-cobalt				**Publ.**
Process	**Feed**	**Products**	**Abbreviation**	
Pressure oxidation	CI	CSHH, gold	POX-CI	I
	CII		POX-CII	new
Atmospheric leaching	CI	CSHH, gold	ATM-CI	new
	CII		ATM-CII	II
Roasting-leaching	CI	CSHH, gold, sulfuric acid	RLP-CI	new
	CII		RLP-CII	II
Spent battery				
Synergistic	NiMH, RCo	REE double sulfate, Cu, Mn, Co, and Ni sulfates, Li carbonate	SYN-RCo	III
	NiMH, RNi	REE double sulfate, Cu, Mn, Co, and Ni sulfates, Li carbonate	SYN-RNi	new
Internally reducing (Fe/Cu)	RCo	Mn, Co, and Ni sulfates, Li carbonate	INT-RCo	IV
	RNi		INT-RNi	IV

3.2.4. Impact assessment categories and models

The CML v.4.8 (2016) midpoint method was used for the classification and characterization of the impacts, while optional steps – weighing and normalization – were excluded. The impact categories were selected separately for primary and secondary process modeling, and the shared category indicators were as follows: cumulative energy demand (CED, MJ), acidification (AP, kg SO_2-eq), eutrophication (EP, kg PO_4-eq), global warming (GWP, kg CO_2-eq), tropospheric ozone depletion (ODP, kg R11-eq), and stratospheric photochemical oxidant, or smog, creation potential (POCP, kg Ethylene-eq). These impact categories have been recommended by Santero and Hendry (2016) for mineral processing studies and deemed reliable by the ILCD guidelines (EC-JRC-IES, 2010b).

In addition to the mentioned indicators, it was considered that human toxicity (HTP, kg DCB-eq) and freshwater aqueous ecotoxicity potential (FAETP, kg DCB-eq) are relevant for primary production due to the presence of toxic elements like arsenic and copper in the ore, and the use of cyanide in gold processing. While toxicity categories are more uncertain than AP, EP, GWP, ODP, and POCP (EC-JRC-IES, 2010b), they are useful complementary indicators if the results are interpreted critically. The supporting indicators for black mass processing were human toxicity, abiotic depletion of elements (ADPe, kg Sb-eq), and fossil depletion (ADPf, MJ), which are particularly important in the context of electrification.

3.2.5. Sensitivity analysis

The sensitivity of the models has been assessed in several ways in the publications, e.g., sensitivity to allocation procedures, feed composition, process parameters, and system boundaries. One significant source of uncertainty has been the treatment of the organic phase in the models, and, based on the findings of **Publication IV**, the sensitivity of the models was assessed with respect to some assumptions made about the modeling of solvent extraction and organics. The role of SX has been unclear since the organic phase is circulated in the process, leading to lower reagent consumption than indicated by the mass flows, and the fact that the datasets for extractants are scarce and approximations at best. The following points were considered:

- *Default*: 1-10% of the circulating organic is replaced, data for Cyanex 272 and D2EHPA from Cao et al. (2023), TBP by own calculations (Section 3.4.2), and kerosene from Ecoinvent 3.8. The baseline assumption is that 5% of the organic needs to be replaced.
- *None*: Organic not included at all in the LCI.
- *Proxy chemicals:* The organic extractants are modeled with the "organic chemical" dataset in Ecoinvent.

3.3. Process modeling, software, and databases

All process simulations were conducted with HSC Sim 9 or 10; the specific version is provided in each of the publications. The simulations were harmonized and run with HSC 10.0.8.5 and the impacts were calculated using GaBi 10.5.0.78. with background data from Ecoinvent 3.8 (Ecoinvent, 2023). Most of the units were modeled with the reaction model units in HSC. Only the metallurgical processing, including the treatment of side-streams such as off-gas, was modeled with HSC. Auxiliary data was obtained by stoichiometric calculations, adapting literature data, and estimates.

HSC Sim is a typical thermodynamic software suite for calculating mass and energy balances: the output from one unit is the input for the next. The hydrometallurgical models are built around reactions. The calculations are done by defining all the chemical reactions and how much they proceed, with inputs such as chemicals and energy, temperature and pressure, and distributions of species between different phases. The parameters, i.e., as in **Table 4**, can be defined by controlling the relevant variables. For instance, the pH of a solution may be controlled in several ways, such as the extent that chemical reactions occur within the system, or the input of acid or alkali. The parameter tables and model assumptions of each modeled process is available in each of the **Publications**.

HSC Sim does not calculate the electricity consumption of equipment such as agitators, and the power consumption of the processes was estimated by scaling the process to industrial throughputs and determining the dimensions of the main equipment with a +15% or +20% design factor and a constant for the auxiliary equipment. The main equipment comprised reactors, thickeners, filters (pressure or disc filters), electrowinning equipment, crystallizers, and centrifuges. The methodology, while highly uncertain, is based on the physical relationships between equipment dimensions and throughput, but the availabilities of different process units may vary and affect the dimensions of other units. The availabilities were assumed to be 8000 hours annually in all units, which is not realistic but provides a good enough estimate. The calculations are provided in **Publications I** and **III**, as well as by Elomaa et al. (2019 a).

3.4. Life cycle inventory analysis

Calculating the LCI was one of the objectives of this work. Most background data for chemicals originated from the Ecoinvent 3.8 database, and the lacking datasets were obtained from the literature or estimates that are described in this section.

3.4.1. Electricity modeling

The electricity mixes were modeled regionally in accordance with the stated boundaries: 2030 onwards; Finland and Europe. The electricity mix was used only for the processes within the boundary, and it should be observed that the background processes, such as chemicals, were market averages taken from the Ecoinvent 3.8 database. There is consequently a temporal mismatch between the background and the foreground, which must be considered during the interpretation phase, particularly for the electricity intensive background items. The effect of de-carbonizing the background was further investigated in **Publication III** by means of a sensitivity analysis.

The forecasts were obtained from the Ministry of Economic Affairs and Employment of Finland (2019) and the European Commission's reference scenario 2020 (De Vita et al., 2021), which predict that in 2030, 91% of Finnish and 76% of European electricity will be produced by renewable or nuclear energy. The reports state that 8% of EU's power would come from natural gas, which has previously been treated as a transition fuel. Due to the rapid shifts in the global political landscape, the references should be treated as potentially outdated with some caution. The key points are, however, the increase in the importance of wind and solar power in the European production mix, and the intermittent increase in nuclear power in Finland until certain aging power plants are closed in the mid-2040s. The mixes for 2030 are provided in **Table 7**.

Table 7. Electricity modeling for 2030 in Finland (Ministry of Economic Affairs and Employment of Finland, 2019) and the EU (De Vita et al., 2021).

	Wind	**Hydro**	**Bio**	**Solar**	**Peat**	**Coal**	**Gas**	**Oil**	**Nuclear**	**Other**
FI	19%	15%	12%	1%	2%	2%	4%	0%	44%	1%
EU	30%	12%	5%	12%	-	8%	15%	0%	17%	1%

3.4.2. Organic extractants

One current shortcoming of the analysis is the lack of representative data on the organic extractant used in solvent extraction. The organic chemicals included in the inventories were D2EHPA, Cyanex 272, tributyl phosphate (TBP), and kerosene, of which only kerosene has database data. Approximate datasets for D2EHPA and Cyanex 272 have been compiled by Cao et al. (2023), and are provided in **Table 8** along with the estimate for TBP.

The data for TBP was modeled in this work by assuming stoichiometric reactions between n-butanol and phosphoryl chloride and neutralization of the formed hydrochloric acid with sodium hydroxide. There is an Ecoinvent dataset for triphenyl phosphate, which has been used as a proxy by Moréno-González et al. (2023). Part of the dataset was used to breach the gaps in the reaction equations. The data is therefore only an estimate that has not been validated.

Table 8. LCI for the organic chemicals used in SX, compiled from Cao et al. (2023), stoichiometric calculations, and Ecoinvent 3.8 database.

Input /kg chemical	D2EHPA	Cyanex 272	TBP	Unit
Electricity	6.12	20.05	1.50	MJ
Heat, steam	-	-	0.20	MJ
Heat, natural gas	-	-	2.15	MJ
Tap water	-	0.12	0.03	kg
Sodium hydroxide	0.46	-	0.45	kg
Hydrochloric acid	0.63	-	-	kg
Soda ash	-	0.35	-	kg
Lime, hydrated	-	0.24	-	kg
Phosphorus	-	0.26	-	kg
Hydrogen	0.97	-	-	kg
Nitrogen	-	-	0.02	kg
Phosphoryl chloride	0.76	-	0.58	kg
n-Butanol	-	-	0.83	kg
3-methyl-1-butanol	-	1.90	-	kg
Acetaldehyde	1.89	-	-	kg

In addition to the above datasets, sensitivity analysis was conducted using "market for organic chemical" as a proxy for the extractants and the modifier to see the effect. Kerosene was modeled with market kerosene, and the consumption of the organics was varied between 1% and 10%. The decomposition of the organic varies between individual reagents, process conditions, and process media, but is typically in the range of the total organic.

3.4.3. Gold-cobalt inventories

The stages included in the gold-cobalt studies were mining and beneficiation (**Table 9**), sulfide oxidation by pressure or atmospheric oxidation, or roasting and leaching, gold cyanidation and recovery, and the refining of CSHH.

The mining and beneficiation stages were not modeled in detail, and instead, data for open cast mining of refractory sulfide gold ores was used as a proxy (Norgate and Haque, 2012) It is noteworthy that the actual mine for the arsenical gold-cobalt ore will be an underground mine, which is indicated to have lower environmental impacts than open pit mines, but no publicly available data was found for the underground mining of gold. The data is therefore only a conservative estimate of the approximate magnitude of the mining impacts. Chromium steel, electricity, and chemicals are used for the grinding and flotation of the ore, and a generic inorganic chemical dataset was used for the various flotation chemicals.

Table 9. Data for mining and beneficiation of raw materials CI and CII for 1 tonne of concentrate. Data adapted from Norgate and Haque (2012).

	CI	**CII**	**Unit**	**Outflow**	**CI**	**CII**	**Unit**
Ore	2.25	1.96	t	Tailings	1.25	1.09	t
Diesel	751.30	652.97	MJ	Concentrate	1.00	1.00	t
Blasting	5.39	4.68	t				
Electricity	218.38	189.80	MJ				
Cr-steel	2.25	1.96	kg				
Chemical	0.25	0.22	kg				

The compiled inventories for the hydrometallurgical processing and the transport of the cobalt sulfide product for 500 km are provided in **Table 10**. The process consists of sulfide oxidation and dissolution, cobalt sulfide precipitation and transport, refining of CSHH, and gold recovery by a conventional cyanide process. The simulation models for both raw materials are presented in detail in **Publication II**, and the only difference between CI and CII is the minerology and raw material grade. Transparent inventories of each stage for the CII scenarios are also available in the supplementary information of **Publication II**. More sulfuric acid is produced than consumed in leaching in the RLP process, which explains its negative values in the RLP-CI and RLP-CII scenarios.

The emissions to freshwater were estimates, obtained by calculating the soluble metals remaining in the wastewater from effluent treatment and in the moisture of solid residues. The emissions are therefore not an absolute truth, but since the modeling method is consistent, the values can be used for internal comparisons between the scenarios. The destruction of cyanide to cyanate and thiocyanate was modeled, for instance, assuming that the wastewater contains approximately 0.5 mg/L of weak acid dissociable (WAD) cyanide, and that 15% thiocyanate decomposes to cyanate and sulfate in the INCO process (Mudder et al., 2006). Cyanide and thiocyanate oxidize first to cyanate, which has no characterization factors, and was therefore not included, although it does not share the toxicity of cyanide.

Table 10. Compiled harmonized LCI for primary cobalt scenarios, per FU (1 kg CSHH).

	POX-CI	**POX-CII**	**ATM-CI**	**ATM-CII**	**RLP-CI**	**RLP-CII**	**Unit**
Concentrate	16.69	120.31	18.55	131.12	18.79	131.08	kg
Electricity	33.96	204.45	38.43	273.90	25.31	199.72	MJ
Steam	1.2	14.27	1.32	9.67	2.62	14.83	MJ
Natural gas	0.06	0.47	0.07	0.57	0.07	0.43	kt
Air (700 kpa)	1.82	11.99	5.95	3.87	70.52	188.27	kg
Oxygen, liquid	7.81	35.45	4.37	19.15	0.62	0.57	kg
Tap water	99.46	45.45	59.88	34.96	70.17	46.82	kg
Activated carbon	3.14	23.47	3.45	2.72	22.71	1.19	g
Sulfuric acid	1.6	1.15	0.85	3.08	-5.92	-7.93	kg
Lime	4.45	21.83	1.80	12.51	2.35	8.25	kg
Caustic soda	0.53	1.06	1.04	2.94	0.99	1.58	kg
Hydrogen sulfide	0.16	0.22	0.13	1.27	0.21	0.24	kg
Kerosene	0.19	0.20	0.19	0.20	0.19	0.20	kg
Cyanex 272	0.14	0.15	0.14	0.15	0.14	0.15	kg
TBP	0.02	0.02	0.02	0.02	0.02	0.02	kg
Sodium cyanide	32.39	200.07	71.09	389.64	17.79	360.25	g
Hydrochloric acid	89.38	11.95	67.44	44.55	72.11	31.42	g
Sodium sulfite	80.13	519.54	51.13	337.65	63.87	940.65	g
Lead nitrate	3.88	24.75	1.99	13.25	3.44	51.34	g
Copper sulfate	1.99	42.79	2.22	33.11	2.45	43.79	g
Iron sulfate	-	-	-	-	0.51	1.00	kg
Transport, 500 km	0.20	0.19	0.24	0.24	0.24	0.23	t.km
Outflows	**POX-CI**	**POX-CII**	**ATM-CI**	**ATM-CII**	**RLP-CI**	**RLP-CII**	**Unit**
CSHH	1.00	1.00	1.00	1.00	1.00	1.00	kg
Gold bullion	0.42	1.62	0.42	1.60	0.42	1.62	g
Copper sulfide	0.10	0.17	0.11	0.16	0.11	0.19	kg
Gold tailings	31.15	186.49	25.57	170.37	18.41	170.31	kg
Solid waste	0.46	3.17	0.18	2.50	4.54	3.99	kg
Spent carbon	30.32	23.64	33.14	29.96	45.41	20.88	g
Wastewater	91.70	340.26	31.79	142.83	146.82	302.05	kg
Carbon dioxide	0.03	0.15	0.06	0.35	0.19	0.35	kg
Co(II), freshwater	13.43	20.1	20.73	43.67	19.72	42.66	mg
As(V), freshwater	5.21	1.99	3.14	0.72	5.11	0.59	mg
Cu(II), freshwater	0.55	17.54	0.35	6.45	0.79	10.82	mg
Sulfate, freshwater	0.61	1.13	0.76	0.22	0.51	0.64	kg
Cyanide, freshwater	12.34	69.05	11.12	64.46	39.72	62.65	mg
Thiocyanate, freshwater	185.60	100.22	150.57	79.76	136.91	70.50	g

The inventory for the sulfuric acid production in the RLP scenarios is presented in **Table 11** per 1 kg sulfuric acid (98%, without water). The data also includes arsenic removal from the sulfur dioxide-bearing gas. The sulfuric acid in the other scenarios is modeled with Ecoinvent's market data.

Table 11. Life cycle inventory data for producing sulfuric acid from roasting off-gases, for 1 kg sulfuric acid.

Inflow	Value	Unit	Outflow	Value	Unit
Gas (8 vol.% SO_2)	10.27	kg	Sulfuric acid	1.00	kg
Electricity	0.74	MJ	Steam	11.34	MJ
Steam	3.57	MJ	Sulfur dioxide	8.70	g
Compressed air, 700 kPa	9.06	kg	Wastewater	6.26	g
Oxygen, liquid	6.49	g	As(V) to water	0.04	ug
Process water	2.37	kg	Sulfate to water	4.94	mg
Cooling water	13.96	kg	Arsenate waste	18.79	g
Lime as CaO	22.08	g			
Ferrous sulfate	24.67	g			

3.4.4. Black mass treatment inventories

The inventories for the treatment of spent batteries are presented in **Table 12**, where it can be observed that the internally reducing (INT) and synergistic (SYN) scenarios are quite similar. The INT scenario has more copper in circulation, leading to higher consumption of iron and hydrogen peroxide. The outflows, on the other hand, seem to be more dependent on the feed. A higher nickel content in the Li-ion waste (RNi) affects the wastewater composition in addition to the products. More nickel is released, while the water contains less cobalt and manganese. It should, again, be highlighted that the modeling of the wastewater is simply for internal comparison.

Iron and additional copper were assumed to be fed as scrap rather than virgin metals. The copper scrap would ideally be sourced from the separated current collector foils, which would avoid the need for external metal sources. Some black masses contain enough metallic reductants without any additional metal feed (Guimarães et al., 2022), so the metal feeds are for low-copper black mass.

Table 12. Life cycle inventories for the black mass recycling scenarios.

Inflows	**INT-RCo**	**INT-RNi**	**SYN-RCo**	**SYN-RNi**	**Unit**
Li-ion black mass	1.00	1.00	1.00	1.00	kg
NiMH black mass	-	-	0.75	0.75	kg
Heat, steam	8.40	9.26	10.00	9.34	MJ
Electricity	2.18	2.26	2.19	2.41	MJ
Process water	27.28	28.68	33.41	37.80	kg
Copper scrap	0.06	0.06	-	-	kg
Iron scrap	79.97	79.96	3.83	3.83	g
Sulfuric acid	2.74	2.81	3.98	3.99	kg
Caustic soda	1.80	1.81	1.94	1.93	kg
Lime	0.09	0.09	0.01	0.01	kg
Soda	0.16	0.17	0.18	0.18	kg
Hydrogen peroxide	0.03	0.03	0.00	0.00	kg
Kerosene	1.92	1.94	1.37	1.38	kg
D2EHPA	0.12	0.12	0.16	0.16	kg
Cyanex 272	0.17	0.17	0.06	0.06	kg
TBP	0.07	0.07	0.04	0.02	kg
Outflows	**INT-RCo**	**INT-RNi**	**SYN-RCo**	**SYN-RNi**	**Unit**
Manganese sulfate	46.04	64.92	46.74	65.50	g
CSHH	774.39	101.34	845.40	142.57	g
Nickel sulfate	109.12	710.91	2043.08	2717.4	g
Lithium carbonate	114.36	115.32	123.32	126.66	g
REE precipitate	-	-	324.25	323.86	g
Copper powder	-	-	4.31	4.31	g
Sodium sulfate	3.36	3.22	3.60	3.57	kg
Leach residues	0.66	0.66	0.69	0.69	kg
Neutralization waste	0.37	0.38	53.58	0.54	g
Wastewater	12.37	13.45	37.16	37.24	kg
Cu(II) freshwater	29.39	29.24	1.93	1.94	mg
Co(II) freshwater	101.86	12.66	96.14	12.37	mg
Ni(II) freshwater	16.19	100.87	243.52	324.63	mg
Mn(II) freshwater	8.41	11.80	21.18	29.62	mg

4. Results and discussion

The harmonized results are presented in this section for both Au-Co ore processing and Li-ion battery recycling. The following findings from **Publications I-IV** were implemented in the harmonized scenarios:

a) **Publication I**. The impacts of hydrometallurgical processing tend to decrease when the raw material grade increases.
b) **Publication II**. Cobalt co-product should be recovered from Au-Co concentrate according to the environmental impacts. Sulfide intermediate provides benefits against hydroxide or aqueous solution products.
c) **Publications III** and **IV**. Synergistic NiMH and Li-ion black mass recycling is beneficial vs. virgin processing, as is internally reducing Li-ion processing.
d) **Publication III**. Crystallization from waste effluent is the preferred method for obtaining sodium sulfate to be used in REE precipitation in NiMH and Li-ion recycling.
e) **Publication IV**. Decreasing downstream impacts of recycling Li-ion black mass hydrometallurgically is possible by optimizing the final leaching acidity.
f) **Publication IV**. Manganese SX is an appropriate compromise for manganese purification and recovery from black mass leaching solutions.
g) **Publication IV**. Organic extractants should be included in the LCI of solvent extraction processes.

Recommendations were made on process improvement based on their combined technical and environmental benefits according to the impact assessment and sensitivity analyses; see Sections 4.1 and 4.2.

4.1. Environmental impacts

The results for Au-Co ores are presented in the following section, 4.1.1, and the results for Li-ion battery recycling in Section 4.1.2.

4.1.1. Gold-cobalt ore scenarios

The impacts of the six different scenarios: two raw materials (high-grade cobaltite concentrate CI and lower grade CII) and three processes (POX, atmospheric reactor leaching ATM, and roasting-leaching RLP), are presented in **Figure 12**, with the impacts sub-divided and allocated between gold and cobalt sulfate heptahydrate (CSHH). It is not straightforward to select a preferred process due to the variation between products and impact categories. **Figure 12** shows the impacts for 1 kg CSHH and the respective amount of gold, **Table 13** only for 1 kg CSHH, and **Table 14** for 1 kg gold.

Overall, the higher-grade concentrate CI was associated with significantly lower impacts across the spectrum than the lower-grade, but more realistic, CII concentrate. POX had consistently the lowest toxicities and eutrophication potential (**Figure 12c, d, and f**), but also performed the best for the low-grade concentrate CII in the closely linked acidification (**Figure 12a**) and photochemical oxidant creation (**Figure 12h**), and for CI in global warming (**Figure 12e**). Of the studied processes, POX had the highest cumulative energy demand for CII. This indicates that pressure oxidation would be a particularly interesting option for high-grade concentrates.

Roasting-leaching had the lowest impacts in cumulative energy, but it was also favorable for CI in terms of acidification and photochemical oxidant creation, despite being the only scenario with direct SO_2 emissions. It was nevertheless the highest in the two aforementioned categories for CII, which, along with the contribution analyses in **Figures 13** and **14**, would imply that this is due to the crediting of sulfuric acid manufacture as “avoided burdens”, which is discussed in more detail below.

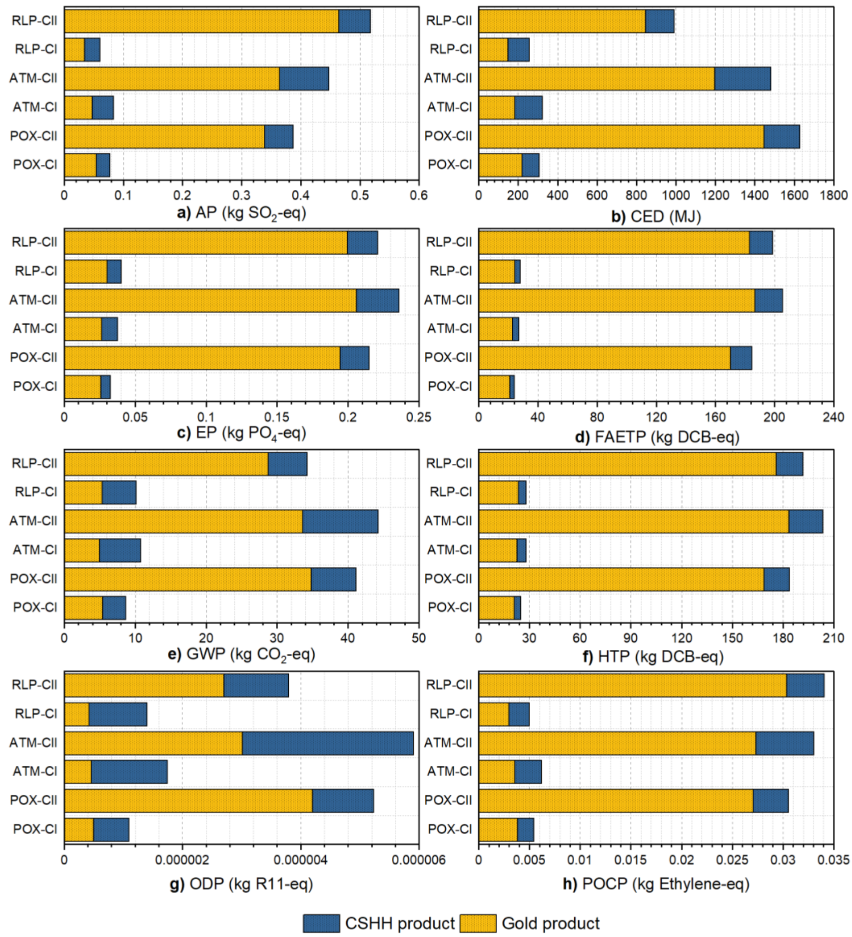


Figure 12. Impacts of 1 kg CSHH production in three different processes (POX, ATM, RLP) for two raw materials, CI and CII: **a)** Acidification, **b)** Cumulative energy demand, **c)** Eutrophication, **d)** Freshwater aqueous ecotoxicity, **e)** Global warming, **f)** Human toxicity, **g)** Ozone depletion, **h)** Photochemical ozone creation.

Atmospheric leaching had the highest impacts in GWP and ODP for both feeds but also the highest EP and toxicities for CII, and the highest POCP for CI. It was the lowest in none of the impact categories, but it should be observed that **Figure 12** shows the results for 1 kg CSHH and the recovered amount of gold. Looking at cobalt alone, POX appears the best process for CI rather consistently and both RLP and POX have the lowest impacts in four out of eight impact categories for CII, leaving them tied.

The results are therefore sensitive to cobalt but not gold recovery, see **Tables 13** and **14**. Gold recovery was approximately the same across the investigated scenarios, but there was some variation in cobalt recovery. The ATM scenario had the lowest cobalt recovery and POX the highest, which explains the obtained results. This can be presumed realistic, given that gold in the material is free-milling, but cobaltite is difficult to dissolve.

Table 13. Harmonized impacts for 1 kg CSHH with CI and CII raw materials.

	POX		ATM		RLP	
	CI	**CII**	**CI**	**CII**	**CI**	**CII**
Cobalt recovery (%)	92.3	94.0	85.9	86.7	85.9	85.6
AP (kg SO2-eq)	2.32 E-2	4.77 E-2	3.63 E-2	8.37 E-2	2.34 E-2	4.64 E-2
CED (MJ)	85.57	182.13	138.44	285.53	104.87	137.23
EP (kg PO4-eq)	0.68 E-2	2.04 E-2	1.10 E-2	3.00 E-2	0.96 E-2	2.09 E-2
FAETP (kg DCB-eq)	2.97	14.45	4.04	18.47	3.57	15.52
GWP (kg CO2-eq)	3.20	6.30	5.76	10.61	4.65	5.35
HTP (kg DCB-eq)	3.69	15.05	5.30	20.16	4.55	15.74
ODP (kg R11-eq)	0.60 E-6	1.03 E-6	1.30 E-6	2.89 E-6	0.97E-6	1.09 E-6
POCP (kg Ethene-eq)	1.63 E-3	3.51 E-3	2.62 E-3	5.74 E-3	1.92 E-3	3.22 E-3

The harmonized results for gold (**Table 14**) are in line with **Publication II**, which studied the impacts from the perspective of gold. The results for pressure oxidation are also consistent with **Publication II**: it is indicated to be an intensive process aside from the emissions to water (particularly EP, HTP, and FAETP), while roasting-leaching has low energy and climate change impacts. Atmospheric reactor leaching, on the other hand, falls in the middle in all but toxicity impacts, making it a worthy compromise if the extraction of cobalt can be increased. Otherwise, the most environmentally viable choice is between pressure oxidation and roasting-leaching.

Table 14. Harmonized impacts for 1 kg gold with CI and CII raw materials.

	POX		ATM		RLP	
	CI	**CII**	**CI**	**CII**	**CI**	**CII**
Gold recovery (%)	97.7	97.7	97.5	97.6	97.4	97.5
AP (kg SO2-eq)	128.77	205.55	113.67	154.89	64.22	192.06
CED (MJ)	522,000	877,000	440,000	509,000	251,000	464,000
EP (kg PO4-eq)	60.96	117.94	63.46	117.61	63.69	119.00
FAETP (kg DCB-eq)	49,900	103,200	54,900	117,500	54,700	110,000
GWP (kg CO2-eq)	12,900	21,100	11,900	14,300	9740	16,300
HTP (kg DCB-eq)	50,200	102,000	54,200	108,000	51,700	106,000
ODP (kg R11-eq)	1.18 E-3	2.55 E-3	1.09 E-3	1.28 E-3	0.83E-4	1.59 E-3
POCP (kg Ethene-eq)	9.04	16.39	8.53	11.62	3.68	14.71

The contributions of each process stage (Figure 13) highlight that mining and beneficiation, regardless of the poorly representative model, is the most intensive step in the entire process chain in all but CED, GWP, and HTP, and particularly highly represented in terms of toxicities and eutrophication. The notable difference between CI (1.35% cobalt) and CII (0.20%) is that the role of cobalt refining in the impacts is far more substantial for CI (28-41% GWP) than for CII (2.6-8.6%). Gold refining, on the other hand, is better represented for CII (20-27% GWP), possibly due to the higher content of inert tailings that are treated for gold recovery.

The "avoided burden" credit for sulfuric acid in the RLP scenario exceeded the impacts of its production across all the studied impact categories, shown in **Figures 13 e** and **f** as negative percentages for sulfuric acid. A larger amount of pyrrhotite was present in CI, and therefore the negating effects were much more substantial for CI than for CII. The boundary does not include infrastructure, however, and a larger content of sulfur dioxide-generating minerals requires larger sulfuric acid production capacity.

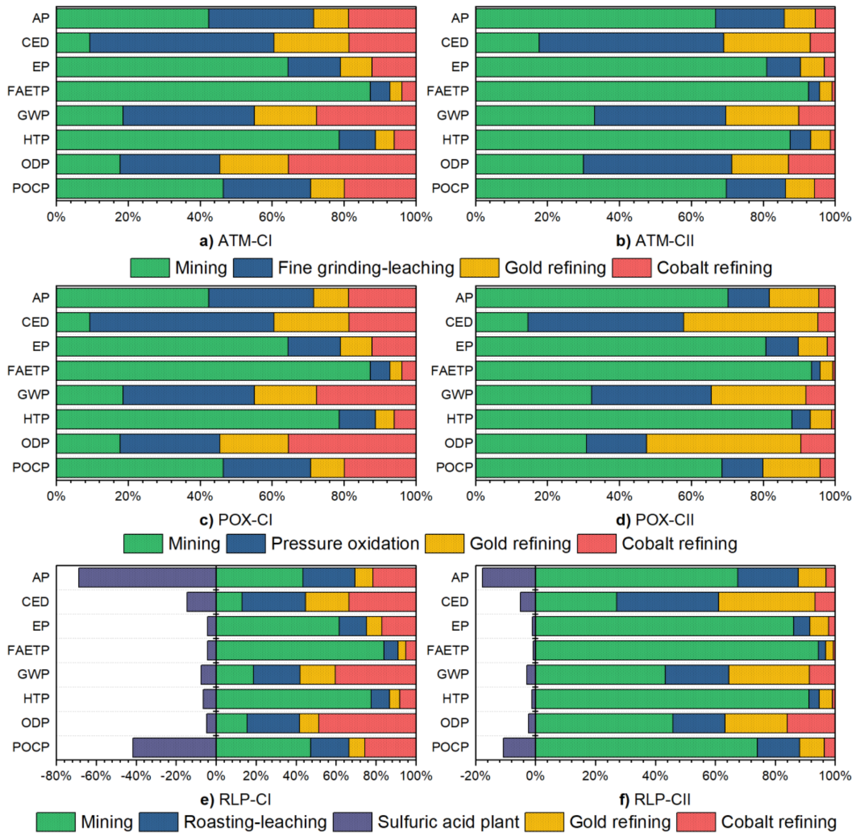


Figure 13. Wider process stage contributions to the impacts: **a)** ATM-CI scenario, **b)** ATM-CII, **c)** POX-CI, **d)** POX-CII, **e)** RLP-CI, **f)** RLP-CII.

A breakdown into individual feeds and direct emissions is provided in **Figure 14**, which shows that the hotspots are largely the same as those in **Publications I** and **II**. The impacts are divided rather evenly between several consumables, of which electricity, oxygen for POX and ATM, air for RLP, sulfuric acid, caustic soda, and sodium sulfite stand out as major contributors. As a new addition to the compendium, it was found that organics contribute far more than originally thought in **Publications I-II** when the makeup of all the organic in circulation was 5%. This is despite the system containing only a relatively small solvent extraction circuit to purify re-leached cobalt sulfide. Furthermore, while copper sulfate is only a minor additive in the cyanide destruction process, it contributes as much as 6-8% of CI and 20-30% of the toxicity categories for CII.

Although the calculations of the foreground emissions are highly uncertain, the processes, except for RLP, had only minor direct scope 1 emissions. RLP was associated with minor SO_2 emissions, as seen in the well-represented "Others" category in **Figures 14 e** and **f**, but these were more than mitigated by the sulfuric acid credit. The emissions to water were presumed to be minor due to the relatively strict legislative landscape of Finland, although not all aqueous species were accounted for in the analysis, such as thiocyanate and sulfate. These have no emission factors in the CML 2016 methodology but are important for environmental permits. Natural gas and other carbonaceous fuel burning processes were accounted for in the "Heat" category rather than in the foreground.

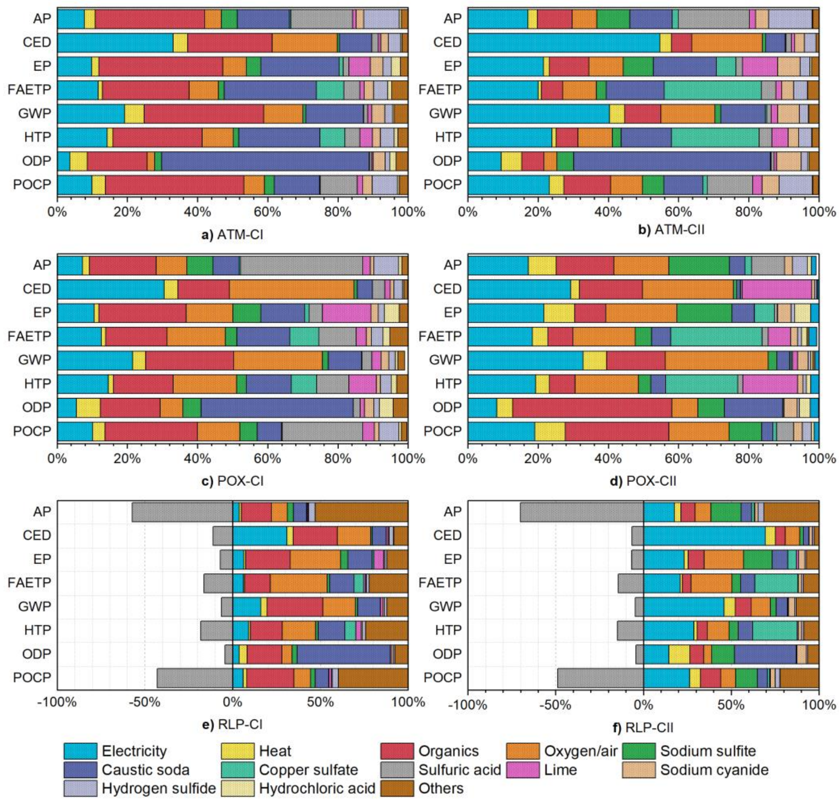


Figure 14. Contribution breakdown into individual feeds. "Others" contains foreground emissions, water, transport, iron sulfate, activated carbon, and lead nitrate: **a)** ATM-CI scenario, **b)** ATM-CII, **c)** POX-CI, **d)** POX-CII, **e)** RLP-CI, **f)** RLP-CII.

Only conventional cyanide leaching and carbon adsorption process were considered for gold in the context of this compendium and **Publications I-II**, but cyanide-free options like chloride (Elomaa et al., 2020; Rinne et al., 2021) and thiosulfate (Cairncross and Tadie, 2021) have also been studied with LCA outside of this thesis. It appears that chloride processes are too chemically intensive to compete with cyanidation despite the fast kinetics (Rinne et al., 2021). The requirement for high copper concentration in the cupric chloride leaching solution limits the usefulness in the case of the specific concentrates that do not contain much copper: as observed, a small copper sulfate feed can even be surprisingly significant for the impacts of the process.

Overall, it cannot be said conclusively that one of the processes is greener than the others without implementing some other selection criteria. Pressure oxidation appears, however, to have the lowest impacts, particularly when the feed is particularly high-grade in cobalt. Roasting-leaching may have some benefits for lower grade concentrates, while atmospheric reactor leaching could be a flexible option if the extraction of cobalt can reach the level of the other two options. The findings also do not support the exclusion of solvent extraction chemicals from the LCA models. It is suggested that the metallurgical industry would greatly benefit from primary data from organic chemical manufacturers in order to build representative process models and LCI. This is investigated further in the sensitivity analyses.

4.1.2. Black mass scenarios

The impact analysis of black mass recycling scenarios is presented in **Figure 15,** along with the credits for each of the products: lithium carbonate, manganese sulfate, cobalt sulfate heptahydrate, nickel sulfate hexahydrate, as well as the SYN scenario-limited rare earth double sulfate concentrate and copper powder products. The analysis showed that the internally reducing INT process had slightly greater environmental impacts than SYN processes, but nevertheless the impacts of recycling do not exceed the corresponding virgin metal production, except for INT scenarios in ODP, and INT-RNi in fossil depletion, shown in **Figure 15**.

It is worth noting that the leaching of NiMHs is more acid-consuming in comparison with Li-ion battery active material leaching: 1 mol of NiMH anode consumes 7.5 mol and the cathode 0.5 mol of sulfuric acid, whereas the Li-ion graphite anode is inert, and the cathode consumes 2 mol of sulfuric acid. This may partly explain why the downstream impacts of SYN scenarios are lower than those of INT, as the consumption of environmentally intensive sodium hydroxide is lower in the subsequent steps due to the higher pH of the PLS. A clearer comparison would probably be obtained by harmonizing the final rather than the starting acidity. The impacts of the low-acid processing of RCo material in the INT system are presented in **Publication IV**, and it was seen that this recycling approach could also bring depletion below the impacts of virgin production.

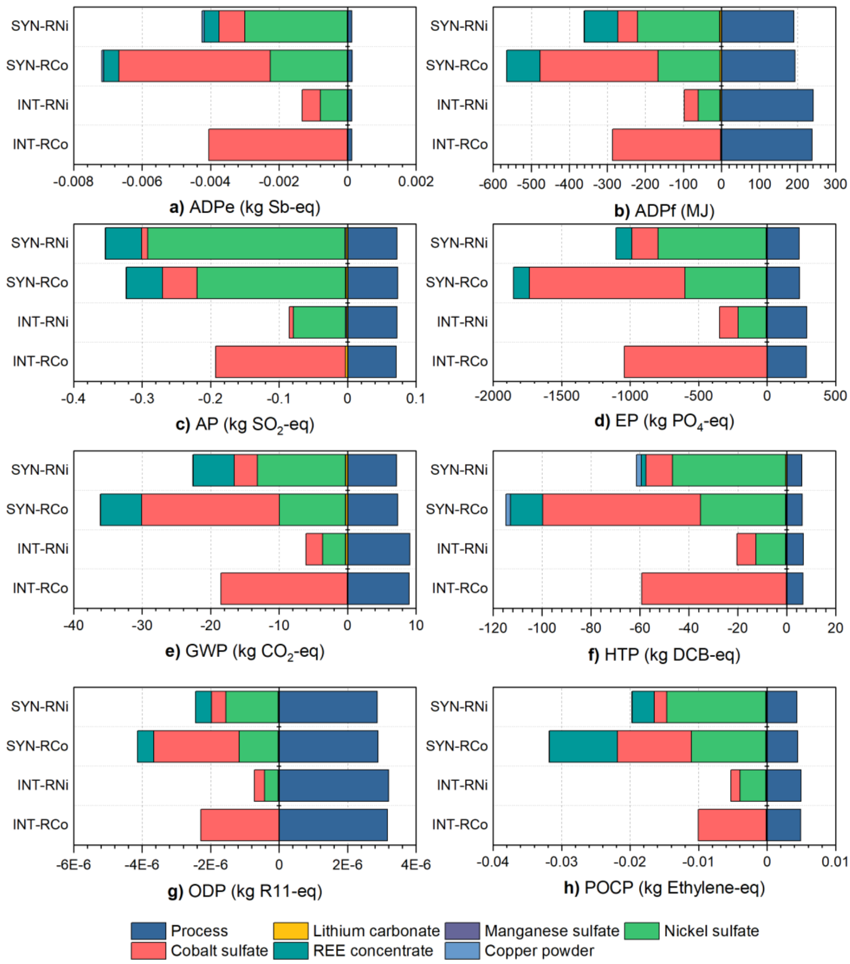


Figure 15. Impact assessment of black mass recycling scenarios per 1 kg Li-ion black mass feed, with "process" referring to the recycling process impacts: **a)** Abiotic depletion of elements, **b)** Fossil depletion, **c)** Acidification, **d)** Eutrophication, **e)** Global warming, **f)** Human toxicity, **g)** Ozone depletion, **h)** Photochemical oxidant creation.

Another aspect to notice is that the scenarios all have very different product baskets, and the intensity of nickel and CSHH production was overrepresented in the credits. Lithium carbonate, manganese sulfate, and copper powder contributed very little to the credits, but REE precipitate, which was credited as a concentrate, was more significant than cobalt for SYN-RNi in certain impact categories, such as global warming, acidification, and photochemical oxidant creation. The comparison of INT and SYN baskets is unfair for this reason, but not without some value. The integration of NiMH and Li-ion waste in the same hydrometallurgical process is relatively simple, and REEs can be recovered using the sodium sulfate salt produced in the process.

The contribution analyses shown in **Figure 16** do not reveal anything new about the processes that was not evident from **Publications III** and **IV**: the impacts are dominated mainly by sodium hydroxide/caustic soda, sulfuric acid, and organic production. Organics were not included in **Publication III**, but, based on the updated analyses in **Publication IV** and this thesis summary, they should have been. Of the studied impact categories, organics are the least significant for abiotic depletion of elements, where they account for 20-25% of the impacts across the scenarios, less for SYN than INT, making them the biggest single contributor to the process. Direct manganese oxidation to manganese dioxide and re-leaching and refining it in another circuit would decrease the significance of organics a little, although with the loss of some valuable cobalt and nickel, as determined in **Publication IV**.

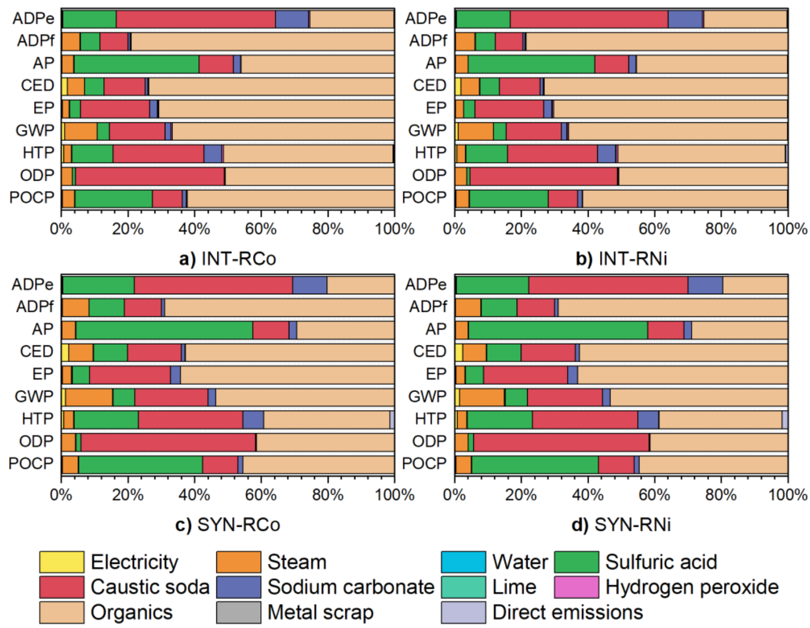


Figure 16. Contribution breakdown into individual inputs and direct emissions.

It is worth factoring in that the acidity of the leaching solution can be further decreased so that very little excess acid is consumed. Porvali et al. (2020 b) optimized acid consumption so that the final pH of the leaching solution was above 3, which, according to **Publication IV**, clearly decreases the impacts of the Li-ion recycling process. The effect of optimizing acidity also affects the downstream process by decreasing the consumption of neutralizing chemicals, thus effectively lowering the environmental impacts. Caustic soda is another hotspot in the process, particularly for ADPe and ODP, so finding ways to decrease the need for pH adjustment is an effective way to develop the process further. This would also decrease sulfuric acid consumption.

The two recycling processes investigated had very similar environmental impact contribution profiles, and the major differences between them lie in the product baskets and the resulting recovery credits. Synergistic processing of NiMHs and Li-ion batteries (SYN) consumes more sulfuric acid, which can be considered a weakness since the internally reducing (INT) process focused solely on the Li-ion battery can be even further optimized in regard to acid consumption. The biggest problem with the SYN process is not environmental, but the fact that the availability of waste NiMHs will decrease over time as hybrid vehicles will increasingly be powered by Li-ion batteries. The calculations made in **Publication III** may be outdated regarding the tonnages of Li-ion batteries in 2030 (estimated 33,600 t NiMHs and 205,900 metric tons of Li-ion batteries), but the difference in waste volumes is vast, and currently the focus should be on the dedicated recycling of Li-ion batteries.

4.2. Modeling of the organic

Goal IV of this thesis summary was to evaluate the data gaps and modeling approaches to suggest improvements in the methodology. The modeling of SX processes has evolved during the work on these publications, from the organic-less black box model in **Publication III** to the inclusion of specific datasets in **Publication IV**. The challenge of modeling SX is that the degradation of the organic is dependent on the process conditions, dissolved species, presence of solids, and other factors that are difficult to assess experimentally, and not only on the organic extractant itself. The organic is circulated in the process, but losses occur due to degradation and crud formation, and the extent of this is unknown. Furthermore, LCI data for extractants is lacking.

The default model included organic datasets from Cao et al. (2021) for Cyanex 272 and D2EHPA, and a dataset for TBP produced for this thesis, see **Table 8**. As discussed in Section 3.2.5, sensitivity analysis was conducted by changing the default consumption of organic (5% of organic in circulation) to 1% and 10% to assess the sensitivity of the model. Additionally, the results were analyzed by excluding the organic completely or modeling the extractants with the generic “chemical, organic” dataset from Ecoinvent 3.8. The results are presented in **Figure 17**. The contribution analyses of all Au-Co and black mass scenarios showed very similar contributions by the organics, which is why the analysis was conducted only for POX-CII and INT-RCo. The response would be similar across the other scenarios.

In **Figure 17**, “10%” and “1% makeup” refers to the difference to the baseline 5% of consumed organic when modeling the organic with the LCI from Section 3.4.2. The “generic” dataset assumes 5% organic consumption using the “market for organic chemical” dataset from Ecoinvent, and “No organic” excludes the LCI for organics totally from the analysis.

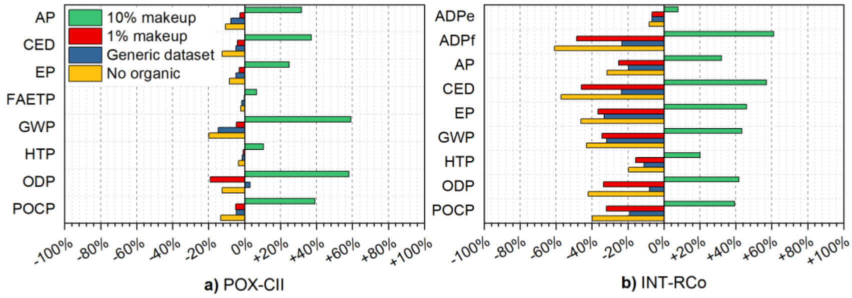


Figure 17. Response of the LCIA to changing organic consumption from the baseline 5% in circulation or modeling the organic with a generic dataset or not at all: **a)** POX-CII, **b)** INT-RCo.

The sensitivity analysis presented above does not support the exclusion of the organic from the LCI, nor the use of generic datasets. The POX-CII scenario was less sensitive to the exclusion (-20% GWP) or the use of generic chemical (-15% GWP) than INT-RCo (-43% and -33% GWP respectively), but the difference to the baseline was still significant. The decrease in organic consumption did not affect the model much either (-5% GWP) but an increase led to a significant response (+59%). This would indicate that 5% is a safe assumption for a typical case, but it should be noted that POX-CII was assumed to only use Cyanex 272 and TBP in one SX circuit.

INT-RCo contained three SX circuits: one with D2EHPA, one with Cyanex 272 and TBP, and one with D2EHPA and TBP. The model was, unsurprisingly, more sensitive to both the changing of dataset and to varying the organic consumption. The response to an organic consumption increase was similar to POX-CII (+43% GWP), but the model was more sensitive to a decrease (-34% GWP). Assuming no organic led to a -43% change in global warming impacts from the default method, and a generic dataset -33% change.

The results show that the organic phase does matter, despite the seemingly low consumption. Therefore, the recommendation is that the organic be included in both recycling and primary ore processing studies. Nevertheless, a significant knowledge gap remains: the degradation behavior of the organic phase. Some rules of thumb, e.g., "1-10% of all organic is makeup", can be made, but as seen from the sensitivity analysis, variation in the assumed percentage alone can lead to massive shifts. Both primary data from organic extractant manufacturers and the behavior of typical extractants would therefore be critical for the better modeling of SX in LCA in general.

4.3. Sources of uncertainty

Since the goals and the overall modeling methods varied between primary and secondary raw materials in this study, the possible ways that uncertainty exists in model variables and parameters is evaluated separately. The analysis is only qualitative, but quantitative methods such as data quality indicators could also be used (Aromaa et al., 2021).

4.3.1. Uncertainty for primary ores

The primary gold-cobalt ore processes were modeled assuming “best case scenarios”, where each of the studied options is technically viable and results in high yields in typical operating conditions. The “similarity” of the ore to Blackbird concentrate was the basis of the HSC model, and some approximation was made by assuming the behavior of cobaltite to be similar to other arsenical minerals such as arsenopyrite and enargite. No experiments were made, and it was presumed that the processes are scalable, and work as intended.

The mining and beneficiation stages were modeled with proxy data for open pit mining, which is a poor fit for this case since the specific mine in question is planned to be underground. There is no known LCI data for the underground mining of gold, but the impacts to the environment are presumably lower, although the power consumption is likely to be higher. The current model may therefore overestimate the impacts of mining by some degree. Primary data from underground mines could be used instead, or the model should be updated with specific input/output data once that becomes available.

As was seen from the models, pressure oxidation led to the highest cobalt recovery, making it the preferred option for cobalt (but not for gold) in the analyses. Assuming roasting-leaching or atmospheric tank leaching can reach similar levels of extraction, they are likely to become more environmentally viable. RLP especially appears to have an edge as a flexible state-of-the-art process with fairly good environmental performance despite the poorer cobalt recovery.

The impacts were allocated economically between gold and cobalt at solid/liquid separation after cobalt leaching so that sulfide precipitation and refining impacts were solely subdivided to cobalt and the impacts of cyanidation to gold. As discussed in **Publication IV**, the allocation could also be done after mining since gold extraction is not dependent on sulfide oxidation. However, allocation was done at the said point since their oxidation also destroys species that can consume excess cyanide.

Sulfuric acid manufacturing was provided with an avoided burden credit in the roasting/leaching scenario, which greatly benefited the option. Substitution, rather than allocation, was used since sulfuric acid is a minor by-product of the operations. Excluding the credit, however, would substantially increase the acidification and photochemical oxidant creation impacts in particular of the RLP scenario.

4.3.2. Uncertainty for black mass waste

In battery recycling, the greatest challenge is that the hydrometallurgical black mass processes do not exist on scale, and some of the unit processes, like manganese SX, are not in industrial practice on a large scale. This is somewhat different even for the Au-Co scenarios, which all are industrially operated for other types of ores. Hydrometallurgical processing of black mass is not a mature technology, which affects the interpretation of the results.

The scaling up was done using the simulation, but as noted in **Publications I-IV**, the methods for calculating the electricity and heat consumption by the process are extremely uncertain. The power consumption of the process is only indicative, but it may be surmised from the analyses of **Publication III-IV** and the compendium that hydrometallurgical black mass processes are intensive in terms of chemicals but not energy. The leaching reactions are exothermal and external heating may possibly not be needed, but this is not certain. The heating of the crystallizer units was also modeled only with heat flows and not physical steam, which makes the heat balances unreliable.

The case studies were conducted gate-to-gate, including only the hydrometallurgical process, although the effects of system boundary expansion to include pre-treatment were analyzed in **Publication III**. Pre-treatment may consist of any number of stages, greatly affecting the composition of the black mass and therefore also the hydrometallurgical processing. Black masses with high aluminum and content can make the material more self-reducing and therefore suitable for the INT process (Chernyaev et al., 2021), but only copper can be recovered in practice and aluminum is precipitated as a waste product (Chernyaev et al., 2023). The black mass would ideally therefore be low in aluminum, and copper could theoretically be supplied as scrap and recovered for re-use from the solution.

Another issue with the system boundary is in the comparison of the process to primary metals. The recovery of copper, and perhaps aluminum, is associated with large recovery credits, as observed in **Publication III**, Dunn et al. (2012), and Rajaeifar et al. (2021). In **Publication IV**, the comparison was used to assess whether optimizing recovery with a more intensive process was worth it from an environmental standpoint, but the comparison may be misleading without including the pre-treatment stages. Some valuable losses and recovery also occur during mechanical treatment, even if it is presumed that pre-treatment is much less environmentally taxing than the hydrometallurgical process.

5. Critical outlook

The limitations of the presented research (publications, compendium) have been recognized throughout the work, and recommendations for future studies could be made based on the findings. Results are only as good as the data behind them, and challenges with data quality in this research can be found in both the process simulations and the LCI data used to model the background processes. The challenges with the specific methodologies used in each of the simulations and LCA has been discussed in **Publications I-IV**, and challenges with, for example, the dimensioning of equipment are not discussed further, and instead a wider view has been adopted. Recommendations have been made based on the observed limitations.

First, the studies are all prospective and the processes were scaled up to industrial scale using process simulations. While the methodology can be highly accurate, the energy balances are uncertain. The process simulations were partly conducted with industrial estimates and the simulations could be improved further by bench scale experiments of the whole process chain. Pilot scale experimental data would be invaluable in enabling the comparison of different scales.

A notable challenge with process simulation is the skills needed to reliably conduct the analysis. It was observed throughout the work that a simple leaching step can be modeled in several different ways with the simulation tool used, and the author's method of modeling alone developed significantly throughout the work on the thesis publications, leading to a need to harmonize the models for a meaningful comparison of the results. Nevertheless, this flexibility is also one of the strengths of simulation-based LCA, since the models can be updated as more knowledge is obtained. Similarly, the method can be applied with highly uncertain or more detailed process data, depending on the goals of the study.

As was observed with the organic extractants, the results are dependent on the assumptions, but it may be difficult to recognize which ones are significant. Whereas the organics were significant for the black mass processes, they were not in the case of the gold-cobalt ores. This difference was due to the volume of the treated solution, which was small for gold-cobalt ores due to the production of a relatively pure intermediate that was refined using an SX-based process. In a similar way, based on the contribution analysis a very small addition of copper sulfate to cyanide destruction dominated the toxicity impacts of cyanidation. These examples, nevertheless, imply that additives and chemicals that may seem to be insignificant due to re-use or low consumption can be highly impactful on the results, and these assumptions should be tested whenever possible.

The studies are future-oriented and set in 2030, whereas most of the data for the background and utilities apart from electricity has been modeled with current technologies. The role of the background should not be underestimated, given that many of the chemicals, such as sodium hydroxide, are energy intensive to produce and therefore would greatly benefit from a green electricity production mix. The development and adoption of new technologies, like hydrogen, also play a role in this uncertainty especially beyond 2030.

A notable shortcoming of the case studies is that the system boundaries were limited to hydrometallurgical processing, or poorly representative proxy data was used for pre-processing in the case of Au-Co ores. Pre-treatment affects the composition of the raw material, so the black box approach leaves much to be desired for the optimization of the entire process. As a downstream process stage, hydrometallurgical processing can nevertheless inform the pre-processing of composition preferences or vice versa, as in the case that high grade concentrates are best treated by pressure oxidation, and aluminum is a harmful impurity in black mass processing.

The studies are limited to an environmental LCA of the studied processes and therefore exclude social and economic aspects. However, both of these missing pillars of sustainability would be invaluable in assessing the impacts of both cobalt mining in Finland and the recycling of batteries within Europe, considering the social and economic challenges of strategic battery metal extraction around the world. The implementation of methods such as LCC and SLCA should be considered in future work to provide a more holistic view of the processes and a basis for multi-criteria analysis.

It can be surmised that the largest challenge with any LCA, prospective or not, is the quality of the data. Process simulations can be extremely powerful to model the foreground processes, but the LCA practitioner is nevertheless reliant on patchy or outdated background data in practice due to time and resource limitations. The simulations themselves contain uncertainties that need to be analyzed by the user, which necessitates skills in process engineering, simulation, and LCA as well if the same user completes the entire study. This knowledge intensity may be considered both a strength and weakness of the methodology, since a carefully done study can be extremely enlightening regarding the possible outcomes, but may also lead to erroneous conclusions.

6. Conclusions

Cobalt is primarily sourced from the Democratic Republic of the Congo, and alternative raw materials and the recycling of Li-ion batteries will be required in Europe to ensure the availability of the metal. New raw materials and the development of new processes is time-consuming, and the environmental impacts of extractive industries are an increasing concern even during process development. The prospective life cycle assessment of black mass recycling and rare gold-cobalt ore processing has been considered in this thesis in the context of an environmentally sustainable battery value chain for electrification.

Simulation is a flexible way of scaling up processes and obtaining inventory data on emerging technologies. In this thesis, process simulations were built with Metso's steady-state modeling tool HSC Sim 10, and the impact assessment step was conducted in GaBi with background data from the reputed Ecoinvent database. The strength of process simulation is that it can provide transparent data that may be used to interpret the results of the life cycle assessment and provide exact recommendations for further process development. The tool is highly powerful for the process industry, but it requires both intensive process knowledge and skills in simulation. This was demonstrated throughout the publications, and ultimately harmonization of the models and practices was required for the compendium.

In this compendium, ten simulations were assessed: six for Au-Co ores, and four for black mass. The flowsheets were drawn based on the findings from the publications. **Publication I** considered the pressure oxidation of high-grade Au-Co concentrates, while **Publication II** recommended that cobalt should be recovered as cobalt sulfide intermediate after either pressure oxidation, atmospheric tank leaching, or roasting-leaching. For black masses, **Publication III** recommended the crystallization of sodium sulfate salt instead of leaving it in effluents in the synergistic processing of NiMH and Li-ion black mass waste, while **Publication IV** suggested solvent extraction with D2EHPA for manganese purification before cobalt and nickel. In addition to the scenario analysis, the implications of the modeling of organics in solvent extraction were studied in detail in the compendium, based on the many modeling methods used in the publications.

The treatment of Au-Co ores was modeled with two feeds (low- and high-grade concentrate) and three models based on the eight scenarios given in **Publication II**, which showed a clear preference for sulfide intermediate recovery from cobalt leaching solutions. The findings in the harmonized flowsheets did not strongly suggest any single process: pressure oxidation was preferable for cobalt recovery from high-grade concentrates, but roasting-leaching and pressure oxidation were equally viable for the low-grade feed. Assuming that the recoveries of atmospheric tank leaching and roasting-leaching may be further improved, they are likely to become the preferred option over intensive but robust pressure oxidation. Only conventional cyanide leaching was considered for gold in this thesis. High-grade concentrates were associated with substantially lower hydrometallurgical impacts than low-grade concentrates, but low-grade material is a more realistic feed material. Based on the findings, the first and foremost goal of process improvement should be maximizing the extraction of cobalt.

Two black mass processes were modeled: the synergistic processing of NiMH and Li-ion black mass (**Publication III**), and the internally reducing processing of Li-ion black mass (**Publication IV**). The results showed that the synergistic process led to slightly lower impacts than the internally reducing process and far higher recovery credits, but the internally reducing process is more realistic due to the low availability of waste NiMH batteries as early as in 2030. Instead, research efforts should focus on optimizing the leaching step to minimize the acid consumption in Li-ion black mass leaching, which would also positively affect the downstream impacts of the process. **Publication IV** showed that some valuable metal losses can be tolerated if the process conditions can be kept milder in this way.

The studies identified several weaknesses in the modeling practices used and some improvements that could be suggested. Solvent extraction modeling was developed during the course of the work, starting with a simple black-box model in **Publication III** that did not include organic at all, to the inclusion of organic extractants in the LCA stage of **Publication IV**. The sensitivity analysis for solvent extraction modeling presented in this compendium revealed that the exclusion of organic extractants or their modeling with generic LCA datasets would lead to poor accuracy in the results. Despite the circulation of the organics, the extractants used, D2EHPA and Cyanex 272, as well as the modifier TBP, contributed significantly to the impacts of all the studied scenarios, and the models were sensitive to the organic feed in general. Unfortunately, it is challenging to assess the consumption of organic without full-scale production, leaving a significant source of uncertainty for any prospective analysis. Furthermore, primary LCI data of even common extractants is missing, and the industry should seek to obtain this data from manufacturers to improve the quality of metallurgical LCA.

The studies did not consider holistic sustainability, which would also require the assessment of social and economic impacts of the processes. Future assessments should increasingly be based on multiple methodologies to better aid decision-making and avoid inconclusive findings, as with the Au-Co concentrate treatment. The simulation-based methodology can, however, be invaluable for obtaining data for other types of assessments provided the limitations are correctly recognized.

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Aalto-DT 164/2024

ISBN 978-952-64-1964-0 (printed)
ISBN 978-952-64-1965-7 (pdf)
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)

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