



Horizon 2020
Programme

ION4RAW

Research and Innovation Action (RIA)

This project has received funding from the European
Union's Horizon 2020 research and innovation programme
under grant agreement No 815748

Start date : 2019-06-01 Duration : 54 Months
<http://ion4raw.eu>

Life Cycle Assessment

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ION4RAW - Contract Number: 815748

Project officer: Floriana La Marca

Document title	Life Cycle Assessment
Author(s)	Mrs. Mathilde LEGAY, Mathilde Legay (LGI)
Number of pages	39
Document type	Deliverable
Work Package	WP7
Document number	D7.1
Issued by	LGI
Date of completion	2023-12-07 23:05:52
Dissemination level	Public

Summary

The ION4RAW project centers on utilising an innovative mineral processing technology to recover valuable by-products from primary sources. This approach leverages Deep Eutectic Solvent (DES) ionic liquids and advanced electro-recovery methods to extract Critical Raw Materials such as bismuth (Bi), tellurium (Te), antimony (Sb), and also aims to reclaim silver (Ag). The cradle-to-gate Life Cycle Assessment (LCAs) of in the ION4RAW process encompasses every process step, from the extraction of copper at El Porvenir, to the production of an alloy at the electrowinning stage. Intermediary steps include Crushing, Grinding, Leaching, DES/solid filtration, Electrowinning, residual solids valorisation and DES recovery. Initially, a first LCA of the alloy production in the ION4RAW process is performed at laboratory scale. This LCA has evaluated the environmental burdens and provided recommendations to the process scale up. Throughout the project, when faced with choices between different process conditions, LGI has evaluated potential trade-offs and offered guidance on the most sustainable process routes to recover the alloy, and in the future, the individual metals. As the project progressed, LGI conducted a LCA based on medium scale experiments, in order to anticipate the potential impacts of the process at pilot scale that will be further developed. The primary function is to produce 1 kg of metals together after electrowinning: 33 % (w/w) copper, 41 % (w/w) bismuth, 4% (w/w) antimony, 2% (w/w) tellurium, and 19% (w/w) silver. Secondary functions consist of recycling the DES at 93% (w/w), the additive at 76% (w/w), and solids without residual DES as inert filler in the construction industry. The LCAs at laboratory scale and pilot scale are compared to reference scenarios, that include the recovery of 1kg of copper cathode (International Copper Association, 2021), and the recovery of 1kg of separated by-products (tellurium, antimony, silver, bismuth) at the factory gate (Philip Nuss; Matthey Eckelman, 2014). The Recipe Midpoint method, using the software OpenLCA 1.10.2 is used with the database Eco-invent v3.6. Life Cycle Inventory: Data collection for the Life Cycle Inventory has encompassed information gathered at both laboratory and medium scales, and hypotheses from partners to foresee the pilot scale potential results. Main hypotheses include the implementation of the ION4RAW technology close to a copper mine similar than El Porvenir in Europe. The close...

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D7.1 Life Cycle Assessment

Project type: Research and Innovation Action
Start date of project: 01/06/2019
Duration: 54 months

WP n° and title	WP7 – Sustainability assessment and exploitation
Responsible Author(s)	Mathilde Legay (LGI)
Contributor(s)	
Dissemination Level	Public deliverable

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EXECUTIVE SUMMARY

The ION4RAW project centers on utilising an innovative mineral processing technology to recover valuable by-products from primary sources. This approach leverages Deep Eutectic Solvent (DES) ionic liquids and advanced electro-recovery methods to extract Critical Raw Materials such as bismuth (Bi), tellurium (Te), antimony (Sb), and also aims to reclaim silver (Ag).

The cradle-to-gate Life Cycle Assessment (LCAs) of in the ION4RAW process encompasses every process step, from the extraction of copper at El Porvenir, to the production of an alloy at the electrowinning stage. Intermediary steps include Crushing, Grinding, Leaching, DES/solid filtration, Electrowinning, residual solids valorisation and DES recovery.

Initially, a first LCA of the alloy production in the ION4RAW process is performed at laboratory scale. This LCA has evaluated the environmental burdens and provided recommendations to the process scale up. Throughout the project, when faced with choices between different process conditions, LGI has evaluated potential trade-offs and offered guidance on the most sustainable process routes to recover the alloy, and in the future, the individual metals. As the project progressed, LGI conducted a LCA based on medium scale experiments, in order to anticipate the potential impacts of the process at pilot scale that will be further developed.

The primary function is to produce 1 kg of metals together after electrowinning: 33 % (w/w) copper, 41 % (w/w) bismuth, 4% (w/w) antimony, 2% (w/w) tellurium, and 19% (w/w) silver. Secondary functions consist of recycling the DES at 93% (w/w), the additive at 76% (w/w), and solids without residual DES as inert filler in the construction industry.

The LCAs at laboratory scale and pilot scale are compared to reference scenarios, that include the recovery of 1kg of copper cathode (International Copper Association, 2021), and the recovery of 1kg of separated by-products (tellurium, antimony, silver, bismuth) at the factory gate (Philip Nuss; Matthey Eckelman, 2014).

The Recipe Midpoint method, using the software OpenLCA 1.10.2 is used with the database Eco-invent v3.6.

Life Cycle Inventory:

Data collection for the Life Cycle Inventory has encompassed information gathered at both laboratory and medium scales, and hypotheses from partners to foresee the pilot scale potential results.

Main hypotheses include the implementation of the ION4RAW technology close to a copper mine similar than El Porvenir in Europe. The close proximity to the mine eliminates the need for transportation between beneficiation, leaching, and electrowinning. The chemicals are assumed to be globally sourced without specific geographical constraints.

At Laboratory scale process conditions, the LCA takes into account the following experiments:

- The ore extraction, crushing, grinding and flotation of the copper ore are conducted at El Porvenir. These operations are assumed to be taking place in Europe.
- DES Leaching on 1 g of ore is conducted at TECNALIA laboratory (3:1 oxidant :solid ratio) at room temperature.
- Electrowinning is conducted at 50°C for 90 minutes at SINTEF laboratory.
- DES/solid filtration, DES recovery and residual solids valorisation are conducted at LUREDERRA laboratory.

The Pilot-scale process conditions relied on hypotheses from medium-scale and laboratory scale:

- The pilot scale LCA used the same hypotheses for the concentrate conditions as for the laboratory scale LCA.
- The LCA takes into account the data from DES Leaching conditions (2:1 oxidant :solid ratio) at TUF laboratory for 1kg of ore with controlled cooling to keep the exothermic reaction at 45°C. Based on this dataset, it is theorised that the 0.8 oxidant to solid ratio, leading to successful by-products recoveries by TECNALIA, would be effective at the pilot scale. Thus, the LCA made assumptions regarding DES Leaching conditions, projecting the use of a 0.8 oxidant to solid ratio.
- Data on the DES/solid filtration are from the experiments conducted at TUF laboratory.
- Due to experimental constraints, the hypotheses for electrowinning are the same as for laboratory scale, with less temperature variation due to the fact that the warm leachate is already at 45°C before electrowinning.
- DES recovery and residual solids valorisation at LUREDERRA laboratory.

The Life Cycle Impact Assessment results are highlighted in Table 1.

Table 1. Results of the Life Cycle Impact Assessment at laboratory and pilot scales

	ION4RAW laboratory scale	ION4RAW pilot scale	Bi	Te	Sb	Ag	Cu	Unit
			(Nuss & Eckelman, 2014)	(Nuss & Eckelman, 2014)	(Nuss & Eckelman, 2014)	(Nuss & Eckelman, 2014)	(International Copper Association, 2021)	
climate change	6,11E+04	9,39E+03	5,9E+01	2,2 E+01	1,29E+01	1,96 E+02	4,1E+00	kg CO2-Eq
freshwater ecotoxicity	2,23E+04	8,91E+03	-	-	-	-	-	kg 1,4-DCB-Eq
freshwater eutrophication	9,70E+01	2,52E+01	2,2E-02	8,9E-01	2,4E-01	3,6	2,70E-03*	kg P-Eq
ozone depletion	7,06E-03	1,10E-03	-	-	-	-	1,20E-10	kg CFC-11-Eq
metal depletion	1,22E+02	1,85E+01	-	-	-	-	-	kg Fe-Eq
ionising radiation	3,12E+04	4,63E+03	-	-	-	-	-	kg U235-Eq
photochemical oxidant	1,40E+02	2,20E+01	-	-	-	-	-	kg NMVOC
human toxicity	8,92E+04	2,66E+04	-	-	-	-	-	kg 1,4-DCB-Eq
terrestrial acidification	2,53E+02	3,93E+01	3,8E-01	2,5	2,2E-01	8,5	6,1E-02	kg SO2-Eq

Results interpretation

The collated process data has provided partners with an initial assessment of the ION4RAW process impacts at laboratory scale. Recommendations for upscaling regarding DES Leaching have been to minimise oxidant and additive quantities to mitigate freshwater ecotoxicity and eutrophication during upscaling.

Observations of reduced environmental impact from laboratory to pilot scale indicate increased efficiency. However, compared to established technologies for by-products and copper recoveries, the ION4RAW process necessitates further optimisation efforts.

To enhance the recovery of valuable metals like silver and tellurium, it is advised to refine the electrowinning process at pilot scale. Additionally, optimising energy usage in cooling the DES Leaching process is recommended, potentially achieved by reducing oxidant levels to mitigate heat generation and cooling needs.

Other recommendations, such as recirculating the metal bearing DES, adding an extra metal refining step, and investigating other washing agents have been done. Other feedstocks are recommended to be studied. Optimised conditions should be studied under the “safe and sustainable by design” (SSbD) framework developed by the European Commission.

Keywords

Life Cycle Assessment, Metallurgy, Deep Eutectic Solvents

Abbreviations and acronyms

Abbreviation	Meaning
Bi	Bismuth
CFC-11	chlorofluorocarbon-11
CO ₂	Carbon dioxide
Cu	Copper
DB	Dichlorobenzene
DES	Deep Eutectic Solvent
Fe	Iron
GHG	Greenhouse Gas
GWP	Global Warming Potential
H ₂ O	water
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life cycle impact assessment
NH ₃	ammonia
NO _x	Nitrogen oxides
P	Phosphate
Pb	Lead
POCP	Photochemical Ozone Creation Potential
Sb	Antimony
SO ₂	Sulfur dioxide
SO _x	Sulfur oxides
SSBD	Safe and Sustainable By Design
Te	Tellurium
U	Uranium
Zn	Zinc

1 INTRODUCTION

1.1 The ION4RAW Project

The ION4RAW Project is dedicated to developing a cost-efficient and environmentally friendly mineral processing technology to recover by-products from primary sources. Joint recovery of by-products from primary sources that belong to the Cu-Ag-Au group is proposed. Most of the targeted by-products elements are Critical Raw Materials such as bismuth (Bi), antimony (Sb). Accompanying major product metals, copper (Cu), silver (Ag), lead (Pb), and zinc will also be recovered by this process. Other by-product metals may also be recovered, e.g. tellurium (Te).

The project runs duration is four years and a half and involves thirteen partners from six countries across the European Union as well as the United Kingdom and Peru. The consortium brings expertise spanning technical research institutes and universities, companies from the mining sector and consultancies.

1.2 Deliverable Objectives

Under Work Package 7 (WP7), Task 7.1 specifically focuses on conducting a Life Cycle Assessment (LCA) to analyse the environmental impacts associated with the ION4RAW process. This task aims to assess and gauge the environmental performance of the Ion4Raw process.

The LCA for the ION4RAW process at both laboratory and pilot scales involves a series of steps:

- The ore extraction, crushing, grinding, flotation processes are modelled based on data from WAI and BRGM.
- DES leaching, DES/solid filtration, electrowinning, residual solids valorisation and DES recovery are evaluated based on laboratory-scale data from TECNALIA, SINTEF, LUREDERRA and TUF, who provide data from WP4, including input material requirements, material yield, energy consumption, wastes and emissions.
- The updated based on data from medium scale experiments (TUF), to anticipate the pilot-scale process, and on hypotheses validated by TECNALIA.
- Data on background processes (energy requirement, pollutant release) is investigated by a literature review prioritising EU datasets (Life cycle Data Network). Ecoinvent database also enables access to specific data.

The interpretation of the results makes it possible to provide key insights on environmental factors in order to optimise the process from laboratory scale to medium scale and pilot scales. These findings inform decisions regarding the most suitable parameters to optimise (ex: DES, use of additive and oxidant, and optimal recovery choices between by-products, if the metals were to be separated). LCAs at laboratory scale and pilot scale are compared with current technology to recovery copper, tellurium, bismuth, antimony and silver.

The interpretation of results is carried out carefully by analysing the dataset and performing a sensibility analysis, collaborating with partners who have fed the dataset. IDENER reviews the LCA.

2 Methods

2.1 Methodology overview

The goal of this deliverable is to assess the environmental impacts of the ION4RAW process at laboratory scale and pilot scale.

The deliverable follows **ISO 14040 and 14044** standards on LCA and provides the framework for this task.

For evaluating environmental sustainability, the EC recommends employing the standardised life cycle assessment (LCA) methodology (ISO 14040/44). This comprehensive approach aims to assess all potential environmental impacts of a product or process throughout its life cycle, uncovering any potential shifting of burdens between stages or impact types.

The ISO standards outline specific steps for conducting an LCA study:

- **Goal and scope definition:** This involves setting the context, objectives, target audience, system boundaries, functional unit (used for comparing systems providing the same function), and other methodological choices.
- **Life cycle inventory (LCI):** Quantification of all input and output flows from the Laboratory scale and Pilot-scale processes, supplemented by generic data to reflect upstream and downstream processes (background data, like making hypotheses on electricity supply chain or waste treatment processes).
- **Life cycle impact assessment (LCIA):** Classification of emissions and used natural resources from the LCI step into impact categories. These are characterised based on their effect and the reference unit for each impact category (e.g., converting physical units from LCI such as mass to impact units like kg CO₂ eq. using characterisation factors).
- **Results interpretation:** Analysis of LCA results based on study goals and evaluation quality. This may involve contribution analysis, gravity assessment, sensitivity analysis, or uncertainty analysis to draw relevant conclusions.

LCA application is iterative, allowing LGI to revisit earlier stages to refine assumptions, gather more data, or test new scenarios, thereby enhancing the study's accuracy and reliability.

2.2 Management

2.2.1 Interviews

In order to understand each step of the process, interviews were conducted with technical WPs. Following up on these, each partner has provided updates regarding the inputs and outputs of each process step.

2.3.3 Validation process

In order to make sure data is reliable, LGI has been working in close collaboration with LUREDERRA, TECNALIA, SINTEF and TUF. Partners have frequently been asked to update their results. They have also been asked whether they require a comparison between different parameters of a process step to choose the most sustainable process.

The data collection milestone was reached in November 2021 for the process at laboratory scale, and in November 2023 at pilot scale.

As part of the risk assessment, partners have been asked to assess the quality of the data, in order to ensure the data representativity.

2.3 Goal and Scope definition

2.3.1 Context

The following process is studied at laboratory and pilot scales, described in Figure 1.

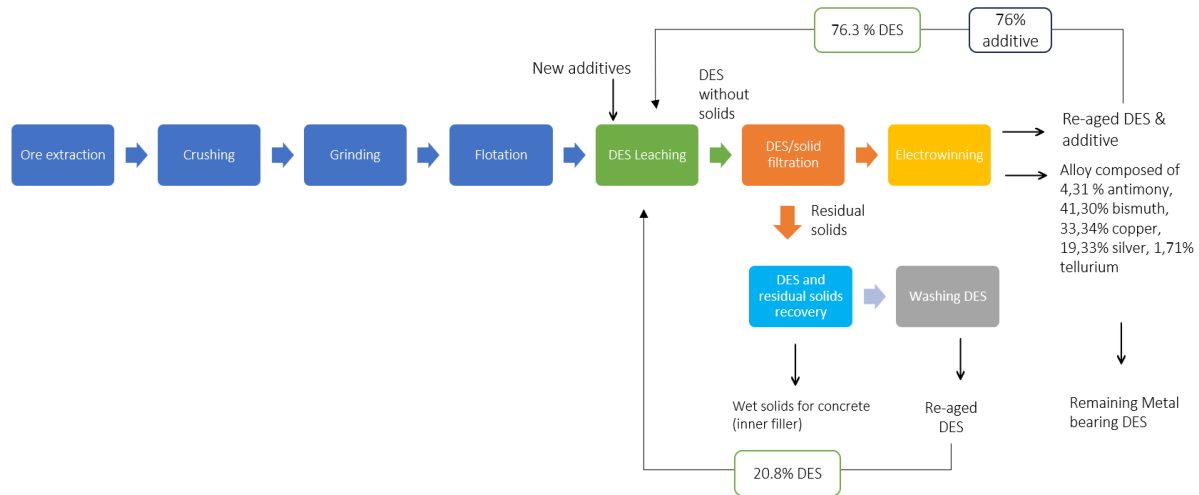


Figure 1. ION4RAW process description

2.3.2 Target audience

This LCA is intended for researchers and the metallurgy industry.

2.3.3 System boundaries

The LCA is performed to measure the impact of metal production from **cradle to gate**. The analysis of upstream processes assesses the environmental impact of the following process steps:

- Extraction of the mineral ore,
- Crushing,
- Grinding,
- Flotation,
- DES Leaching,
- DES/solid filtration,
- Electrowinning,
- DES and residual solids recovery,
- And DES washing.

2.3.4 ION4RAW process functions

The primary function is to produce 1 kg of metals together after electrowinning: 33 % (w/w) copper, 41 % (w/w) bismuth, 4% (w/w) antimony, 2% (w/w) tellurium, and 19% (w/w) silver. Secondary functions consist of recycling the DES at 93% (w/w), the additive at 76% (w/w), and solids without residual DES as inert filler in the construction industry.

Within the process, physical allocation is applied to both DES/Solid Filtration and DES and residual solids steps.

No allocation is applied to the following reference flows:

- crushed ore regarding the crushing step,

- ground ore at the grinding step,
- beneficiated ore at the flotation step,
- leachate, at the leaching process, prioritising the importance of the leachate over the recovery of residual solids,
- washed DES for the DES recovery,
- alloy production via electrowinning, as the focus is on the recovery of metals, with the metal-bearing DES being potentially valuable for further processing.

2.3.5 Impact categories

The LCA adopts the ReCiPe MidPoint methodology. The selection of indicators is determined through a literature review of existing processes and includes the following:

- **Climate change**

Climate change is defined as the changes in global temperature generated by the emission of GreenHouse Gases (GHG). The main unit is in kg CO₂ equivalent.

- **Freshwater ecotoxicity**

Freshwater ecotoxicity highlights the maximum concentrations of chemicals the marine ecosystems can handle. The main unit is used as a reference 1,4-dichlorobenzene (1,4 DB) and is thus expressed in 1,4-dichlorobenzene equivalent (1,4-DB).

- **Freshwater eutrophication**

Freshwater eutrophication is the presence of chemical nutrients, such as ammonia, nitrates, nitrogen oxides and phosphorous, in a river or marine environment. This results in a decrease in both species abundance and water quality and potential excessive growth (ex: algae.) The main unit is Kg P equivalent.

- **Metal depletion**

Metal depletion is the decrease in the amount of non-renewable raw materials and is characterised based on their rate of extraction and estimated reserves. The unit is Fe kg equivalent.

- **Human toxicity**

Human toxicity quantifies the potential impact of a product or process on human health due to exposure to toxic chemicals throughout its life cycle. It considers the potential adverse effects such as cancer, mutations, and developmental disorders, among others and can be divided into cancer and non-cancer categories. Carcinogens increase the risk of cancer, while non-carcinogens cause other adverse health effects such as skin irritation, respiratory problems, or nervous system disorders. Human toxicity can be expressed in several ways depending on the study objectives, the scope and boundaries of the study, the availability of data and the intended audience for the results. In this study, the main unit is used as a reference 1,4-dichlorobenzene (1,4 DB) and is thus expressed in 1,4-dichlorobenzene equivalent (1,4-DB).

- **Ionising radiation**

Ionising radiation is related to the impacts the emissions of radionuclides in a product have on human health and ecosystems. The indicator relates to different radiations, coming from natural sources and human-made sources (nuclear power generation, manufacturing, ...) The unit is given in kg of uranium 235.

- **Ozone depletion**

Ozone depletion measures the potential impact of a product or process on the Earth's ozone layer caused by the emission of ozone-depleting substances (ODS). It is typically expressed in terms of its ozone depletion potential (ODP), which measures the relative ability of a chemical to destroy ozone molecules in the atmosphere in comparison to that of chlorofluorocarbon-11 (CFC-11) and is thus expressed in kg CFC-11-eq.

- **Terrestrial acidification**

Acidification is caused by the reaction of acidic gases such as sulphur dioxide (SO₂) with water in the atmosphere to form a process named as acid deposition. Rain falls can be at a considerable distance from the original source of the gas. This results in varying degrees of ecosystem impairment, contingent upon the specific characteristics of the landscape ecosystems. Gases responsible for acid deposition encompass ammonia (NH₃), nitrogen oxides (NO_x), and sulfur oxides (SO_x). The potential for acidification is quantified using the reference unit of kilograms of SO₂ equivalent

3 Comparison to current technology

To assess the sustainability opportunities for the ION4RAW technology, the current recovery of copper, tellurium, silver, bismuth, and antimony has been studied.

3.1 ION4RAW as a process to recover main metals and by-products with a DES

3.1.1 *Current processing steps to recover copper and its by-products*

Copper is primarily produced as the main product from copper mines, although smaller amounts of copper are also obtained as a by-product from zinc, lead, nickel, and gold mines.

In order to produce primary copper, copper-bearing ores must first be removed using one of three basic methods: open pit mining, underground mining, or leaching processes. The most popular mining method, open pit mining, which produces 90% of the world's copper, is appropriate for low-grade ores that are found close to the surface. After the ore is mined, it is crushed and ground, and then concentrated using flotation. (Screen2, 2023)

Two processes, pyrometallurgical operations and hydrometallurgical processes, are used to transform the concentrated ore into pure copper. Both methods produce refined copper cathodes as the final product. The primary copper production routes via pyrometallurgy and hydrometallurgy are illustrated in the Figure 2.

A variety of cradle-to-grate LCA publications on copper production from primary sources are available in the literature. The functional unit of these studies is usually 1 kg of copper cathode. However, impacts from copper extraction and copper production are site-specific and mainly depend on the type of mining, the type and grade of ores exploited and the type of metal processing technology.

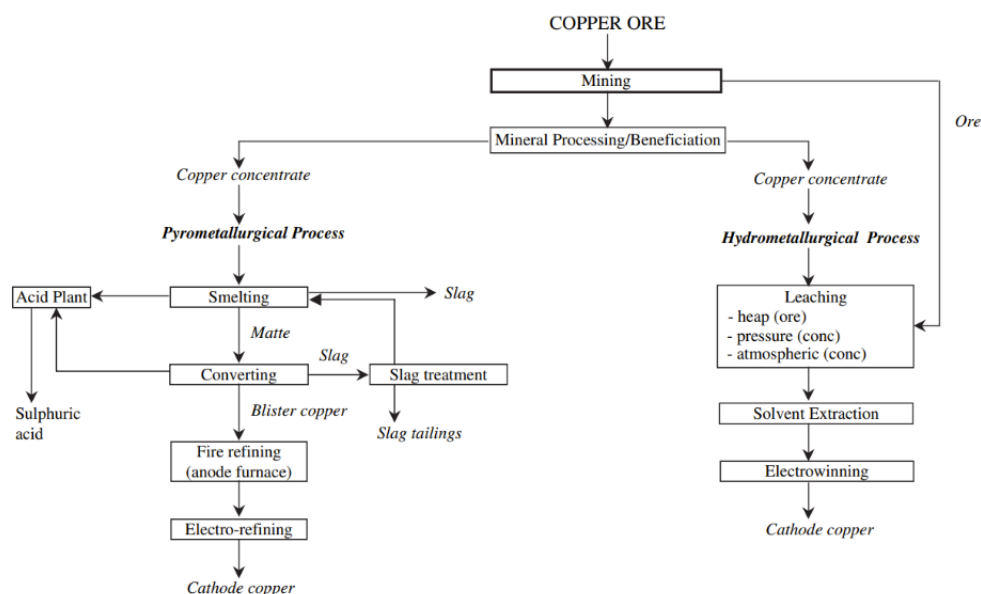


Figure 2. Main processing routes for copper production (Norgate, Jahanshahi, & Rankin, 2007)

A LCA on copper cathode production (**International Copper Association, 2021**)¹ takes into account representative data from 2013 with all technological routes (pyro and hydro), and many coproducts to produce 1,000 kg of copper cathode:

- Mining: oxide ore,
- Concentration: molybdenum concentrate,
- Smelting processes: iron silicate in slag, lead/tin alloy, steam,
- Sulfuric acid plant: sulfuric acid production
- Electrolytic refining: precious metals (via anode sludge), nickel sulfate and copper sulfate.

This LCA highlights the key impacts of the copper production from 2013 data in Table 2 and **Figure 3**.

Table 2. Impacts of copper cathode production (International Copper Association, 2021)

	Results per Tonne of Copper Concentrate (28% Cu)	Results per Tonne of Copper Cathode	Unit
Global Warming Potential (GWP 100 years)	1.100	4,100	kg CO ₂ eq
Eutrophication Potential	0.73	2.7	P eq
Ozone Depletion Potential	1.7E-08	1.2E-07	Kg CFC-11 eq
Acidification Potential	8.2	61	Kg SO ₂ equivalent
Photochemical Ozone-Creation (POCP)	0.60	3.5	Kg ethene-equivalent

¹ Data is currently not yet available on the Life Cycle Data Network

Figure 5: Relative Results for Copper Cathode, by Category

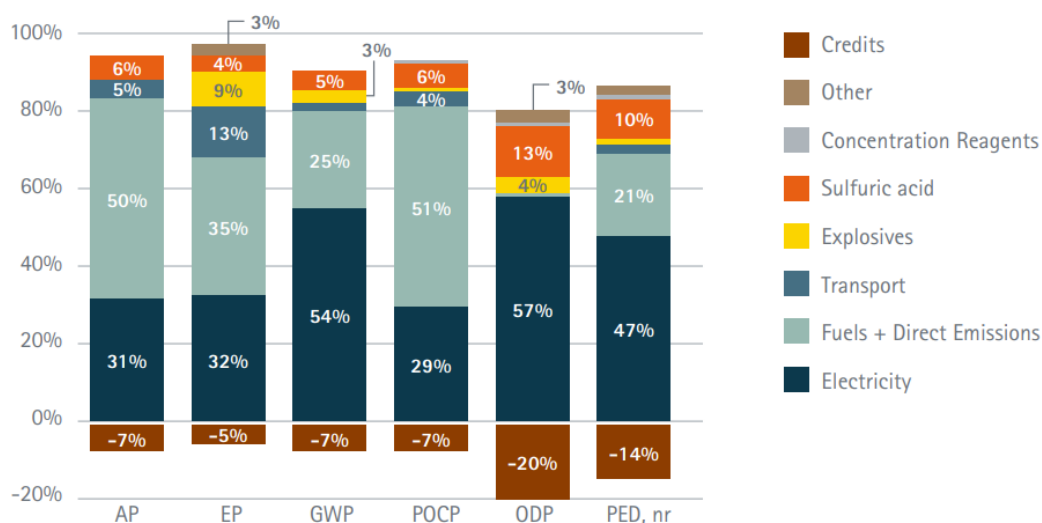


Figure 3. LCA Results for Copper Cathode, by Category (International Copper Association, 2021)

The impacts associated with copper cathode production are the following ones:

- **Climate Change:** GreenHouse Gas emissions from purchased electricity play the most substantial role. Consequently, the environmental footprint of copper production is significantly shaped by the composition of the electricity grid in the production region. Beyond electricity, diesel combustion during mining also represents a significant contributor to environmental impact.
- **Eutrophication:** The impact on eutrophication is largely influenced by NOx emissions, mainly from diesel combustion, prevalent during both mining operations. In certain cases, NOx emissions are released during the intermediate transport of concentrate to the smelter. Electricity usage contributes to approximately one-third of this impact, especially in regions where coal power plants dominate the electricity grid composition.
- **Acidification and Photochemical Ozone Formation:** When sulfur dioxide emissions are released directly during smelting, they notably impact the environment, especially in categories like Acidification Potential and Photochemical Ozone Creation Potential. However, the extent of this impact heavily relies on the specific regulations in a region and the technologies implemented for sulfur removal.
- **Ozone Depletion:** impacts are almost entirely due to the release of R 114 (dichlorotetrafluorethane) emissions and are highly dependent on the presence of nuclear power plants within the electricity grid. With the large contribution of emissions attributable to purchased electricity, the study results highlight a role for the copper industry to play in advocating for renewables in the regions in which copper producers operate.
- Human Toxicity and Metal Depletion values lack robustness in literature review. **(International Copper Association, 2021)**

However, another study (Philip Nuss; Matthey Eckelman, 2014) has investigated human toxicity and uses data from the 2008 production mix for 63 metals, 2006-2010 price data for allocation, and available LCI data at the time of publishing the paper. The study indicates that the production of 1kg of copper leads to a **Human Toxicity** of about **2.7E-04 CTUh/kg**.

3.1.2 Current methods to recover by-products of copper

By-products are recovered through different methods, depending on the materials:

- **Bismuth:** as a by-product, bismuth supply chain is firstly dependent on primary production of lead and tungsten, but also copper, tin and gold. There is no primary production of bismuth.
- **Antimony:** the majority of antimony comes as a co-product or by-product, mainly from gold mines and is produced during gold-antimony concentrates refining. In 2018, 56% of antimony was produced as a by-product of gold, 32% was produced as a host metal and 12% was produced as co-product or by-product of lead, tin, silver and mercury (Screen2, 2023).
- **Silver:** About 20% of annual supply comes from copper mines, about 30% is produced at lead and zinc mines, and 30% of the annual supply comes from primary silver mines. (Mining Intelligence, 2019)
- **Tellurium:** Tellurium is mainly produced worldwide as a by-product of electrolytic copper refining, with smaller amounts obtained as a by-product of refining gold, lead, or other metals. When copper is refined electrolytically, tellurium, being insoluble, settles to the bottom of the electrolytic cell as anode slimes. These slimes are further processed to extract tellurium, resulting in products like crude tellurium dioxide (which contains about 70% Te), copper telluride (which has a Te content of 20-45%), or low-grade tellurium concentrates (which contain roughly 10% Te), which are then refined to yield tellurium metal. (Screen2, 2023).

By-products being produced differently depending on the method, they have different impacts. At the time of writing this deliverable, there is a limited availability of data to thoroughly evaluate the current impacts associated with the recovery of bismuth, tellurium, silver, and antimony. The previously mentioned study uses economic allocation to evaluate the environmental impacts of the by-products (Philip Nuss; Matthey Eckelman, 2014), highlighted in Table 3.

Table 3. Impacts for the recovery of metals (per kg of metal at the factory gate) (Philip Nuss; Matthey Eckelman, 2014)

	Bismuth	Tellurium	Antimony	Silver
Global Warming Potential (kg CO ₂ eq/kg)	58.9 kg	22	12.9	196
Freshwater Eutrophication (kg Peq/kg)	2.2E-02	8.9E-01	2.4E-01	3.6
Human Toxicity (CTUh/kg)	1.7E-05	1.8E-03	4.2E-04	6.9E-03
Terrestrial Acidification (kg SO ₂ eq/kg)	3.8E-01	2.5	2.2E-01	8.5

4 ION4RAW Laboratory scale Life Cycle Inventory

The Life Cycle Inventory of the project is carried out in this section for the results of the process obtained at laboratory scale.

4.1 Geography of the process

Process stages, including extraction, crushing, grinding, and flotation, are intended to be at a single European location, eliminating transportation by processing minerals directly at the mine site. Electricity delivered at high voltage is taken into account. Chemicals' environmental impact, sourced globally, is estimated using data from ecoinvent.

4.2 Ore Extraction

Definition

Ore extraction requires a certain amount of energy and generates mining waste such as tailings and waste rocks. Tailings are mainly composed of milled rock particles. According to Cumbrex, waste rock is usually placed on waste dumps, which usually need to be monitored to avoid creating pollutants like acid water causing metal mobilisation.

Most of the targeted by-products elements are Critical Raw Materials such as bismuth (Bi), antimony (Sb), copper (Cu), silver (Ag), tellurium (Te). Other metals such as lead (Pb), and zinc (Zn), iron (Fe) are also recovered by this process, but are not deposited after electrowinning.

Inputs/Outputs

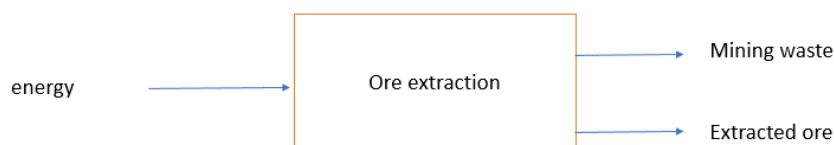


Figure 4. Flows during ore extraction

Available data

- Data on extraction, and cadmium concentration has been provided by WAI.
- Data regarding El Porvenir ore has been provided by BRGM and contains a percentage of each mineral phase obtained with XRD (calcite, dolomite, siderite, quartz, k-feldspar, ca-amphibole, illite, smectite, chlorite, gypsum, galena, sphalerite, pyrite and magnetite).
- Data regarding galena composition and sphalerite composition has been provided by BRGM.

Hypotheses

- The LCA focuses on the extraction happening at the mine El Porvenir, assuming that the mine could be similar in Europe.
- The energy consumption from a copper mine operation (sulfide ore) is taken to account as a primary basis. Electricity, high voltage and medium voltage, and diesel burned in building machines represent the energy consumption due to transportation in the mine and the required electricity for engines.

- For underground mining purposes, a 10% mining dilution is considered for El Porvenir: for one mined ton, there is 100 kg of tailings, considered at the flotation step.
- Chlorite, smetite, illite are assimilated into clays
- Amphibole and andradite are neglected
- Magnetite is assimilated to pyrite: stoichiometry is taken into account, 1M of Magnetite being equivalent to about 3M of pyrite
- The elementary flows, such as ferric oxide, copper, zinc, silicon dioxide, etc., are integrated as inputs to assess the resource depletion impact.
- Siderite (FeCO_3) is assimilated to Iron (Fe).
- As the energy estimated to produce 1kg of copper concentrate (25% copper) in Europe (Ecoinvent) is the following ones, the same values are taken and multiplied by the quantity of copper in the ore:
 - electricity, high voltage : 0,14589 kWh
 - electricity, medium voltage: 0.09778 kWh
 - diesel, burned in building machine: 0.00033 kWh,

Potential improvements in future LCA work

Taking into account amphibole, andradite, magnetite, siderite is important in further work.

4.2 Crushing

Definition

The extracted ore from El Porvenir is fed into a jaw crusher in order to reduce the size of masses for subsequent usage by liberating the Critical Raw Materials.

Inputs/Outputs



Figure 5. Flows during Crushing

Hypotheses

- The energy is consumed in Europe.
- No mass is lost or added during crushing, as there is minimal sample loss during crushing (ultrafine as dust, <0.1%) according to WAI.

Available data

- WAI has provided data on the energy consumption from El Porvenir mine

4.3 Grinding

Definition

The crushed ore is ground in order to increase the surface area to have better chemical reactions.

Inputs/Outputs

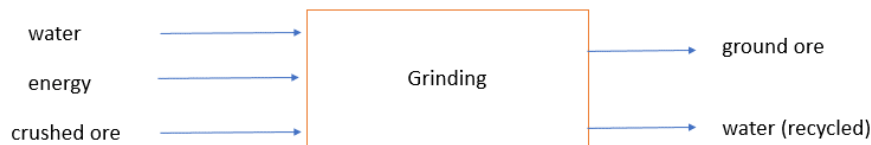


Figure 6. Flows during Grinding

Hypotheses

- No mass is lost during grinding since grinding is performed wet and in a closed circuit, according to WAI.
- All the water is reused in flotation.
- Water is estimated to come from a river in Europe. The coefficient from Ecoinvent excludes Switzerland.

Available data

WAI has provided data on energy consumption, yield, and water consumption.

4.4 Flotation

Definition

Froth flotation separates the ore into a concentrate and a waste stream, tailings. The concentrate is also called beneficiated ore.

Inputs/Outputs

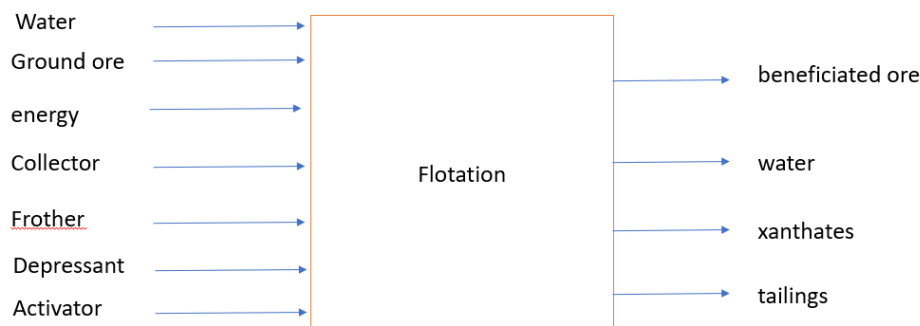


Figure 7. Flows during Flotation

Hypotheses

- The depressant and frother are accounted according to data given by WAI.
- Water coming in the process comes from grinding.
- As weights of collector and activator have very small values compared to the other inputs, they are neglected.

- There is no mass loss during the running of the pilot plant
- Xanthates being biodegradable, it has no impact on the effluent.
- The hypothesis is made that Cu Zn and Pb recovery have no problem with emissions or effluents
- Tailings are accounted as sulfidic tailings from a copper mine, from the ecoinvent database. cadmium and arsenic are taken into account in the tailings.
- Water is accounted as wastewater.

Available data :

- WAI has provided concentrations, ores weights and the consumed energy.

Potential improvements in future LCA work

- Even though their concentration is minimal, the use of collector and activator in flotation should be taken into account into account to evaluate water-related impacts.

4.5 DES synthesis

The synthesis of the DES is confidential and is only available to consortium members.

4.6 DES Leaching

Definition

The leaching process enables the dissolution and recovery of metals concentrate through the use of the Deep Eutectic Solvent. DES Leaching on 1 g of ore is conducted at TECNALIA laboratory (3:1 oxidant :solid ratio) at room temperature.

Inputs/Outputs

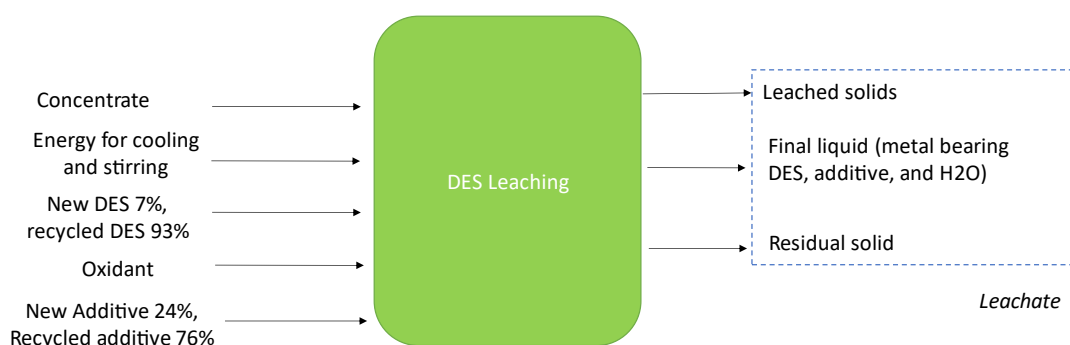


Figure 8. Flows during DES Leaching

Hypotheses

- Since the DES is reused at 93% in a loop circuit, only 7% of new DES is estimated to enter the DES Leaching process.
- Since the quantity of additive recovered in the whole ION4RAW process is about 76% (see stage "DES recovery"), 24% of new additive is estimated to enter the DES leaching step.

- The chemicals' origin remains unknown, so their environmental footprint is based on a worldwide estimation in ecoinvent.
- TECNALIA provided the assumption that total energy comes from the maintenance of temperature, and stirring, assumed to be at 0.27 kW/kg of concentrate for 1hour of DES Leaching.
- At laboratory scale, a reactor of 100 L has been taken as a reference to unify the calculations of agitation and temperature-related energy.
- The oxidant is consumed completely and transformed into water. Water is not considered to be evaporated and is considered as part of the leachate.

Available Labscale data

- Tecnalia has provided the DES leaching conditions.

Potential improvements in future LCA work

- Tecnalia has provided the leaching condition standard deviations.
- The energy requirements for the pilot-scale LCA will be tailored to the specific reactor used.
- Assumptions exclude traces of DES in wastewater from filtration and DES washing stages, since DES recovery is likely to use water as a washing solvent. However, future investigations should consider potential DES traces in water if using DES as a washing agent proves unsuccessful.
- During leaching, the stability of additives might be affected by pH fluctuations and compound formations with dissolved elements, especially chloride. This aspect requires further investigation, including at the pilot scale.

4.7 DES/solid filtration

Definition

DES/ solid filtration is carried out to separate the insoluble solids from the metal-pregnant DES after the leaching.

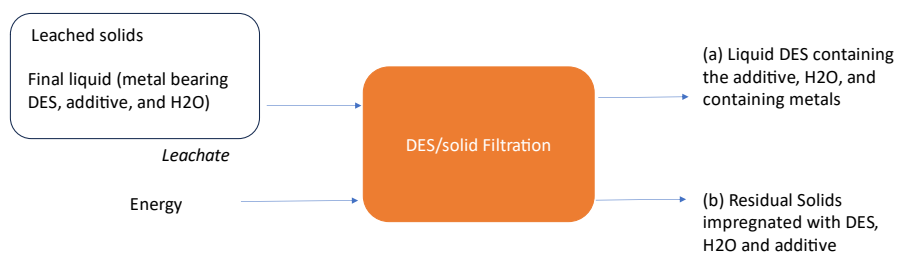


Figure 9. DES/solid filtration

Hypotheses

- The energy value is given by LUREDERRA.
- At the filtration stage, the additive concentration is assumed as similar in both phases:
 - o (a) liquid DES without solids, containing metals,

- (b) residual solids impregnated with DES.
- Similarly to the leaching step, the oxidant is assumed to have reacted completely so will be taken into account as water.
- The metals composition of the liquid DES without solids is the same as the one in the leachate.
- Energy to filter is estimated to be 0.05 kWh.

Available data

- LUREDERRA has provided all the required data.

Potential improvements for future LCA work

- LUREDERRA has assessed the data quality as good or high quality. There are uncertainties regarding the pump consumption, estimated at small-scale. According to LUREDERRA, with greater quantities, the consumption per treated material will be lower.

4.8 Metal Recovery via electrowinning

Definition

The metal recovery stage aims to recover metals dissolved in the DES via electrowinning.

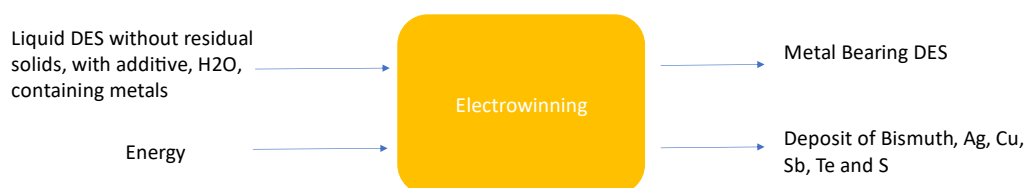


Figure 10. Metal recovery

Hypotheses

- The estimated value to heat up the leachate from room temperature to 50°C is estimated by LGI based on specific heat capacity of water-based solvent (4.186 J/g°C), and is about 0.036 kWh/kg, calculated according to the following formula, where the energy needed for solution is assumed equivalent to the needed electricity (J), the mass is the mass of the leachate (g), and dT represents the temperature change.

$$Energy = mass \times specific\ heat\ capacity \times dT$$

- The electricity to deposit the by-products is calculated based on the formula, where the energy consumption is the amount of energy used in the process, measured in units like watt-hours (Wh), E_{cell} is the cell voltage measured in volts (V), n is the number of electrons transferred in the electrochemical reaction per molecule/ion, F is Faraday's constant, CE is the Current efficiency, and $Mat(Metal)$ is the amount of metal produced or deposited during the electro-winning process.

Energy consumption = $E_{cell} \times n \times F / (CE \times 3600 \times Mat(Metal))$. Higher oxidation states for copper and iron are not taken into account. $n=1$ for copper and $n=2$ for iron.

- Energy for stirring is considered as 0.05 kWh/kg of leachate.
- Metal bearing DES, containing arsenic, cadmium, iron, lead and zinc is not considered as a waste since it can be recovered in another process, or recovered back through DES Leaching.

Available data

- SINTEF has provided the required data.

Potential improvements for future LCA work

- There is a need to optimise the process conditions. In the chosen hypotheses, the experiment lacks optimisation concerning cathode area and time. If the aim were to deplete more, conducting a longer experiment or employing a larger cathode area could have been possible. This would have essentially allowed more charge/current through the system, leading to increased recovery.
- For instance, had SINTEF utilised twice the current in the 25 mL experiment, it could have potentially resulted in up to a twofold increase in metal recovery and production, contingent upon batch electrolysis variations.

4.9 DES and residual solids recovery through filtration



Figure 11. Solid/DES/solvent filtration

Definition

Solids leaving the DES/ solid filtration stage will be impregnated with DES, which needs to be recovered. This stage comprises the following steps :

- The first step consists of filtering the solid with residual DES mixture to recover separately from the solid with residual DES mixture, the clean DES without solid, and a wet solid composed of traces of DES.
- Then, the wet solid is dried in the oven. The wet solid is washed in deionised water as a washing solvent. Then, the wet solid is dried in the oven.
- The solid is will be used as a filler in cement.

Hypotheses

- The energy of heating and filtration is neglected, since drying is made in an oven at 80 °C for 2 hours and oven at 150 °C for 1 hour but could dry out without oven.
- Cadmium, arsenic, lead, iron, and zinc emissions to water are not accounted, since most of them are estimated to remain in the metal bearing DES that will be further processed.
- Solids without residual DES are assimilated to inert fillers for the global market, from ecoinvent database. They are considered as avoided products.
- The wet solid is washed with deionised water as a washing solvent, and the hypothesis is made that no DES remains in deionised water. According to TECNALIA, this hypothesis is relevant since in the future, fresh DES could be used as washing agent and the metals dissolved in the impregnating DES would be recirculated to a new leaching cycle.
- Energy to filter is estimated to be similar to the DES/solid filtration, 0.05 kWh.

Available data

- LUREDERRA has provided all the required data.

Potential improvements in future LCA work

- LUREDERRA has assessed the data quality as good or high quality.
- There are uncertainties surrounding pump consumption estimates at a small scale. LUREDERRA suggests that with larger quantities, the consumption per treated material will decrease.

4.10 DES recovery through washing

Definition

The DES is recovered within the process through DES dilution with water and vacuum distillation.

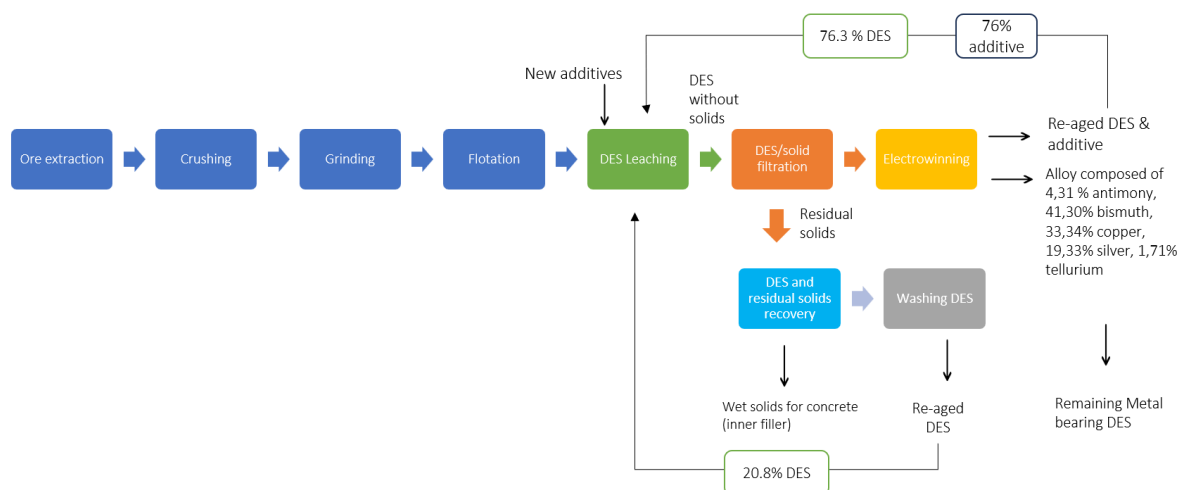


Figure 12. DES recovery

Hypotheses

- The DES is obtained from metal recovery and the recovery of DES and residual solids at 93% and 7% is considered as new input, according to LUREDERRA.

- Similarly, the additive is considered to be recovered at 76% as new input for 24% of its initial value. (see Leaching process), according to LUREDERRA.
- Energy consumption of the distillation is estimated by TUF. The energy consumption for 7h of vacuum distillation at 70 degrees is estimated to be 1.89 kWh.
- Cadmium and arsenic emissions to water are accounted and are estimated based on the concentration in the leachate after electrowinning.

Potential improvements in future LCA work

- TUF and LUREDERRA have assessed their data as good or high quality.

5 Laboratory-scale Life Cycle Impact Assessment

5.1 All Impacts categories

Figure 13 shows the results of the laboratory-scale life cycle impact assessment. Most environmental burdens fall on washing DES, Electrowinning, and the ore extraction, crushing, grinding, and flotation. The valorisation of inner filler, credited on the graph, is not seen to have impacts.

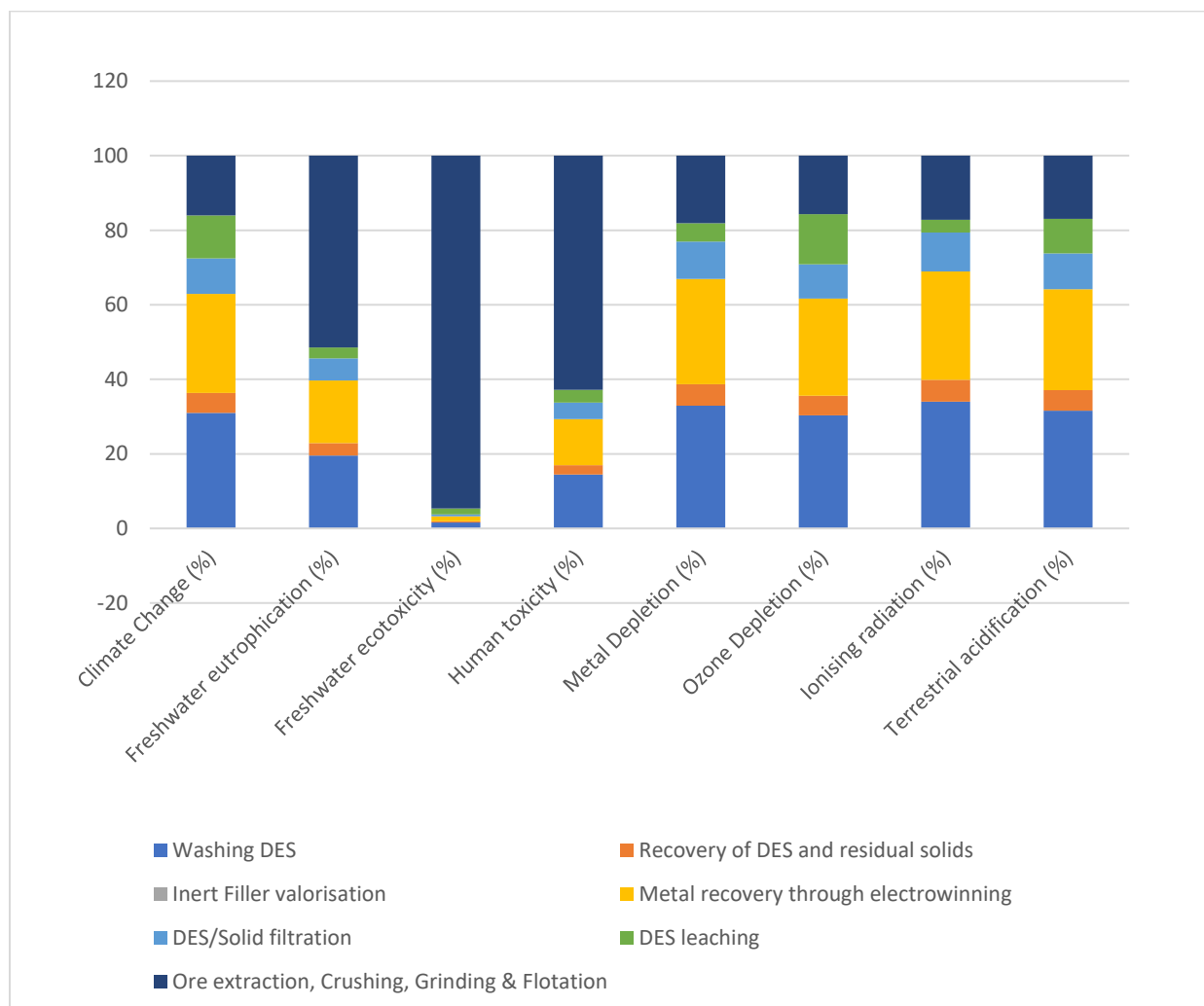


Figure 13. Results of the LCA at laboratory scale

Since the energy is produced in Europe with a variety of energy sources, all environmental impacts are highly impacted by the amount of electricity used in the whole process:

- **DES washing** is very energy intensive since it takes place for 7 hours at 70°C at laboratory scale.
- **Electrowinning** is also important due to the small amount of recovered alloy in the conducted experiments.
- **DES/ solid filtration** is also important due to the important electricity used at laboratory scale, for a small amount of recovered quantities.
- **DES Leaching:** the environmental impact of DES Leaching with a 3:1 oxidant:solid ratio primarily stems from oxidant use, contributing to GWP, freshwater eutrophication, ecotoxicity, human toxicity, ozone depletion, terrestrial acidification, and ionising radiation impacts. Recycling 93% of DES and 76% of additive minimises their contributions.
- **Ore extraction, crushing, grinding, flotation:** there are important freshwater ecotoxicity impacts, human toxicity and freshwater eutrophication impacts are due to sulfidic tailings disposal at flotation stage.

Comparison with current copper & by-products recoveries

Comparing the ION4RAW process with current copper and by-products recovery methods requires caution due to different boundaries, hypotheses, allocation methods, and data timeframe. Future comparisons should consider innovative technologies such as bioleaching.

All environmental burdens are highly important compared to the recovery of copper (International Copper Association, 2021), tellurium, bismuth, silver, and antimony (Philip Nuss; Matthey Eckelman, 2014). The main reason is that the process takes place at laboratory scale, involving small volumes. When scaling up, the energy deployed in the process per amount of volume might improve. The process needs to be further optimised to recover valuable by-products, and separate them. Additionally, the by-product recovery is more energy intensive than copper recovery, due to the lower quantity of by-products compared to the copper content in the ore.

5.2 Recommendations for medium scale

The gathered process data has allowed partners to generate an initial assessment of the process impacts. Recommendations for optimising laboratory-scale operations have been conveyed to TECNALIA and have been outlined in the recent technical report and the presentation at the TARANTULA clustering event, delivered in April 2023.

The subsequent suggestions for scaling up the technology at medium scale have included:

- Focus on maximising the recovery of valuable by-products, maximising their economic potential, and reducing the environmental burden,
- Within the leaching process, a crucial emphasis has been placed on minimising the oxidant quantity during leaching. This adjustment has aimed to decrease both freshwater ecotoxicity and freshwater eutrophication.
- Additionally various alternative conditions have been examined to assess diverse parameters in the DES Leaching step, aiding Tecnalia in pinpointing specific laboratory-scale conditions that minimise environmental impacts.

6 Pilot scale LCA

6.1 Geography of the process

Similarly to the LCI at laboratory scale, the European energy mix is taken into account. Electricity delivered at high voltage is taken into account. No transportation is considered during the different steps of the process, and the chemicals' origin is based on a worldwide estimation inecoinvent.

6.2 Ore extraction, grinding, flotation

The same hypotheses and data are taken for pilot scale from laboratory scale.

6.3 Leaching

Different conditions apply compared to laboratory scale LCA.

Values are taken from the medium scale experiments for the solid/oxidant ratio LCA using the 2:1 non optimised leaching (medium scale, conducted by TUF), and prospective hypotheses made in collaboration with partners. The medium scale volumes are 33% smaller than the pilot scale.

Keeping all the other values for TUF experiments, the most promising conditions for pilot scale are considered: the **solid: oxidant ratio 1:0.8**, leading to recoveries similar to those obtained with the solid: oxidant ratio 1:2, is considered, as recommended by TECNALIA.

For this ratio, the **temperature is set at room temperature and endogenously raised up to 45°C**. Since the reaction is exothermic, the temperature is controlled by refrigeration to this temperature. The electricity necessary to the DES Leaching process is due to stirring and cooling. Values provided by TUF at medium scale (9.54 kWh) are considered.

Potential improvements in future LCA work

The required energy for refrigeration at a oxidant: solid ratio 0.8 would be lower than those suggested by TUF, since there will be less oxidant reacting and generating heat. It will be worth considering real pilot scale energy consumption in the future.

6.4 DES solid filtration

Values are provided for the medium scale experiments, by TUF. The energy for pumping 1L for 1hour is estimated at 0.04 kWh, since LUREDERRA has suggested that the pumping of 3kg for 1hour at pilot scale will require 0.12 kWh.

6.5 Metal recovery through electrowinning

Since the electrowinning step on the optimised leachates from the 1: 0.8 solid: H₂O₂ ratio has not been carried out, the same experiments at laboratory scale are considered for the LCA.

However, different values of electricity are considered:

- Energy for stirring is considered as 0.2 kWh (taking into account the 0.2 kW value for stirring which was previously advised by TECNALIA for laboratory scale leaching experiments.)
- The energy needed to warm up 1kg of leachate from 45°C to 60°C will be approximately 0.0174 kWh, based on the formula previously mentioned in the section “electrowinning at laboratory scale.”

Potential improvements for future LCA work

As pumping will be conducted at pilot scale, it is important to replace the pumping electricity in the LCA. Moreover, it is important to include the real pilot scale data.

6.6 DES and residual solids recovery

Same conditions as for laboratory scale apply for the yield. However, the energy for pumping 1L for 1hour is estimated at 0.04 kWh, since LUREDERRA has suggested that the pumping of 3kg for 1hour at pilot scale will require 0.12 kWh.

6.7 DES recovery through washing

Same yields as for laboratory scale are taken into account. In order to improve the pilot-scale experiments, LGI has taken the values from the experiments conducted at laboratory scale. Together with TUF, LGI has proposed a decrease in distillation time, from 7hours to 2hours, leading to the same DES recovery.

Potential improvements for future LCA work

Verification at the pilot scale is necessary to ascertain water content in DES washing.

7 Pilot-scale Life Cycle Impact Assessment

7.1 LCIA

Results about the pilot-scale LCIA are expressed in Table 4. The results suggest significant differences in environmental impacts between the laboratory and pilot scales across various parameters, with some categories showing substantial reductions or alterations in impact values at the pilot scale compared to the laboratory scale.

Table 4. Results of the Life Cycle Impact Assessment at laboratory scale and pilot scale

	ION4RAW laboratory scale	ION4RAW pilot scale	Bi (Nuss & Eckelman, 2014)	Te (Nuss & Eckelman, 2014)	Sb (Nuss & Eckelman, 2014)	Ag (Nuss & Eckelman, 2014)	Cu (Internation al Copper Association, 2021)	Unit
climate change	6,11E+04	9,39E+03	5,9E+01	2,2 E+01	1,29E+01	1,96 E+02	4,1E+00	kg CO ₂ -Eq
freshwater ecotoxicity	2,23E+04	8,91E+03	-	-	-	-	-	kg 1,4-DCB-Eq
freshwater eutrophication	9,70E+01	2,52E+01	2,2E-02	8,9E-01	2,4E-01	3,6	2,70E-03*	kg P-Eq
ozone depletion	7,06E-03	1,10E-03	-	-	-	-	1,20E-10	kg CFC-11-Eq
metal depletion	1,22E+02	1,85E+01	-	-	-	-	-	kg Fe-Eq
ionising radiation	3,12E+04	4,63E+03	-	-	-	-	-	kg U235-Eq
photochemical oxidant	1,40E+02	2,20E+01	-	-	-	-	-	kg NMVOC
human toxicity	8,92E+04	2,66E+04	-	-	-	-	-	kg 1,4-DCB-Eq
terrestrial acidification	2,53E+02	3,93E+01	3,8E-01	2,5	2,2E-01	8,5	6,1E-02	kg SO ₂ -Eq

Figure 14 shows the distribution of impacts at pilot-scale. Ore extraction, crushing, grinding and flotation is responsible for a significant part of the environmental impacts, followed by DES Leaching. Electrowinning is responsible for a small part of the environmental impacts. DES/solid Filtration, washing DES, recovery of DES and residual solids do not carry important burdens.

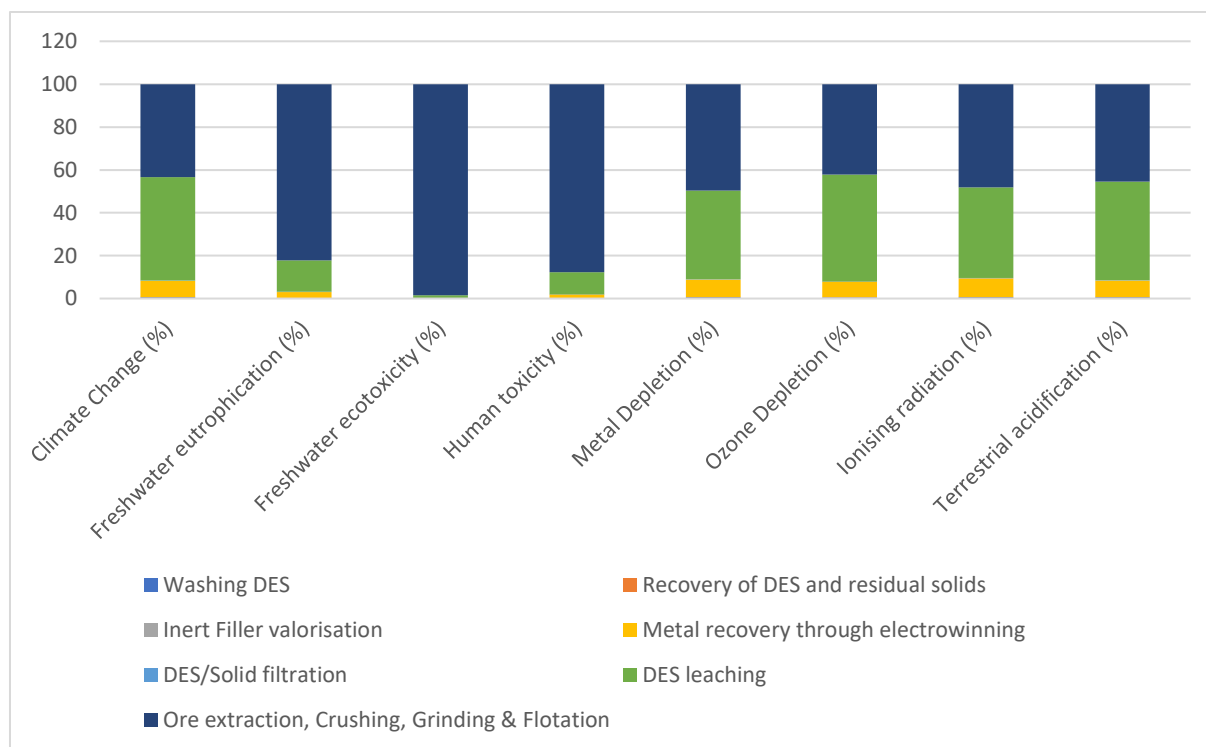


Figure 14. Pilot-scale LCIA

7.2 Results Interpretation

This LCA conducted at the pilot scale builds upon findings from both the medium-scale experiments and anticipated outcomes at the pilot level. It emphasises the expected environmental impacts at the pilot scale pending confirmation of the experiments.

The environmental impact reductions from laboratory scale to pilot scale indicate a potential environmental advantage and improved efficiency. However, compared to the current technologies to recover by-products and copper, the ION4RAW process highlights a need for further optimisation.

- **DES Washing:** Taking into account the laboratory-scale experiment, but within a reduced timeframe of 2 hours instead of the previous 7 hours, this step carries less environmental burdens than at laboratory scale.
- **Leaching Process:** The pilot scale LCA indicates a heightened significance in leaching compared to the laboratory scale LCA, despite the reduction of oxidant use, from 3:1 to 0.8:1 oxidant: solid ratio. This increase is attributed to the introduction of cooling and stirring mechanisms, intensifying the environmental burdens of this stage.
- **Electrowinning:** Environmental impacts remain consistent with those observed at the laboratory scale, indicating comparable impacts at the pilot stage.
- **Filtration:** Foreseen impacts during filtration appear to decrease due to a foreseen reduction in electricity consumption for processing 3 kilograms of leachate, due to pumping a larger amount of liquid compared to laboratory scale.

- **Flotation, Crushing, Grinding and Ore extraction:** Notable environmental impacts arise during the flotation stage. Freshwater ecotoxicity, human toxicity, and freshwater eutrophication are significant concerns owing to sulfidic tailings disposal.

8 Sensitivity Analysis

As part of the risk assessment, partners have given their standard deviations and have assessed the quality of the data, to ensure the data representativity.

8.1 Results uncertainties linked to results at laboratory and medium scale

Uncertainties arise from laboratory-scale and medium-scale results, requiring replication and further optimisation:

- Filtration energy requirements are anticipated to decrease at a larger scale, deviating from laboratory conditions.
- Predictions suggest lower DES recovery through washing; alternative conditions might offer improvements beyond the initial 7-hour distillation hypothesis.
- The values of electricity consumed during DES washing at laboratory scale and pilot scale should be confirmed at pilot scale.
- Laboratory uncertainties are addressed by BRGM, LUR, TECNALIA, and SINTEF for each dataset through standard deviations that appear in Table 5. Data quality assessment has been done by LUREDERRA and TUF, and the following standard deviations have applied. A Monte Carlo analysis should be done in the future.

Table 5. Data quality assessment and hypotheses

Data quality	Standard deviation hypotheses
High	5%
Medium	10-20%
Low	25-50%

8.2 Pilot scale uncertainties

Several hypotheses need to be confirmed after the pilot-scale experiments:

- Verification of successful electrowinning conditions at the pilot scale is necessary.
- The stability of additives during the leaching process might be compromised due to pH fluctuations and the formation of compounds, particularly with dissolved elements like chloride.
- The amount of energy needed for the DES Leaching will be lower than assessed in the pilot-scale LCA, since there will be less oxidant reacting during the exothermic reaction.

8.3 Uncertainties due to the path to market

Several uncertainties can be drawn upon the hypotheses :

- Future optimisation of the ION4RAW process, if available on the market by 2030, will lead to different environmental results in regards to GWP, due to potential changes in emission factors. It's advised to maintain current emission factors due to uncertainties in prospective factors.
- The significance of technology decarbonisation may vary, with potentially greater importance in regions that rely on low-carbon energy sources.

8.4 Potential improvements for future LCA work

Various hypotheses have been considered for the laboratory-scale and pilot-scale LCAs. The following areas need to be improved:

- Current assumptions overlook DES presence in wastewater from filtration and DES washing stages, presuming DES usage as a washing agent will be foreseen in the future. However, should the exploration of DES as a washing agent prove unsuccessful, future assessments should consider potential traces of DES in water and their associated environmental impact.
- Actual heating values for electrowinning need consideration. Duration for maintaining a constant temperature during electrowinning warrants consideration.
- Scaling energy requirements for pumping and stirring from laboratory to pilot scale should be evaluated.
- After the electrowinning process, the recovery of metal-bearing DES at laboratory scale and pilot scale is accounted for only 76.3% of DES recovery without any washing. If a washing step was implemented to retrieve the DES and main metals in the future, this process modification must be factored into the Life Cycle Assessment. Additionally, it's essential to acknowledge that the metal-bearing DES should be classified as waste after undergoing 5-10 cycles.
- The ION4RAW process currently leads to an alloy production. To foresee the metal separation, a future LCA should take into account the by-products recovery with economic allocation (Table 6).

Table 6. Economic allocation to be considered in the next LCA based on the metal price (in USD/ KG) (USGS, 2022)

Raw Material	Metal Price in 2022	coefficient
Bismuth	8.58	0.011
Copper*	8.8	0.0114
Antimony	13.86	0.0179
Tellurium	66	0.085
Silver	675	0.87

9 Ecodesign recommendations in the ION4RAW project

The following recommendations are drawn for the upscaling of the ION4RAW technology, building upon the LCA based on medium scale results and hypotheses, and the LCA at laboratory scale:

- **Washing DES:** Other strategies to wash the DES with less energy should be investigated. It is recommended by LGI and TUF to improve the energy used in distillation by reducing the time from 7h to 2h or reducing temperature.
- **Electrowinning:** A priority consists of improving the metal recoveries through electrowinning. Further experiments must be conducted at twice the amount of charge, in order to have twice more metal recoveries. As recommended by SINTEF, electrowinning should be at 60°C at pilot scale to get higher recoveries, estimated to be 3 times more important than at room temperature. An emphasis on high economic value by-products, (silver, tellurium) is recommended.
- **DES Leaching:** During the leaching process, it is advised to reduce the amount of oxidant, prior to reducing the additive. Reducing the oxidant concentration will induce less heating during the reaction, and thus less energy consumption to cool the reactor down.
- **Energy consumption:** The electricity should be as much as possible decarbonised for the whole ION4RAW process and at the mine. Renewable energy or low carbon energy are strongly suggested. Moreover, the electrification of trucks in the mine, that currently run at diesel, is recommended.

The following options should be explored to valorise the results of the ION4RAW project:

- **Higher by-products recovery:** Given the market demand for high-purity bismuth, tellurium, silver, copper, and antimony, an additional refining step for metals is strongly advised. Maximising the recovery of by-products, particularly those with substantial economic value such as silver and tellurium, should remain a focus for optimisation. Ensuring the purity of secondary materials is crucial for creating long-lasting products.
- **Recirculation of metal bearing DES:** Further efforts should concentrate on recovering metals after the electrowinning step. It's suggested to recirculate the metal-bearing DES multiple times (approximately 5-10 times) to enable further leaching and subsequent metal valorisation. According to Tecnia, post-electrowinning metal washing is essential to enhance DES leaching efficiencies. This washing process should prioritise energy efficiency. Recovering main metals could involve methods such as chemical recovery (e.g., precipitation steps, pH adjustments).
- **DES washing using DES:** Exploring the possibility of utilising DES for washing instead of deionised water warrants investigation as an alternative approach. The environmental impacts and theoretical laboratory conditions (energy consumption, yields) would have to be studied.
- **Industrial symbiosis:** In order to improve the process sustainability, tailings recovery and copper refining by-products valorisation could be foreseen:
 - The recovery of tailings from mines would lead to less freshwater toxicity and human toxicity. Since the concentration of metals in tailings has a significant influence on Climate Change, studying the cut-off grade is essential to reach the breakeven point of reprocessing. Additionally, it will be important to pursue mineral valorisation after processing of low-grade ores in concrete. Other applications for the construction industry could also be foreseen.
 - The recovery of metals from anode slimes, slags, and flue dust will also be valuable.
 - The implementation of a ION4RAW process for various feedstocks will need to be studied through the safe and sustainable by design framework developed by the European Commission.

10 CONCLUSION

The laboratory scale LCA and the pilot scale LCA have been conducted and compared to current processes to obtain bismuth, tellurium, antimony, silver, and copper.

The process data has been collected and has enabled partners to have a preliminary estimate of the process impacts. Advices on the Laboratory scale optimisation have been provided to TECNALIA and other partners. Recommendations have been made to decrease the amount of oxidant and additive in order to reduce both freshwater ecotoxicity and freshwater eutrophication in the upscaling phase.

The environmental impact reductions observed from the laboratory scale to the prospective pilot scale phase demonstrate a promising environmental advantage and enhanced efficiency. Nevertheless, in comparison to existing technologies for recovering by-products and copper, the ION4RAW process underscores the necessity for additional optimisation efforts.

It is recommended to improve the recovery of metals during the electrowinning step, with a focus on high value metals, such as silver and tellurium. Monitoring and optimising the energy consumption involved in cooling the DES Leaching process is advised; reducing oxidant concentration might lead to a less heat-intensive reaction, consequently decreasing the need for cooling.

Several post-project activities have been suggested, such as:

- Introducing an additional metal refining step to facilitate metal separation,
- Investigating the recirculation of metal-bearing DES in the DES leaching step, including exploration of an associated washing process, such as alternative methods to recover DES using fresh DES,
- Exploring potential opportunities for industrial symbiosis to share environmental burdens and maximise the valorisation of by-products.

Lastly, as currently hypothesised, the process should be close to a mine with the targeted by-products, in order to avoid transportation, and minimise its potential environmental burden on climate change and eutrophication.

Appendix - Current methods to extract Zn and Pb

Lead and zinc are traditionally mined together in large quantities, although the concentrates produced from these mixed ores are often processed separately to produce refined lead metal (the lead blast furnace process) and refined zinc metal (the electrolytic zinc process). The production routes for lead and zinc are illustrated in Figure 15. Lead is obtained from blast furnace 80% and the smelting process 10%, when zinc is obtained by electrolytic process at 90%, and smelting 8%. (Norgate, Jahanshahi, & Rankin, 2007)

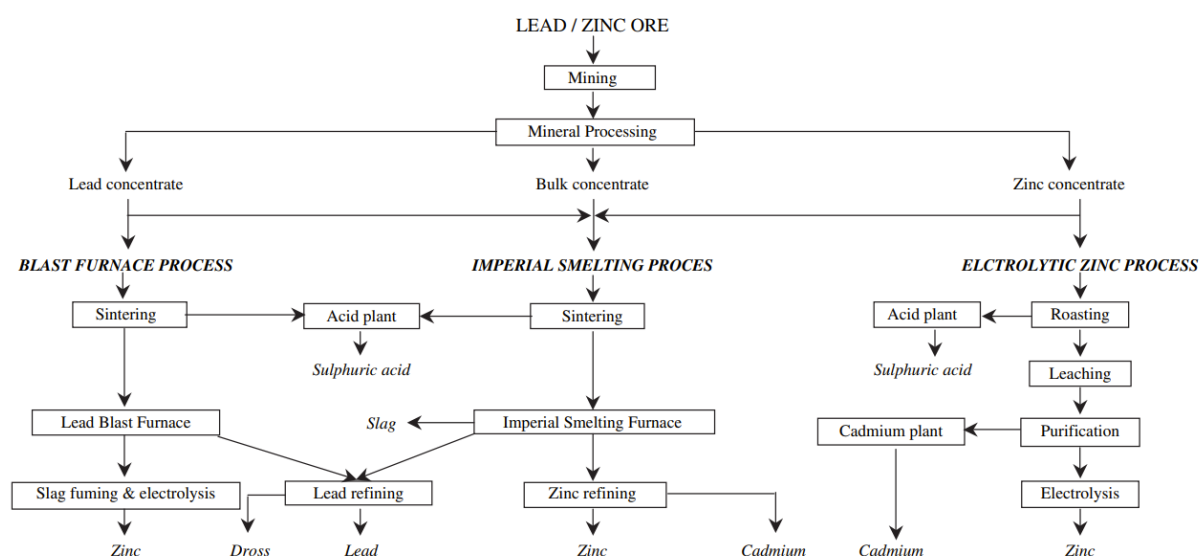


Figure 15. Main processing routes for lead and zinc productions (Norgate, Jahanshahi, & Rankin, 2007)

In the previously mentioned study (Nuss & Eckelman, Life Cycle Assessment of Metals: A Scientific Synthesis, 2014), the environmental burdens are assessed by economic allocation with their by-products (ex: Ge, byproduct of Zn smelting) and are communicated below, for 1kg of each element at the factory gate. (Table 7)

Table 7. Impacts for Lead and Zinc

	Lead	Zinc
Global Warming Potential (kg CO ₂ eq/kg)	1.3	3.1
Freshwater Eutrophication (kg Peq/kg)	2.2 E-03	5.1E-03
Human Toxicity (CTUh/kg)	9.9E-06	5.9E-05
Terrestrial Acidification (kg SO ₂ eq/kg)	2.8E-02	3.9E-02

Appendix - Scenario 1: ION4RAW as a first step before standard processing routes

One potential scenario entails the utilisation of ION4RAW to use the DES to eliminate and sell by-products (silver, tellurium, bismuth, antimony, zinc, and lead) prior to the standard refining processes for copper. Figure 16 provides a high-level flowsheet that illustrates this particular scenario.

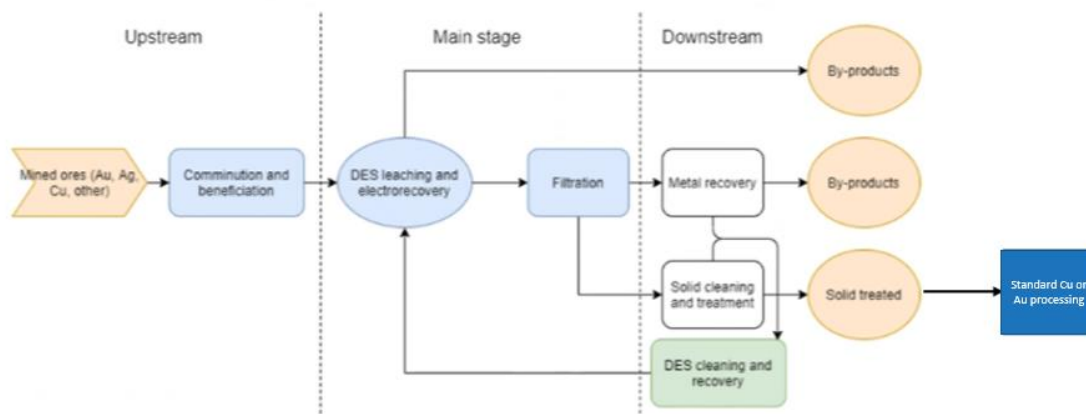


Figure 16. ION4RAW process before standard processing of main metals

The deployment of two processes (one for by-products, one for standard refining) means that there will be environmental impacts of scenario 0 due to by-products through the ION4RAW process, and, if there is enough copper remaining that hasn't been leached nor deposited, environmental impacts due to the obtention of copper via traditional processes. Due to the previous results, the combination of both processes carries too many environmental burdens to be foreseen.

Appendix - Scenario 2: ION4RAW as a tailings treatment technology

10.1.1 Description of the scenario 2

The second scenario foresees ION4RAW process as a solution to treat tailings to recover by-product metals that would otherwise be disposed of as waste. A high-level flowsheet representing this scenario is presented in Figure 17.

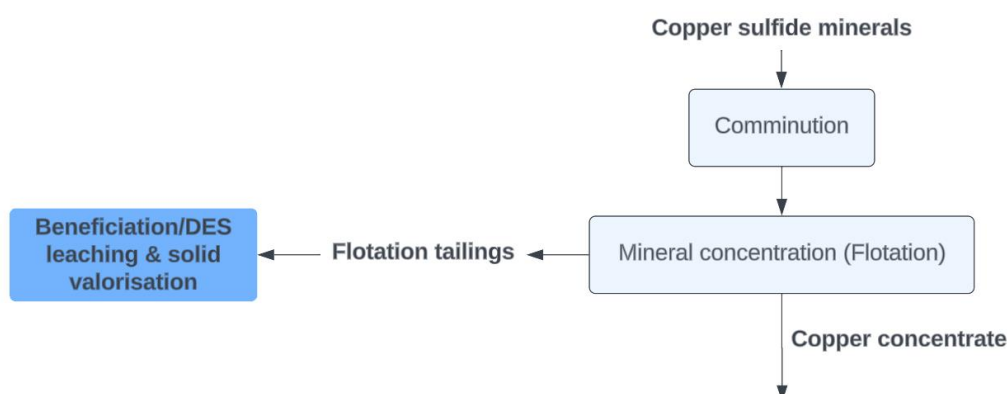


Figure 17. Scenario 2 treatment of tailings flowsheet

10.1.2 Current methods to treat copper tailings while recovering by-products

The reference LCA taken into consideration is a prospective LCA whose functional unit refers to the treatment and management of sulfidic copper tailings arising in the EU in the year 2020/2050. (Raka Adrianto & Pfister, 2022) In this study, the environmental burdens related to the generation of copper tailings are excluded. Different scenarios are foreseen: scenario 0 Business as usual (BAU), scenario 1 BAU toward equitability 2050, scenario 2 mineral valorisation route toward equitability 2050, and scenario 3 metal and mineral recovery route – toward equitability 2050.

Figure 18 illustrates the result for these scenarios. The production of secondary ceramic tiles and CSA cement can save up to around 2 Mt. CO₂ eq. in 2050. Moreover, although a reduction of ecotoxicity impacts is expected, there are still substantial tailings disposal environmental risks. Scenario 3 shows that the extraction of acid-generating compounds and metals from copper tailings can minimise ecotoxicity.

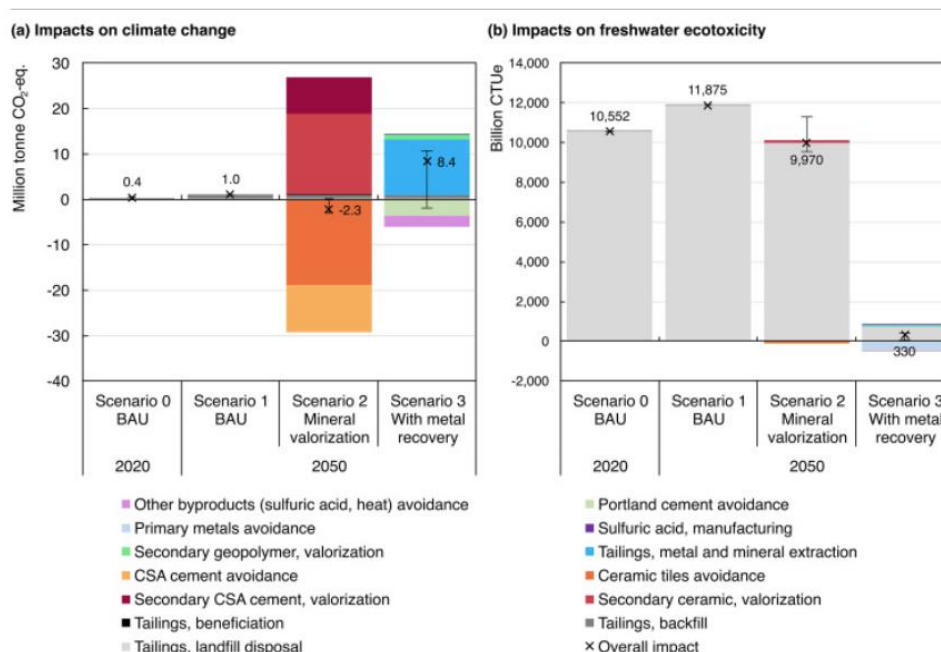


Figure 18. Impacts of tailings reprocessing (million tonne CO₂ equivalent)

Another study highlights the environmental impacts of copper tailings reprocessing, with the recovery of together with sulfuric acid production, ceramic production (3-4t for every tonne of tailings), geopolymers production (0.6-0.7 t for every tonne of tailing), CSA cement (1.56 for every tonne of tailing), with different routes options (Raka Adrianto & Pfister, 2022). The study also reveals that the only recovery of metals in tailings cannot offset the burdens of tailings reprocessing for most environmental impacts.

In fact, Climate Change, Cumulative Energy Demand, and Fossil Depletion Potential have 2-4 times higher values than for primary metal production. However, Human Toxicity and Ecotoxicity have significant lower values. Mineral recovery is essential to bring environmental benefits, and can happen through the valorisation into cement or ceramic tiles. Sulfuric acid can be recovered through sulfur off-gasses that are generated from pyrite roasting process.

Environmental benefits depend on where the process is located (influence of the energy mix & local specificities), on the level of purity that can be achieved in order to use the secondary metals as substitutes for primary metals, on the reprocessing routes, and technology upscaling parameters.

Lastly, tailings reprocessing enables to remove heavy metal in tailings that often leads to groundwater contamination and can have social impacts on communities (access to water and ability to cook in healthy conditions.)

10.1.3 ION4RAW process

As previously stated, the combination of two processes might result in a higher impacts on climate change than having one ION4RAW process to recover main metals together with by-products, depending on the metals recovery rates.

If the ION4RAW process enables a wider recovery of metals, similarly to the reprocessing of sulfidic tailings, the reprocessing of copper tailings thanks to the DES could avoid their disposal in tailings, which can have positive effects on ecotoxicity and human toxicity, taking into account a reduction in the use of oxidant and additive in the ION4RAW process. Mineral recovery into cement is also essential to decrease climate change, cumulative energy demand and fossil depletion potential.

If the reprocessing of tailings with the ION4RAW technology is proven effective in reducing heavy metals and toxic elements in old mine sites, surrounding communities will see their health being less impacted. In some cases, the depollution could enable the appearance of biodiversity, such as new ecosystems and species.

According to the paper below, the break-even point for all indicators, such as Climate Change (CC), Cumulative Energy Demand (CED), Fossil Depletion Potential (FDP), particulate matter formation potential (PMFP), metal depletion potential (MDP), is for a copper grade of 1.2-1.8%. It may be challenging to extract tailings that are less than 1%.

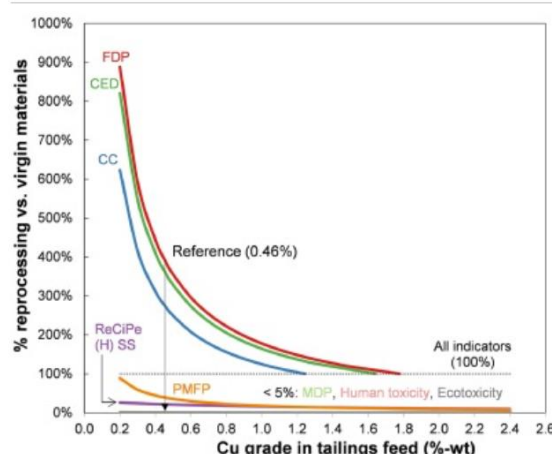


Figure 19. Cu in tailings vs. ratio of reprocessing to metal-only credits (route B without valorisation). MDP, human toxicity, and freshwater ecotoxicity are hardly visible due to low values below 5%. FDP = fossil depletion potential, MDP = metal depletion potential, ReCiPe (H) SS = single score using ReCiPe method at endpoint level. (Raka Adrianto & Pfister, 2022)

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