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Energy Cost Analysis for Extracting Metals from Low Ore Grade Mines and Exploration of Alternative Sources for Sustainable Metal Extraction

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Tesis Doctoral

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Ricardo Magdalena Zarzuela

Directoras

Alicia Valero Delgado

Guiomar Calvo Sevillano

Universidad de Zaragoza / Instituto Universitario de Investigación Mixto CIRCE

2023

Publicaciones

La tesis doctoral se ha llevado a cabo mediante el sistema de compendio de artículos. Estos artículos son trabajos basados en una misma línea de investigación y que han sido publicados en revistas científicas. Se presentan a continuación los detalles de las publicaciones realizadas:

I. **R. Magdalena**, A. Valero, A. Valero, and J. Palacios, "Mining energy consumption as a function of ore grade decline: the case of lead and zinc," Journal of Sustainable Mining, vol. 20, no. 2, pp. 109–121, 2021. https://doi.org/10.46873/2300-3960.1060
Factor de impacto: 0.829 (SJR, Q1: Environmental Engineering)

II. **R. Magdalena**, A. Valero, and G. Calvo, "Limit of recovery: How future evolution of ore grades could influence energy consumption and prices for Nickel, Cobalt, and PGMs," Minerals Engineering, vol. 200, no. May, pp. 1-11, 2023. https://doi.org/10.1016/j.mineng.2023.108150
Factor de impacto: 4.8 (2021 JCR, Journal Impact Factor, Q1: Chemical engineering)

III. **R. Magdalena**, G. Calvo, and A. Valero, "The Energy Cost of Extracting Critical Raw Materials from Tailings: The Case of Coltan," Geosciences, vol. 12, no. 214, pp. 1–15, 2022. https://doi.org/10.3390/geosciences12050214
Factor de impacto: 2.7 (2021 JCR, Journal Citation Indicator, Q3: Geosciences, multidisciplinary)

IV. **R. Magdalena**, A. Valero, G. Calvo, F. J. Alguacil, and F. A. Lopez, "Simulation to Recover Niobium and Tantalum from the Tin Slags of the Old Penouta Mine: A Case Study," Minerals, vol. 11, no. 10, pp. 1–12, 2021. https://doi.org/10.3390/min11101123
Factor de impacto: 2.818 (JCR, Journal Impact Factor, Q2: Geochemistry & geophysics)

V. A. Valero, **R. Magdalena**, G. Calvo, S. Ascaso, F. Círez, and A. Ortego, "Eco-credit system to incentivise the recycling of waste electric and electronic equipment based on a thermodynamic approach," International Journal of Exergy, vol. 35, no. 1, pp. 132–154, 2021. https://doi.org/10.1504/IJEX.2021.115090
Factor de impacto: 1.467 (JCR, Journal Impact Factor, Q4: Thermodynamics)

Además de los artículos mencionados, se han realizado trabajos adicionales complementando la tesis doctoral. Estos trabajos han contribuido en el avance del estudio llevado a cabo, así como ha servido como base para algunos artículos publicados posteriormente. De este modo, se citan a continuación trabajos realizados que han sido presentados en conferencias internacionales.

- **Magdalena, R**. Valero, A. Ascaso, S. Círez, F. Ortego, A. Eco-credit system for incentivizing the recycling of waste electric and electronic equipment based on a thermodynamic approach. *ECOS International Conference.* Wrocklaw, Poland, 23-28 June, 2019.

- **Magdalena, R**. Palacios, J.L. Valero, A. Valero, A. Mining energy consumption as a function of ore grade decline: the case of lead and zinc. *CPOTE International Conference.* Poland, 21-24 September, 2020.
- **Magdalena, R**. Valero, A. Extraction energy as a function of ore grade decline: the case of coltan. *ECOS International Conference.* Taormina, Italy, 27 June – 2 July, 2021.
- **Magdalena, R**. Valero, A. Valero, A. Variation of the specific energy when the ore grade decreases: the case of nickel, cobalt and PGMs. *ECOS International Conference.* Taormina, Italy, 27 June – 2 July, 2021.
- **Magdalena, R**. Iglesias-Émbil, M. Valero, A. Ortego, A. Identification of critical metals and potential bottlenecks in passenger cars through a thermodynamic approach. *ECOS International Conference.* Copenhagen, Denmark, 1-3 July, 2022.
- Torrubia, J. **Magdalena, R**. Energy cost and allocation in mining co-production. The case of PGMs, nickel and copper. *CPOTE International Conference.* Warsaw, Poland, 20-23 September, 2022.
- **Magdalena, R**. Uys, N. Petersen, J. Feasibility of solar photovoltaic energy as an energy source for the electrowinning of zinc in South Africa. *ECOS International Conference.* Las Palmas de Gran Canaria, Spain, 25-30 June, 2023.
- Russo, S. Valero, A. Iglesias-Émbil, M. **Magdalena, R**. Ortego, A. Exergy cost associated with polymers recycling in vehicles: from qualitative to quantitative indicators. *ECOS International Conference.* Las Palmas de Gran Canaria, Spain, 25-30 June, 2023.
- Ortego, A. Rosa, P. Valero, A. **Magdalena, R**. Alcoceba, S. Leading the transition of the European automotive supply chain towards a circular future. *ISIE, International conference on Industrial Ecology*, Leiden, The Netherlands, 2-5 July, 2023
- Ortego, A. Sesana, M. Antonello, V. van Schaik, A. Calabresi, M. Iglesias-Émbil, M. Valero, A. **Magdalena, R**. Alcoceba, S. Disassemblability, recyclability and ecodesign assessment to promote the circular economy in the automotive sector. *ISIE, International conference on Industrial Ecology*, Leiden, The Netherlands, 2-5 July, 2023

Appended publications

The doctoral thesis has been carried out using the article compendium system. These articles are works based on the same line of research and have been published in scientific journals. The details of the publications are presented below

I. **R. Magdalena**, A. Valero, A. Valero, and J. Palacios, "Mining energy consumption as a function of ore grade decline: the case of lead and zinc," Journal of Sustainable Mining, vol. 20, no. 2, pp. 109–121, 2021. https://doi.org/10.46873/2300-3960.1060
Factor de impacto: 0.829 (SJR, Q1: Environmental Engineering)

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III. **R. Magdalena**, G. Calvo, and A. Valero, "The Energy Cost of Extracting Critical Raw Materials from Tailings: The Case of Coltan," Geosciences, vol. 12, no. 214, pp. 1–15, 2022. https://doi.org/10.3390/geosciences12050214
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V. A. Valero, **R. Magdalena**, G. Calvo, S. Ascaso, F. Círez, and A. Ortego, "Eco-credit system to incentivise the recycling of waste electric and electronic equipment based on a thermodynamic approach," International Journal of Exergy, vol. 35, no. 1, pp. 132–154, 2021. https://doi.org/10.1504/IJEX.2021.115090
Factor de impacto: 1.467 (JCR, Journal Impact Factor, Q4: Thermodynamics)

In addition to the mentioned articles, additional work has been conducted to complement the doctoral thesis. These works have contributed to the advancement of the conducted study and have served as a basis for some subsequently published articles. Thus, the following works are cited, which have been presented at international conferences.

- **Magdalena, R**. Valero, A. Ascaso, S. Círez, F. Ortego, A. Eco-credit system for incentivizing the recycling of waste electric and electronic equipment based on a thermodynamic approach. *ECOS International Conference.* Wrocklaw, Poland, 23-28 June, 2019.

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- Russo, S. Valero, A. Iglesias-Émbil, M. **Magdalena, R**. Ortego, A. Exergy cost associated with polymers recycling in vehicles: from qualitative to quantitative indicators. *ECOS International Conference.* Las Palmas de Gran Canaria, Spain, 25-30 June, 2023.
- Ortego, A. Rosa, P. Valero, A. **Magdalena, R**. Alcoceba, S. Leading the transition of the European automotive supply chain towards a circular future. *ISIE, International conference on Industrial Ecology*, Leiden, The Netherlands, 2-5 July, 2023
- Ortego, A. Sesana, M. Antonello, V. van Schaik, A. Calabresi, M. Iglesias-Émbil, M. Valero, A. **Magdalena, R**. Alcoceba, S. Disassemblability, recyclability and ecodesign assessment to promote the circular economy in the automotive sector. *ISIE, International conference on Industrial Ecology*, Leiden, The Netherlands, 2-5 July, 2023

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A todos ellos y a mucha gente que no está aquí, ¡GRACIAS!

A mis abuelos, Miguel, Ana y Jacinta

Porque sin estar, siempre habéis estado

Resumen

En las últimas décadas, los avances tecnológicos han transformado las industrias, desde la fabricación de vehículos a gran escala hasta la producción de dispositivos pequeños esenciales para la sociedad, como móviles, tabletas y portátiles. Los metales, debido a sus propiedades únicas, son esenciales para estos avances, tanto en términos de cantidad como de variedad. Por ello, el aumento anual en la demanda de estos productos ha llevado a una mayor producción de metales, agotando las minas. La industria minera, una de las más grandes y contaminantes a nivel global, se enfrenta a una reducción drástica en la calidad del mineral extraído, lo que requiere más energía para obtener la misma cantidad de metal.

Esta tesis pretende arrojar luz sobre dichos retos, enfocándose en tres aspectos. Primero, se evalúa el comportamiento energético futuro de las minas asociado a leyes de mina decrecientes. Seguidamente, se lleva a cabo un análisis para determinar la viabilidad de extraer metales de los relaves, con un análisis de los químicos y agua utilizada. Para finalizar, se realiza una propuesta basada en la rareza termodinámica para fomentar la recogida de equipos eléctricos y electrónicos, evitando de esta manera su almacenamiento en los hogares y fomentando la recuperación de materias primas esenciales de una fuente alternativa a la extracción primaria.

En particular, se han desarrollado curvas representando los costes energéticos en función de la disminución en la concentración del mineral, para tres grupos diferentes de metales: plomo – zinc, niobio – tántalo, y níquel – cobalto – grupo de los elementos del platino (PGMs). Para cada metal analizado, las curvas muestran la concentración actual de las minas, concentraciones conocidas sobre residuos de mina y concentraciones que denominamos límite, que serían inaccesibles desde un punto de vista energético. Además, se ha llevado a cabo una evaluación económica y una comparación con sus precios en el mercado.

Los estudios del comportamiento energético y de extracción de los metales han sido realizados con un programa especializado llamado Outotec HSC Chemistry. Este programa informático permite el desarrollo de simulaciones para diferentes etapas en el proceso de extracción, siendo posible el cálculo de la energía en cada punto de la simulación. Además, también se puede llevar a cabo el desarrollo de procesos químicos en la etapa de refinado, siendo posible estimar los productos químicos necesarios para el refinado, así como su impacto en el medio ambiente.

Es importante destacar que la viabilidad de extracción de metales depende mucho de la asignación de costes que se considere, haciendo que la extracción de algunos metales sea viable o no. Por ejemplo, se he realizado un análisis de sensibilidad de los precios en el proceso de simulación del níquel, cobalto y el grupo de los platinos. El análisis revela que, si se aumenta un 30% la asignación de costes en el níquel, el precio en el mercado de este metal podría crecer un 7%. Por otro lado, este aumento en la asignación de costes del níquel podría suponer una reducción del 30% y casi del 50% en el precio para el cobalto y el grupo de los platinos, respectivamente.

Para tratar de paliar el problema detectado sobre la demanda de minerales y la reducción de la concentración en las minas, se han propuesto algunas soluciones para

evaluar la viabilidad de extraer ciertos minerales para cubrir la demanda de los metales analizados. La primera solución está basada en extraer metales de los relaves, que hasta ahora eran materiales que se descartaban por tener unas concentraciones muy bajas de metales y por no ser rentables. Hoy en día, hay explotaciones con una ley de mina muy baja, y existen relaves de minas abandonadas que tienen una concentración similar a la de estas minas. En concreto, en esta tesis, se ha llevado a cabo un estudio de una mina abandonada en 1985 (estando activa hoy en día) en Penouta, Galicia, situada en el norte de España, que tenía como objetivo la extracción de estaño. Se ha podido observar que los relaves contienen no solo una concentración significativa de estaño, sino también de niobio y tántalo. De este modo, se ha llevado a cabo una simulación del proceso de extracción, obteniéndose resultados muy prometedores. Por ejemplo, los cálculos realizados indican que por cada tonelada de relaves sería posible recuperar 0,45 toneladas de estaño, 0,05 toneladas de tántalo y 0,03 toneladas de niobio. Además, la eficiencia del proceso refleja una posible recuperación de más del 92% para el estaño, 95% para el tántalo y del 67% para el niobio, con una pureza del 99%, 79% y 98%, respectivamente.

La segunda solución está asociada a la recuperación de materiales esenciales de productos tecnológicos cuando estos llegan a su fin de vida. Algunos dispositivos son enviados a países en desarrollo, otros son llevados a vías de reciclaje, pero también hay muchos que son almacenados en los hogares. Por este motivo, es esencial que dichos dispositivos sean adecuadamente recogidos para su reusabilidad, o en última instancia, para su reciclado. Esta tesis propone una metodología para calcular los incentivos que podrían otorgarse a modo de recompensas a los usuarios para fomentar que los dispositivos electrónicos puedan ser recogidos, reutilizados o reciclados. Este intercambio estaría basado en un sistema llamado "Eco-credits", y la recompensa propuesta depende de la calidad de los metales presentes en el dispositivo, su estado (funcionando para su reusabilidad o no funcionando para su reparación), y su duración (dispositivos más viejos reciben menos créditos). La calidad de las materias primas se evalúa a través del indicador de "la rareza termodinámica", que está basado en el segundo principio. Este indicador se compone de dos términos principales: el coste exergético de reposición y la exergía incorporada al metal. De acuerdo a esta aproximación, es posible evaluar minerales en función de su abundancia en la corteza de la Tierra, así como la exergía que se necesita para extraer minerales de las minas, procesarlos y enviarlos a la industria. es. El objetivo de los "Eco-credits" es fomentar la reciclabilidad de dispositivos y prevenir la pérdida de metales que están simplemente almacenados en hogar.

Los resultados de esta tesis pueden ser valiosos para las compañías mineras, fabricantes y legisladores para comprender los recursos involucrados en la extracción de metales, la distribución de costes y los potenciales impactos medioambientales. Además, la información recogida en esta tesis puede ser relevante para concienciar a la población sobre esta situación, y por lo tanto, animar a una utilización responsable de los dispositivos que contienen metales valiosos.

Abstract

In recent decades, technological advancements have revolutionized industries, from large-scale vehicle manufacturing to the production of small devices crucial to society, such as mobile phones, tablets, and laptops. Metals, owing to their unique properties, are indispensable for these advancements, both in terms of quantity and diversity. Consequently, the annual surge in demand for these products has led to increased metal production, depleting mineral deposits. The mining industry, one of the largest and most environmentally impactful globally, faces a drastic reduction in the quality of extracted minerals, necessitating more energy to obtain the same quantity of metal.

This thesis aims to shed light on these challenges, focusing on three aspects. Firstly, it evaluates the future energy behavior of mines associated with declining ore grades. Subsequently, an analysis is conducted to determine the feasibility of extracting metals from tailings, with an examination of the chemicals and water used. Lastly, a proposal based on thermodynamic rarity is presented to encourage the collection of electrical and electronic equipment, thus avoiding their storage in households and promoting the recovery of essential raw materials from an alternative source to primary extraction.

In particular, curves representing energy costs as a function of decreasing mineral concentration have been developed for three different metal groups: lead-zinc, niobium-tantalum, and nickel-cobalt-platinum group metals (PGMs). For each analyzed metal, the curves depict current mine concentrations, known concentrations in mine tailings, and concentrations referred to as “limit of extraction”, which would be energetically inaccessible. Additionally, an economic assessment and comparison with market prices have been conducted.

The studies on the energy behavior and metal extraction have been performed using specialized software called Outotec HSC Chemistry. This computer program enables the development of simulations for various stages of the extraction process, allowing the calculation of energy at each simulation point. Furthermore, it facilitates the development of chemical processes in the refining stage, making it possible to estimate the chemicals required for refining and their environmental impact.

It is crucial to note that the feasibility of metal extraction depends significantly on cost allocation considerations, making the extraction of certain metals more or less viable. For example, a sensitivity analysis of nickel, cobalt, and the platinum group metals (PGMs) in the simulation process has been conducted. The analysis reveals that increasing cost allocations for nickel by 30% could potentially result in a 7% market price increase for this metal. Conversely, such a cost allocation increase could lead to a 30% reduction for cobalt and almost a 50% reduction for PGMs' market prices, respectively.

To address the identified challenges concerning mineral demand and declining ore concentrations, several solutions have been proposed to assess the feasibility of extracting specific minerals to meet the demand for the analyzed metals. The first solution is based on extracting metals from tailings, which were previously

disregarded due to their low metal concentrations and lack of profitability. Today, there are mining operations with very low ore grades, and abandoned mine tailings have concentrations similar to these active mines. Specifically, this thesis includes a study of a mine abandoned in 1985 (currently active) in Penouta, Galicia, located in northern Spain, with the goal of extracting tin. It has been observed that the tailings contain not only a significant tin concentration but also tantalum and niobium. Consequently, a simulation of the extraction process has been conducted, yielding highly promising results. For instance, calculations indicate that for every ton of tailings, it would be possible to recover 0.45 tons of tin, 0.05 tons of tantalum, and 0.03 tons of niobium. Furthermore, the process's efficiency suggests a potential recovery rate of over 92% for tin, 95% for tantalum, and 67% for niobium, with purity levels of 99%, 79%, and 98%, respectively.

The second solution is associated with the recovery of essential materials from technological products when they reach the end of their lifecycle. Some devices are sent to developing countries, while others are directed to recycling pathways. However, many end up stored in households. For this reason, it is essential that such devices are adequately collected for reuse or, ultimately, recycling. This thesis proposes a methodology to calculate incentives in the form of rewards to encourage users to return electronic devices for reuse or recycling. This exchange would be based on a system called "Eco-credits", with the proposed reward depending on the quality of metals present in the device, its condition (functional for reuse or non-functional for repair), and its age (older devices receive fewer credits). The quality of raw materials is assessed through the thermodynamic rarity indicator, which is based on the second law of thermodynamics. This indicator comprises two main components: the exergy replacement cost and the exergy incorporated into the metal. According to this approach, it is possible to evaluate minerals based on their abundance in the Earth's crust, as well as the exergy required to extract minerals from mines, process them, and deliver them to the industry. The goal of "Eco-credits" is to promote device recyclability and prevent the loss of metals simply stored in households.

The results of this thesis can be valuable for mining companies, manufacturers, and policymakers to comprehend the resources involved in metal extraction, cost distribution, and potential environmental impacts. Furthermore, the information collected in this thesis can be relevant for raising awareness among the population about this situation, thus encouraging the responsible use of devices containing valuable metals.

Acronyms

AI	Artificial Intelligence
ANS	Adjusted Net Savings
BAT	Best available Technology
BAU	Business as usual
BEV	Battery electric vehicles
CE	Circular Economy
condERS	Battery electric with dynamic charging conductive
CRM	Critical raw material
CTC	Certified Trade Chain
DMC	Domestic Material Consumption
DMI	Direct Material Input
DMO	Direct Material Output
DPO	Domestic processed Output
EEE	Electronic and Electrical Equipment
EoL	End of life
EOL-RIR	End-Of-Life Recycling Input Rate
EOL-RR	End-Of-Life Recycling Rate
ERC	Exergy Replacement Cost
EV	Electric Vehicles
GHG	Greenhouse Gas
HHV	High heating value
HSLA	High-Strength Low Alloy
ICE	Internal combustion engine
induERS	Battery electric with dynamic charging contactless inductive
IoT	Internet of Things
ISF	Imperial Smelting Furnace
LCA	Life Cycle Assessment
LOR	Limit Of Recovery
MFA	Material Flow Analysis
ML	Machine Learning
MRD	Mineral Resource Depletion
NAS	Net Additions to stock
NIMBY	Not In My Back Yard
O&M	Operation and maintenance
PGMs	Platinum Group Metals
REE	Rare Earth Elements
RMI	Raw Materials Initiative
SD	Sustainable Development
SIM	Simulation
TMC	Total Material Consumption
TMR	Total Material requirement
URR	Ultimate recoverable resources

VAT	Value Added Tax
WEEE	Waste of Electric and Electronic Equipment

Institutions and agreements

AusiMM	Australasian Institute of Mining and Metallurgy
BGS	British Geological Survey
DRC	Democratic Republic of Congo
EC	European Commission
EPRS	European Parliament Research Services
EU	European Union
G8	Group of 8
IAIA	International Association for Impact Assessment
IEA	International Agency of Energy
IIED	International Institute for Environment and Development
JISEA	Joint Institute Strategic Energy Analysis
JRC	Joint Research Centre
KP	Kyoto Protocol
PA	Paris Agreement
SEEA	System of Environmental Economic Accounting
SIMP	Social Impact Management Plant
SNA	System National Accounts
UN	United Nations
UNEP	United Nations Environment Program
UNFCCC	United Nations Framework Convention on Climate Change
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey

Units

$	Dollars
€	Euro
Δbci	Replacement exergy
µm	micrometer
A	Factor determined for each mineral
bci	Concentration exergy needed to separate an element from a substance
Ca	Aeration factor to account for air in pulp
Cp	Heat Capacity
E	Energy for the concentration and extraction of minerals
Efx	Efficiency factor
Exm	Energy for the concentration and extraction of minerals
F80	Size through the 80% which 80% of the feed passes
g	Grams
GJ	Gigajoules

GW	Gigawatts
H	Enthalpy
h	hour
inh	Inhabitants
K	Ratio between the total and the minimum exergy to extract a mineral
kg	Kilogram
kJ	Kilojoules
km	kilometer
ktons	Kilotons
kWh	Kilowatt hour
l	liters
m3	Cubic meters
Mi	Mine extraction
mi	elements contained in the device
Min	Minutes
MJ	Megajoules
mm	millimeter
Mt	Millions tons
Mtoe	Millions of tons of oil equivalent
MW	Megawatts
ºC	Celsius degrees
P80	Diameter in microns through which 80% of the product passes
Pi	Market price
Q	Flow rate
R	Universal gas constant
R	Rarity of a device
S	Entropy
S	Scale factor
t	tons
T0	Temperature of reference
TheRy	Thermodynamic Rarity
toe	tons of oil equivalent
t-ore	tons of ore
tph	tons per hour
TR	Flotation retention time
t-rock	tons of rock
USD	Dollars
Vf	Flotation volume
W	Work Index
W	Watts
W	Work bond Index
Wi	Bond Index
wt-%	weight percentage
Xc	Concentration of a mineral in Thanatia

Xi	Concentration of a given mineral in grams of mineral per gram or ore
Xm	Ore grade of a mineral in a mine

Periodic table and chemical compositions

Ag	Silver	Mo	Molybdenum
Al	Aluminum	Na	Sodium
Ar	Argon	Nb	Niobium
As	Arsenic	Nd	Neodymium
Au	Gold	Ni	Nickel
B	Boron	Np	Neptunium
Ba	Barium	O	Oxygen
Be	Beryllium	P	Phosphorus
Bh	Bohrium	Pb	Lead
Bi	Bismuth	Pd	Palladium
Br	Bromine	Pr	Praseodymium
C	Carbon	Pt	Platinum
Ca	Calcium	Re	Rhenium
Cd	Cadmium	Rh	Rhodium
Ce	Cerium	Ru	Ruthenium
Cl	Chlorine	S	Sulfur
Co	Cobalt	Sb	Antimony
Cr	Chromium	Sc	Scandium
Cs	Cesium	Se	Selenium
Cu	Copper	Si	Silicon
Dy	Dysprosium	Sn	Tin
F	Fluorine	Sr	Strontium
Fe	Iron	Ta	Tantalum
Ga	Gallium	Tb	Terbium
Gd	Gadolinium	Tc	Technetium
Ge	Germanium	Te	Tellurium
H	Hydrogen	Ti	Titanium
Hg	Mercury	Tl	Thallium
Ho	Holmium	U	Uranium
In	Indium	V	Vanadium
Ir	Iridium	W	Tungsten
K	Potassium	Xe	Xenon
Kr	Krypton	Y	Yttrium
Li	Lithium	Yb	Ytterbium
Mg	Magnesium	Zn	Zinc
Mn	Manganese	Zr	Zirconium
ABS	Acrylonitrile Butadiene Styrene	KF	Potassium fluoride
CaF_2	Calcium difluoride	NH_3F	Ammonium fluoride
CO	Carbon monoxide	NH_4F	Ammonium fluoride

CO_2	Carbon Dioxide	PA	Polyamide
H_2O	Water	PC	Polycarbonate
H_2SO_4	Sulfuric acid	PES	polyester
HF	Hydrogen fluoride	PMMA	Poly(methyl methacrylate)

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Chapter 1. Thesis objectives and structure

1.1. Objectives

It is a fact that the quantity and variety of raw materials demanded by society are growing at unprecedented rates. This is being exacerbated by the shift from fossil fuels to raw materials for the development of decarbonized energy technologies, which puts increased pressure on the mining sector. As a result of this increased extraction, it is expected that global deposits will experience a decrease in ore grades, leading to corresponding increases in extraction costs. The central objective of this thesis is to calculate the specific energy for concentration of different metals as ore grades decline. The assessment must identify the energy required to extract a ton of certain metals, analyzing the curve calculated for important concentrations when this is reduced. Therefore, the thesis serves as a guide for understanding the depletion of mines and gaining insight into the magnitudes of specific energy required for concentration that may be necessary in the future. Moreover, an examination of various strategies to mitigate the depletion of mines has been undertaken. In this context, the feasibility of extracting metals from tailings has been evaluated, alongside the proposition of a methodology for the collection of electric and electronic devices containing critical materials.

From a more specific point of view the thesis has the following goals:

- Calculate the specific energy for concentration for different metals of the periodic table: lead, zinc, niobium, tantalum, and platinum group metals (palladium, platinum, osmium, iridium, rhodium, and ruthenium). This calculation involves different stages of the beneficiation process, such as comminution, concentration, and refining.

- Analyze the impact of the rock generated in a treatment unit of a mine according to the metal obtained, as well as the amount of water and chemicals derived from the refining process.

- Estimate and calculate a viable extraction limit for the metals analyzed in the thesis, considering the best available technology and the feasibility of the process.

- Conduct a sensitivity analysis using different values for the cost allocation in common processes.

- Perform an economic assessment of the extracted metals and compare the extraction costs with the current market prices of the metals.

- Identify secondary resources as a source of metals, such as urban mining or extracting minerals from tailings.

- Analyze the viability in economic and chemical input terms of the new sources of extraction, as well as the metal output in the flowsheet.

- Establish a methodology to incentivize the collection of waste of electric and electronic equipment.

1.2. Thesis structure

This thesis is a compilation of five scientific publications, and several contributions to international conferences. All works are centered around a common line of research, collectively focusing on the potential supply problems in the future when demand increases and ore grades decline. Furthermore, this thesis aims to propose solutions and alternatives to address future challenges related to mineral availability.

A brief history of the mining industry will be explained, as well as the evolution of the sector. A research has been carried out to examine the current state of mines, including an evaluation of the methodologies used in various studies and the projected future outcomes based on the findings of previous authors. The increase of demand of metals will be explained and the main industries and sectors requiring metals due to their importance in their development. This will be addressed in Chapter 2, where a comparison between resources, reserves and prices for metals will be carried out to understand the critical situation for some metals. Finally, this research will provide an overview of new extraction sources in an attempt to identify potential solutions for meeting the future demand.

Chapter 3 will largely be an examination of the methodology applied during the investigation. As the extraction and beneficiation process of different metals will be analyzed, the best available technology has been applied for every simulation in this study, which is described in the corresponding sections. To carry out the simulations, a specialized software called HSC will be used. In this way, in this chapter, this software will be introduced and also explained its functionality, and why it is the most suitable to conduct this study. A review of previous works, which form the basis of this thesis, will also be provided. Finally, a detailed description of the methodology used will be supplied to offer transparency and clarity during the calculation process, including the different assumptions that were considered as the study evolved.

The first metals analyzed have been lead and zinc, as they usually occur together. Therefore, a simulation in HSC has been carried out to determine the energy cost of extraction. This is represented in Chapter 4, and it serves as an introduction to the curves used for the different metals analyzed in relation to specific energy. These curves will serve as a basis for estimating future scenarios.

Chapter 5 will focus on the simulation of the extraction of nickel, cobalt and platinum group metals. After stablishing the state of art for every metal, the simulation will be explained. Curves will be obtained for the three group of metals for different ore grades, finishing the chapter with an economic assessment between the energy cost of extraction and market prices.

The next chapter (Chapter 6) will be carried out to simulate the extraction of tantalum and niobium. Similar work to the previous metals will be assessed. However, since reliable data was provided from a real mine in Spain, a deeper study will be carried out to analyze the feasibility to extract metals from tailings. This could be a viable solution due to the concentration of some metals in tailings. Preliminary results will be shown with an economic assessment to highlight the cost of the process.

Chapter 7 focuses on the search of a solution for the depletion of mines. Following this line, this new chapter will explain the problems derived for the high amount of electric and electronic equipment and the metals embodied in them. Therefore, we will develop a proposal to enhance the collection of these devices by offering incentives, taking into account their state and raw material contents assessed through the thermodynamic rarity approach. This approach considers both the physical scarcity of metals in the Earth's crust and the energy required for mining and extraction. In this way, it could be possible to exchange the device for some reward, and proceed to reuse the device, their components, or send it to a metallurgy plant to recover the metals.

Chapter 8 will outline the various conclusions reached during the thesis, summarizing the results and highlighting the most significant gains obtained during the investigation. Furthermore, the objectives initially described in the research will be reviewed to determine whether they have been achieved or not. Finally, some limitations and considerations will be commented to understand the restrictions found during the development of the thesis. Moreover, a few perspectives for future works will be explained.

Chapter 2. Past, present and future of mines. State of the art

2.1. Introduction to the chapter

To gain a greater context and an understanding of the current state of the mining sector, a review has been carried out. This review begins with a brief historical overview of the mining industry, examining industrial development from the past to present day. Furthermore, it explores the potential future challenges that the mining industry could face in the coming years if the current trends continue under business-as-usual (BAU) conditions. Finally, this review addresses potential barriers that the mining industry may face and outlines the environmental issues and concerns associated with this sector, both in terms of the planet and of society.

2.2. Evolution of the mining sector

Mineral extraction and processing have historically played a vital role in human advancement [1]. The earliest record of rock extraction dates back approximately 40,000 years with the extraction of coal. However, significant developments in mining began later when metals in their metallic state, such as copper, gold, silver, and mercury, became available [2]. According to some authors [3], the earliest recorded mining report was collected by Greek authors, Ptolemy, Strabo and Pliny, which reference iron ores in Triano mount. This is documented in the Book of Natural History by the same author.

Early records show mining to be a slow and arduous process, as long and dangerous tunnels had to be dug manually [4]. The ores obtained from the mines were primarily used to manufacture weapons, jewelry or coins [3]. However, such barriers encouraged technological advancement as well as increasing the production of and demand for certain metals, leading to an upsurge in mining production to meet these metal requirements [3]. Consequently, wars were fought around the world in an attempt to acquire as much land as possible. As a result, metals became a significant source of negotiation due to their inherent properties and the multitude of possibilities they offered [5]. For that reason, when a land was conquered, metals such as gold and iron were exploited and sent to the conquering country to enhance its wealth and enable it to pursue new opportunities and challenges [3], [5].

A significant innovation took place in the mining industry during the 17th century when miners started utilizing explosives for rock fragmentation [4], [6]. This methodology enabled miners to mobilize larger quantities of rock more efficiently and safely, resulting in a significant increase in production. Consequently, there was a corresponding rise in the demand for the extracted metal [6]. In the years that followed, mining techniques continued to evolve, incorporating new processes and innovations in mining. These advancements included the introduction of drilling techniques, lifts, and hydraulic jets [7]. The industrial revolution marked a pivotal moment in the mining industry due to the significant increase in demand for coal. The increase was so significant that the amount of coal production rose from 2,7 million tons in the 1700’s to 250 million tons in 1900 [8]. Mining, as an industry, became indispensable at that time. This trend not only occurred with coal, but also with other metals, like gold, indicating the robustness of mining industry. The scale of the mining business was so large that it gave rise to a period known as the "Gold Rush" in the mid-19th century in the United States. During this time, many Chileans and Mexicans, travelled in their droves to California in pursuit of gold and wealth [9].

Some of the techniques used in the modern mining industry were developed in Germany in the early 1950s for low coal veins [10]. The “Energy Crisis” in 1972 triggered an increase in coal production, with the United States possessing the world's largest coal reserves [11]. In turn, Germany and the United Kingdom started to use the modern long wall mining, which facilitated more efficient production in order to meet the growing demand [11].

Evidently, mining is a very important industrial activity, as it not only enables the processing of raw materials in a specific region for the benefit of society but also should contribute to the local social and economic prosperity [12]. For example, new job opportunities arise, not only in the mining company, but in companies who operate in conjunction with the mine. This situation typically leads to the development of new regulations and taxation systems related to the voluntary corporate social responsibility programs of those companies, which can offer various benefits. [13]. Moreover, the establishment of a mine brings new infrastructure and services to the community, which often benefits local people. For example, the construction of roads, new buildings, shops, and the implementation of high-speed internet cables and public services are all benefits that can be utilized by local residents and workers [14]. Additionally, the wealth generated provides a tourism opportunity for people visiting the mine, creating a positive impact on existing livelihoods [15].

However, when a large scale mine is located in a community, local people are not always consulted over whether they are interested in that mine or prefer to preserve the natural wealth of that site [16]. The community experiences adverse consequences as a result of economic risks, stemming from factors such as reliance on local resources, financial collapse, and worldwide repercussions [17]. Moreover, there is a perception of safety and security risks, and psychological impacts, as reported in the International Institute for Environment and Development (IIED). Entire communities and villages are displaced and resettled in new areas due to the exploitation of this industry, resulting in detrimental effects like the loss of homes and lands, as well as relocation to places with insufficient resources [18].

Another important aspect to consider are the social effects that come with a mine closure. As employment decreases, so does the wealth of the area where the mine was located, leaving behind a high rate of unemployed people. Additionally, several authors [19]–[21] have outlined how a mine closure affects women and gender relations in a community. Mining is widely viewed as a male dominated industry, with the ratio of female workers remaining significantly low [22]. Historically, women did not work in mines due to harsh physical conditions, lack of interest, and family barriers in regards to conciliation [23]. The result of unemployment following a mine closure is disproportionately felt by men [24].

In order to regulate the impacts, the International Association for Impact Assessment (IAIA), as well as scholars working in the field, developed a new approach in 2010s, designed to mitigate the negative effects of the mining industry, while trying to maximize the positive impacts [25], [26]. This methodology is called Social Impact Management Plant (SIMP) and is based both on the previous impacts of the baseline situation and on an evaluation of developing alternatives and management strategies aimed at eliminating or reducing negative impacts at every stage, including the planning phase, exploitation, and closure [17].

In short, mining as an industry has undergone significant changes due to various factors that have forced it to adapt [27], [28]:

- Safety: Mining is a very dangerous job; however, improved technology and the implementation of security measures has made it safer.
- Job development: It is not only miners who work on the beneficiation process of a metal, many different professionals in a variety of sectors are also involved.
- New regulations: The mining industry has had to adapt to the current environment regulations, which consider several aspects such as land reclamation, pollution, water, and soil among others.

These evolving needs, along with business expansion and increased demand for metals, have resulted in the search for more mineral deposits and rising costs [29], not always reflected in commodity prices, as explained in the next section.

2.3. Resources, reserves, and prices of metals

According to the Australasian Institute of Mining and Metallurgy (AusiMM), mineral resources can be assessed through geoscientific studies and information provided by other disciplines. They can be defined as the quantity of a certain mineral which can be found in the Earth's crust [30]. On the other side, the United States Geological Survey (USGS) defines mineral resources as a concentration of naturally occurring solid, liquid, or gaseous material in or on the Earth's crust in such form and amount that economic extraction of a commodity from the concentration is currently or potentially feasible [31].

On the flip side, the assessment of reserves necessitates the consideration of certain specific factors that directly impact the extraction process, including the technology employed and the prevailing market price. As such, mineral reserves constitute the amount of a certain mineral that is viable to extract, technically and economically [32]. Additionally, reserves can be divided into inferred reserves and inferred marginal reserves, depending on the parameters of economic producibility [33].

Since metals will be needed in the future, more extraction will also be needed. Therefore, extracting metals from mines can affect the resources and reserves. Figure 2-1 illustrates the yearly comparison between production and reserves for copper and cobalt over the past 25 years.

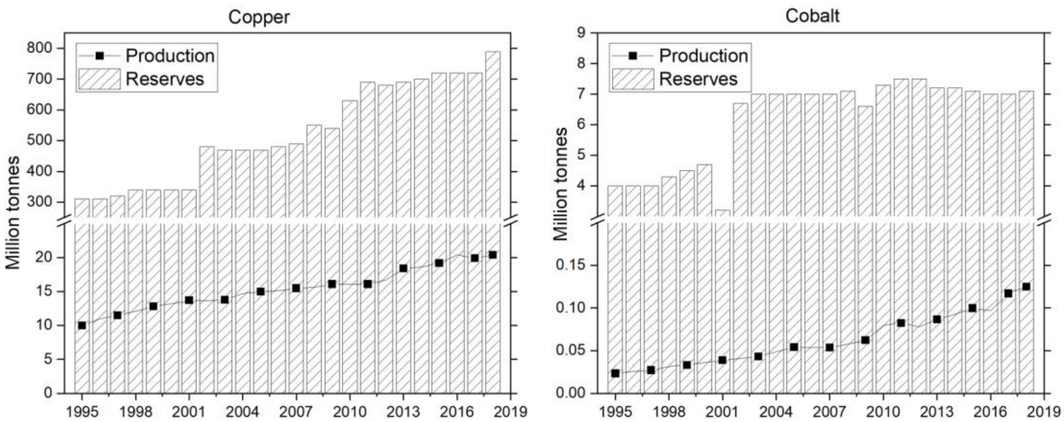


Figure 2-1. Reserves vs Production for copper and cobalt in the last 25 years in million tons (adapted from Minerals yearbook of the USGS).

Copper reserves increased at a faster rate during this period compared to production. In 1995, copper reserves stood at 300 million tons, while in 2018, they reached nearly 900 million tons, marking an increase of almost 300%. In contrast, production in 1995 was 10 million tons, and by 2018, it had doubled, reaching 20 million tons. The situation differs for cobalt; during the same period, reserves increased by 75%, remaining constant for the last 15 years, while production multiplied fivefold.

Metals are not infinite, which means that reserves could eventually reach the maximum amount of a certain mineral available for extraction. In such a scenario, a situation similar to what has occurred with cobalt over the last 15 years could arise: production of cobalt increased while reserves remained constant. Consequently, the impact on reserves would increase exponentially unless additional reserves become available for extraction.

It can be argued that the impact could negatively influence the market prices of the different metals. However, research has shown that price increases can also be influenced by external factors. As such, six metals have been analyzed, as illustrated in Figure 2-2, which compare resources, reserves, and prices (adjusted to the consumer price index (CPI)) for the last 30 years. Resources are highly speculative. As a result, estimations have been modified over time, which is why it appears that resources seem to increase. On the other hand, reserves have been increasing linearly during this time. However, commodity prices are not related to these factors, which can be seen in the examples of copper and cobalt.

Over the last 30 years, copper has been highly representative in understanding changes in these parameters. As illustrated, the availability of resources decreased by more than 40% in 2002, followed by a significant increase after 2012, when resources multiplied by almost four. During this period, the price of copper has experienced several fluctuations, with a difference of 20 times between the lowest and highest prices. However, the availability reserves have been increasing linearly.

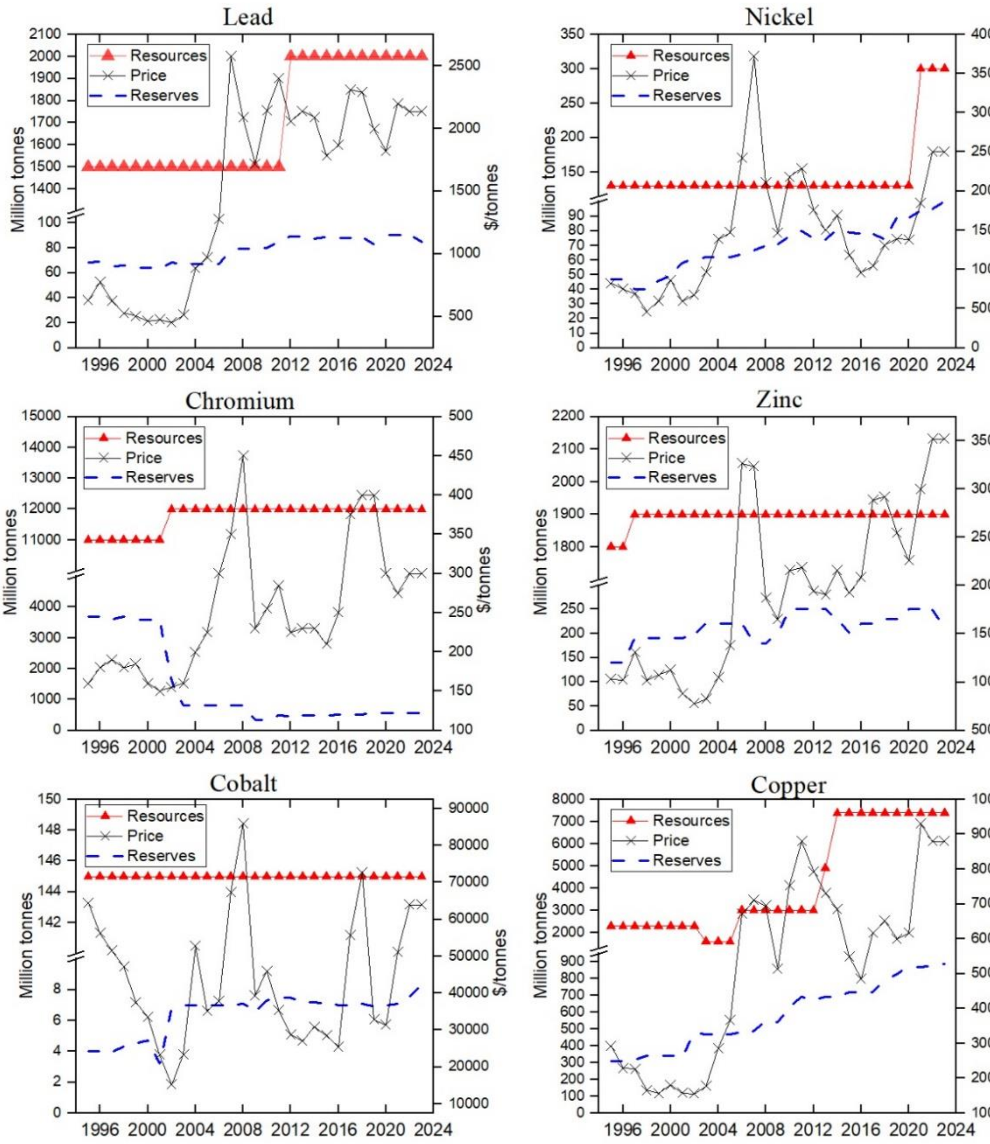


Figure 2-2. Evolution of reserves, resources and updated prices in the last 30 years (adapted from several Minerals yearbook of the USGS).

The case of cobalt is different, as resources remained constant for the timeframe studied. There was an important increase of reserves in 2002. This coincides with a reduction of the price the following year, although it is worth noting that this decrease may also be attributed to other contributing factors. However, as explained above, reserves have remained at an almost constant level (increasing around 1% per year as average). Since then, and as it is possible to see, there have been fluctuations in prices, with considerable peaks occurring in 2008 and 2018, and producing the second lowest price (2016) within the timeframe studied.

It is a fact that various factors can influence the mining sector, which may not have a direct connection to the industry. While these factors encompass costs and mineral extraction from mines [34], [35], two fundamental aspects linked to the mining industry are the commodity's location and the principles of supply and demand. The initial challenge arises from the fact that certain minerals are located in a limited number of countries, granting the producers the ability to dictate the terms of their exploitation [36]. The latter arises from the demand for specific minerals. When multiple buyers seek these minerals, the final price can be established through an auction process in which participants compete by making higher bids. Consequently, the greater the demand, the higher the price [37].

Geo-politics is unquestionably an external factor that significantly influences the challenges associated with mining. Political situations can affect the final price and production of a mineral as illustrated in Figure 2-3 which presents historical data for the price of different metals now over a 30 year timeframe [38]. There is a clear trend among all rising prices, the exception being aluminium which decreases slightly. The graph also shows a fluctuation in prices through the decades, highlighting several peaks during those years as is evident in the example of cobalt. Cobalt experiences a definite peak in 1978, when there was a strong cobalt demand resulting in the copper-cobalt region in Zaire being invaded [39]. Another peak more recently was witnessed in 2008, when there was a deficit of cobalt due to political instability in the Democratic Republic of Congo [39]. As a direct result of daily metal extraction, the concentration and availability of such metals is being reduced and therefore impacting their price. Nevertheless, the various causes for the peaks represented in Figure 2-3, shows that the price of the commodities is not related to the beneficiation process and its costs, but rather from external factors.

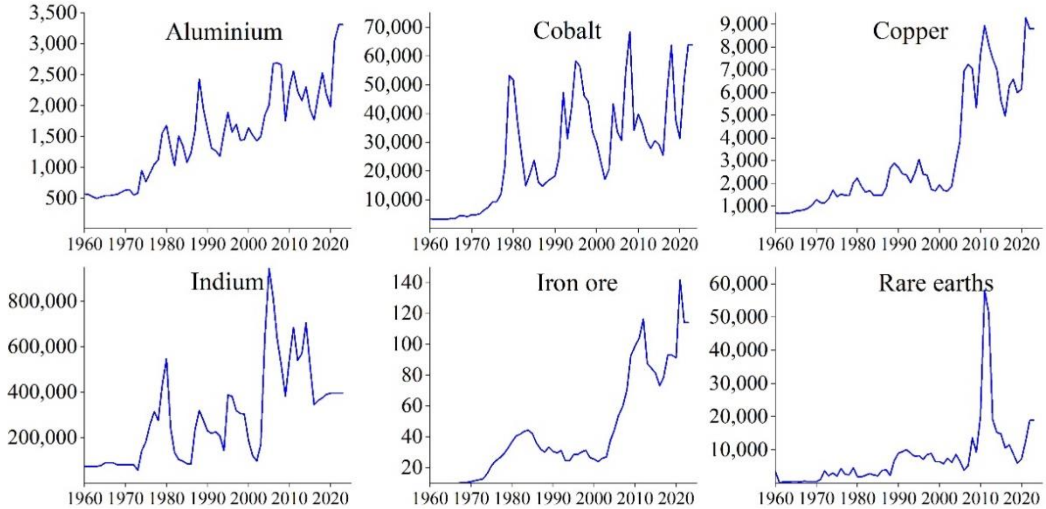


Figure 2-3. Historical price data for different metals (Al, Co, Cu, In, Fe, REEs) (adjusted to the CPI) [$/ton] [38].

During the last two decades, the metals showcased their lowest prices around the year 2000. This phenomenon can be attributed to the simultaneous surge in the global economy, particularly driven by the rapid expansion of electronic trading, and the remarkable growth of the Chinese economy, which was experiencing an annual growth rate of approximately 10%. The influential role of China in the metal sector during that period may provide a plausible explanation for the observed price dynamics [40]. A notable spike has been observed in the years 2007 – 2008 and 2021 in the metals shown in Figure 2-2 and Figure 2-3. This can be explained by the global economic recession in 2007 and by the Covid-19 pandemic in 2020 which affected all sectors [41]. Furthermore, the Ukraine war directly affected the price of nickel. In a timeframe of days, its price more than doubled and has yet to return to pre-war prices [42].

In summary, historical statistics do not clearly indicate that market prices directly correlate with production costs. However, to ensure the profitability of mining activities, prices must always be higher than costs. In this respect, a new challenge is on the horizon in mining: the reduction in ore grade that will lead to increased costs, as is explained in the following section.

2.4. The challenge of ore grade decline

Currently, a significant challenge facing the mining sector is the reduction of ore grade. Ore is defined as a deposit of one or more valuable minerals in the Earth's crust. It is a solid substance containing minerals from which metals can be recovered using a variety of procedures [43]. Therefore, it is possible to say that ore grade is the amount (or share) of a certain mineral in a rock [43]. In this respect, the reduction of ore grade in mines refers to the decline in the quality of a specific ore that is being extracted. A result of this is a clear reduction of the mineral extracted in the deposit exploited. For that reason, it is crucial to ascertain the cut-off grade for minerals. The cut-off grade is defined as the minimum grade that is required in a given mass of rock to classify it as ore [44]. This parameter is crucial because a lower cut-off grade reduces material wastage, but it can also result in slower metal output rates. Conversely, raising this parameter will increase both the volume of waste and the rate of metal production [44].

Some authors have concluded that the ore grade of minerals has decreased over time and this trend is continuing [45], [46]. For example, several authors have carried out analyzes on the evolution of ore grade in relation to copper. Their studies reveal an average reduction of 25% over a ten-year period, spanning from 2003 to 2013 [47]. The reduction of the ore grade is not only shown in the case with copper, but also in several metals that are used in the development of technology, such as gold, zinc and lead [48]–[50]. This decline can be attributed to the current needs of the technological sector of primary raw materials, as Liang et al. explained in their work [51], which characterized the material requirements for low carbon energy technology. This phenomenon is being observed in the long term for copper, zinc, lead, and nickel, while empirical data does not currently show a reduction in the mineral grade in the extraction of iron, aluminum, and manganese [52].

The reduction of ore grades is driving the depletion of some minerals deposits. This depletion is caused by the extraction of the majority of high-grade ore deposits. In this respect, Rotzer et al. [53] state that if lower ore grades must be extracted at a higher cost, the final price of the metal would increase [54], [55].

However, consensus among the authors shows that the concentration in most of mines is much lower than previous years, and minerals must continue to be extracted as they are essential for various industries. For that reason, companies are forced to extract metals from lower-ore grade mines, requiring much more energy and resources to maintain final metal production. Consequently, the operating costs will increase while the benefits mining companies receive decrease, unless prices also increase at a comparable rate.

This situation is fully connected with the environmental impacts of the mining sector, as explained in the next section. If mining companies require more energy to extract minerals (mainly electricity and fossil fuels), more emissions will be released into the atmosphere. Moreover, when the ore grade decreases, a larger volume of rock will be extracted and processed to obtain the same quantity of minerals as would be yielded by a higher ore grade. Therefore, more waste could be generated, and more water could also be contaminated during the process.

2.5. Environmental impacts of the mining industry

The environmental impacts occurring in the mining industry can be classified into 11 major topics [56]: water, land, air and noise pollution, biodiversity, architectural artefacts, deforestation, loss of flora, loss of parks, proliferation of creatures, and landscape destruction.

The impact on water is mainly based on the contamination and scarcity of it. Mines often contain a significant amount of sulfides, which can leach into the water system when water is introduced into the mine. [57]. Even if this water has to be treated before returning it to the system, may end up leading to contamination problems if accidents or leaks occur. Apart from contamination by sulfides, water is also used in the handling and cleaning of the extracted rock, and in the remaining suspended sediments that are not always detected because of their size [58]. Scarcity of this resource is a significant threat to the mining industry, since huge amounts of water are used during the beneficiation process. For example, the amount of water used to extract copper is 12,415 per kg [59]. The United States Environmental Protection Agency (USEPA) reported that 40% of watershed headwaters in Western United States have been contaminated by mining operations [60].

Land impact is referred to the land-based extractive industry. For the mining industry to extract minerals, suitable land in a specific area must be identified. The location must be a natural resource where the extracted material is left as soil mounds leaving the land unsuitable for any other use [56]. As a consequence of this rock extraction, part of it is stored to be added when the mine is closed. In this way, the exploited area is filled in again, allowing these lands to be reused for farming and cultivating plants, etc. [61]. The requirement of land also has significant environmental impacts such as deforestation, loss of flora and fauna.

Furthermore, the mining industry is not only associated with the extraction of the material from Earth, but it also plays a significant role in their transport. Heavy machinery and several facilities are required to treat the extracted rock before transporting it to the next stage of the beneficiation process [62]. Besides, air and noise pollution are linked to the use of heavy machinery and the emissions sent to the atmosphere [63].

Additionally, the mining industry is recognized as one of the largest consumers of energy. According to the Joint Institute Strategic Energy Analysis (JISEA), the mining industry consumes about 38% of total global industry energy use, 15% of the total electricity use, and 11% of the total energy use (in 2012) [64]. Mining energy still strongly relies on fossil fuels, exacerbating the release of greenhouse gases (GHG) to the atmosphere and therefore accelerating climate change. It can therefore be assumed that the mining industry holds a prominent position as one of the most polluting industries on the planet [65].

This industry does not only extract minerals, but also fossil fuels, which are used to generate electricity. Fossil fuels are particularly significant in some countries. This is the case of China, that still mainly relies on the burning of fossil fuels for energy. For instance, in 2017, coal made up 60.4% and 70% of China's energy consumption and primary energy production respectively [66].

As the significance of the mining sector continues to rise, sustainability is becoming increasingly crucial, and innovative approaches must be explored to transform it into a more environmentally friendly industry. Some optimistic forecasts indicate for instance that energy consumption in China's coal mining sector could potentially be reduced by up to 53% by 2050 with energy-saving technologies [66].

An energy transition is therefore necessary in order to limit the extraction and burning of fossil fuels, not only in the mining sector. The emissions released in the atmosphere could be considerably reduced by switching to renewable energies. For this reason, this sector has experienced a significant increase in the last decades, and its growth is expected to continue. The International Agency of Energy (IEA) estimates a total worldwide increase of more than 2,400 GW of wind power by 2030 [67] and more than 5,000 GW of solar technology power [68]. However, this transition to greener technologies has hidden disadvantages, since these technologies require a significant quantity and variety of metals, some of which not easily found on the Earth's crust.

2.6. Raw material requirements for the energy transition

The United Nations Framework Convention on Climate Change (UNFCCC) is the main platform used by different nations from around the world with the shared objective to reduce greenhouse gas emissions (GHG) [69]. The agreement was first reached in 1997, named as The Kyoto Protocol (KP), and came into effect in 2005. Developed nations who were involved agreed to reduce GHG emissions by 5% below their 1990 levels, and established country specific targets depending on individual country goals [70], [71]. However, even if this agreement was a first step in the fight against climate change, it was found to be insufficient, as indicated by the results obtained within the agreed deadline established by the members of the KP [72]. For that reason, there was another important agreement in 2015 in Paris (PA), where again, several industrialized countries agreed not only to reduce their GHG emissions, but also made a firm commitment to maintaining the predicted temperature increase to move below 2ºC above the pre-industrial level, or if possible, limit it to 1.5 ºC [69]. According to some reports from the European Commission (EC) [73], GHG emissions should be cut at least 80% below 1990 if PA was to be accomplished. The three main sectors which utilize the highest energy consumption are industry, transport and heating [74]. In summary, the world must transition to what is commonly referred to as the "green transition". This entails a significant improvement in energy efficiency, a transition to renewable energy sources, or a prioritization of technological advancements to substantially reduce emissions in these sectors [75].

Indeed, the green transition has become an important strategy for sustainable global development and global environmental governance [76]. This transition into a more sustainable society with renewable energies is requiring vast amounts of critical raw materials that are crucial [77]. This is the case of niobium (Nb) or tantalum (Ta), both of which are crucial for renewable energies. Niobium is an essential metal for manufacturing ferroalloys, such as ferroniobium, containing between 60%-70% niobium [78]. It also forms part of the high-strength low alloy (HSLA) steels [79]. However, even if they are included in small quantities on each device, the total amount used at a global scale is considerable. Moreover, their future availability could be dangerously compromised at their primary location as the locations where they are mined are limited [80]. Many countries and institutions consider these minerals to be critical due to their current and future availability, as well as the concentration of their supply. This situation poses a potential risk to many economies [81]–[83].

Other metals that can be named are the so-called Rare Earth Elements (REE). The REEs are a series of seventeen transition metals and they are considered rare due to the scarcity and availability of them in the Earth's crust [84]. Among these metals, Neodymium (Nd) and Dysprosium (Dy) are included, and due to their specific properties, they are used in permanent magnets, making them vital for the development of wind turbines [85]. The presence of these types of metals in wind turbines have been extensively studied by various authors [86]. Studies have determined that for the direct drive model, 650 kg of permanent magnets are required per megawatt (MW) of wind turbine production [87]. Within this total, neodymium accounts for 124 kg/MW, while dysprosium is estimated at 22 kg/MW [88].

However, wind energy is not the only resource affected by the future supply of metals, solar technologies also require a significant amount of metals [89]. Silver and copper in particular, are used for electrical connections, while other metals such as cadmium, indium and gallium are required for the manufacturing of certain types of photovoltaic cells [80]. According to Ortego et al. [90], cumulative material demand in photovoltaic energy technology is projected to increase to over 385 ktons by 2050. Additionally, more than 10,700 ktons of silver, copper, and selenium are expected to see an increase from 2016 to 2050.

Apart from the surge of renewable energy technologies, the number of Electric Vehicles (EV) are expected to increase exponentially in the coming years [91]. Since the advent of the automotive industry, records show high consumption of various types of metals such as iron, aluminium or steel. Although these materials are not considered to be at risk with regards to availability [92], the sector has nevertheless been forced to evolve due to safety and comfortability reasons. Because of this adaption, the automotive industry has become more sophisticated and as a result, has diversified in the types of metals it uses in manufacturing [93], [94]. The European Commission set a target that by 2050 CO_2 emissions should be neutral in Europe. Consequently, road vehicle emissions, which represent 20% of total CO_2 emissions, must be reduced [95]. Therefore, a proposition spearheaded by Europe, and already implemented in some countries like Spain, proposes a ban from 2030 onwards, of the sale of new vehicles that emit more than 123g CO_2 per kilometer. Additionally, it proposes to cease selling vehicles entirely that rely on fossil fuels by 2035 [95]. The consequences of this could be a significant increase in the production of EV in the coming years.

Vehicles in the 21st century not only consist of an engine and wheels, but also include numerous electronic equipment which improves both the quality and security of the vehicle [94]. Electronics are manufactured with various metals that require specific properties for their development. However, due to the trends expected in the coming years, this situation could act as a barrier for developers who require a substantial number of metals. Certain strategic metals like gold and silver, which are used for contacts and welding, as well as indium, find their basic application in the manufacturing of screens and in the infotainment of vehicles [92]. As it is possible to see in Figure 2-4, there are several metals involved in the composition of different vehicles, identifying which are the most used and which could be crucial in the future, not only in the process of manufacturing, but also for the number of vehicles produced every year. Figure 2-4a compares the metal requirement with the global production for different type of vehicles. On the other hand, Figure 2-4b illustrates the weight of type of vehicles, as well as the share of the metals embodied in them [96].

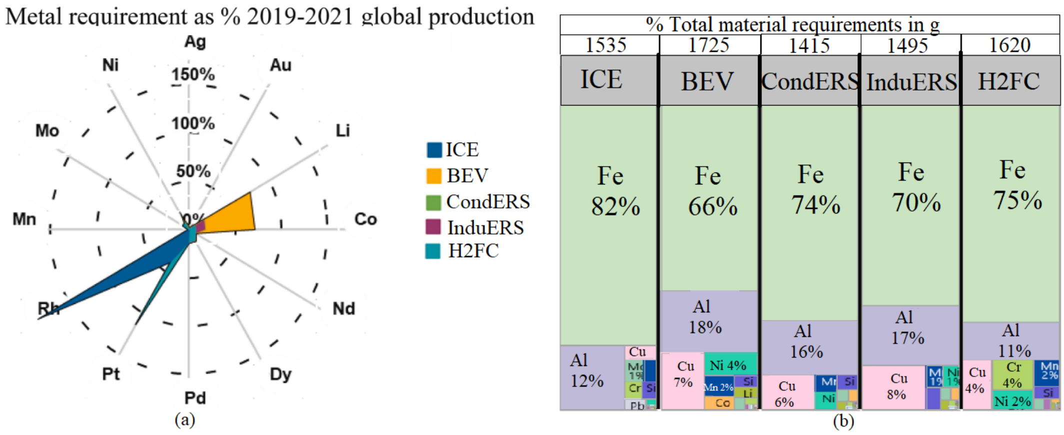


Figure 2-4. Metal requirements embodied in the internal combustion engine (ICE), battery electric vehicles (BEV), battery electric with dynamic charging conductive (condERS), Battery electric with dynamic charging contactless inductive (induERS), and hydrogen fuel cell (H2FC) [96].

Electric vehicles are known for their most critical manufactured component: the battery. As shown in Figure 2-5, the battery system is very complex and it is comprised of several metals [97]. The main disadvantage of this technology is that it is not only using scarce raw materials, but also several kilograms of them in one vehicle. A battery for these vehicles can range from 129 kg up to 734 kg, with an average of almost 350 kg and capacity of almost 50 kWh [98]. This means that an average of almost 11 kg nickel and cobalt, 3.5 kg of lithium, and almost 10 kg of manganese are being used in every vehicle manufactured [97].

This component is essential for the energy transition, as its sustainability may be questionable. Battery manufacturing requires a high volume of energy utilization during the mining process for the metals embodied, significantly impacts reserves, and produces high emissions during its production.

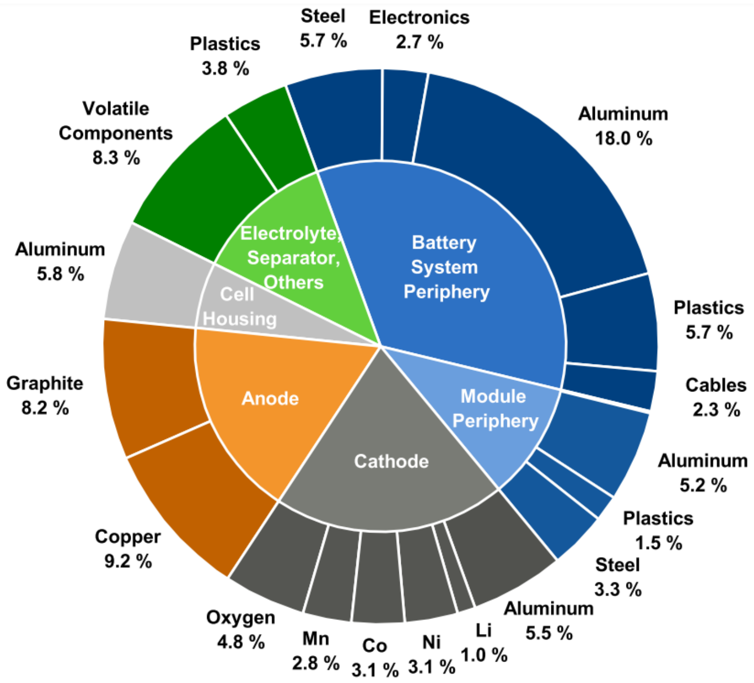


Figure 2-5. Battery system material composition for electric vehicles [97].

2.7. Raw material requirements in Electric and Electronic Equipment

Renewable energies are not the only ones that require vast amounts of raw materials. Digital technologies are also significant consumers of various elements from the periodic table. In this regard, the world has experienced exponential technological advancements, and as it continues to evolve, digital devices have become a permanent fixture in society [99]. The number of connected devices has surged in recent years and an increase of around 3-5% in the production of electric and electronic equipment (EEE) is expected [100]. From around 2 billion devices (primarily personal computers and smartphones) sold in 2000, consumers have driven this number to 22 billion in 2018. According to some estimations, it could even reach 38 billion by 2025 [101].

There are many factors that influence technology advancement such as the needs of the customer, since they demand more efficiency and better experiences. Examples of new technology that has provided for this demand are: Internet of Things (IoT), Machine Learning (ML) or Artificial Intelligence (AI) [99]. Another factor that encouraged technology development is the “Mission Innovation” agreement in Paris in 2015, where global leaders from 20 countries agreed to promote the acceleration of a global clean energy innovation [102].

As previously explained, this agreement accelerated the level of government investment in an attempt to try to produce more clean energy [103]. This agreement was especially present in the electronic and electrical equipment sector (EEE). This has resulted in the EEE sector becoming one of the fastest growing sectors in the world. Technology is more present in every day in society since EEE has made devices more efficient and with better functionalities [104], [105].

However, the advancement of these devices requires the use of more metals, which in turn provide particular properties that allow the manufacturing of more robust, more compact, and more efficient devices [106]–[109]. The penetration of advanced technologies implies using a more significant number and variety of raw materials [90], [110].

2.8. Coupling supply and demand: Raw material criticality

If every device requires this complex assortment of metals to manufacture them, it is reasonable to assume that an increased demand for metals necessitates an increased extraction of metals from mines. According to Calvo et al. [111], the 20th century has been characterized by a drastic increase in global material extraction, a trend which continues to be maintained in this century. An increasing number of metals need to be extracted every year to satisfy the exponential demand, which in turn raises the demand for energy [47], [112].

Technology advancement is not the only element playing an important role in this field. According to the United Nations (UN), the world population could increase to 10.6 billion people in 2050 [113]. Society is requiring more technology every day, which is reflected in an increase of the use of natural resources for their daily lives [114]. The consequence of this growth could drive a higher production and manufacturing of technology devices and therefore, more mineral extraction from mines. This problem is in turn linked to the limited availability of material resources on Earth, some of which are facing or will soon face serious restriction issues when demand exceeds supply [90]. One of these examples is nickel, as it can be seen in Figure 2-6, where the demand could be higher than the production from 2027 onwards, which is likely to be a bottleneck for the availability of this metal.[90].

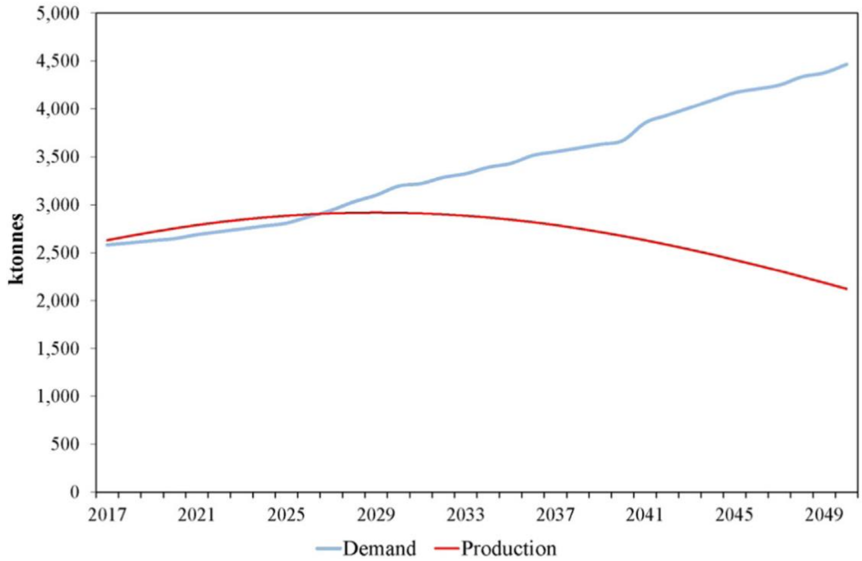


Figure 2-6. Bottleneck calculated for nickel according to the demand and production [90].

The criticality of raw materials has become one of the main concerns for global societies due to the minerals governance versus the transition to a green economy [115]. This is explained for the rapid growth in extracting minerals, since demand projections vary greatly for individual minerals, like a factor of 5-6 for lithium, and a factor of 10-14 for nickel [116]. As of 2022, the United States, the EU, Australia, Japan, and India listed 52 mineral elements as critical. This list is updated in each region periodically, adding or removing critical elements. To assess the situation of materials in the EU, the Raw Materials Initiative (RMI) was launched, with the aim of establishing a list of critical raw materials at the EU level [117]. The materials considered critical are those that hold high economic importance for the EU and pose a significant supply risk.

The first list was released in 2011 and is updated every three years. General information about these lists is collected in Table 2-1, while the critical raw materials (CRM) included in the last report are collected in Table 2-2.

Table 2-1. Information about the different CRM lists published by the EC [117]

Year	Candidates	Critical	%
2011	41	14	34.14
2014	54	20	37.03
2017	78	27	34.61
2020	83	30	36.14
2023	87	34	39.08

Table 2-2. Critical Raw Materials list published by the European Commission [117].

2023 Critical raw materials				
Aluminium	Cobalt	HREE	Niobium	Tantalum
Antimony	Coking coal	Helium	PGMs	Titanium metal
Arsenic	Feldspar	Lithium	Phosphate rock	Tungsten
Barite	Fluorspar	LREE	Phosphorus	Vanadium
Beryllium	Gallium	Magnesium	Scandium	Copper*
Bismuth	Germanium	Manganese	Silicon metal	Nickel*
Boron	Hafnium	Natural Graphite	Strontium	

*Copper and nickel do not meet the CRM thresholds, but are included as Strategic Raw Materials.

As illustrated, the number of CRM included in the most recent list doubles that of the first list published twelve years ago. If this trend continues, it is expected that more metals will be included in any subsequent reports. These lists are key to enabling the European industries to meet the political goals of the EU and also reach the targets of the green and digital transition [117].

The report of the European Commission also mentions the global suppliers of CRM for the EU. It is crucial to anticipate this situation since China is the largest global supplier for the majority of CRMs, such as terbium, dysprosium, cerium, and magnesium, (shares higher than 85%) [117]. In the case of Europe, the main shares come from Poland with a 19% of copper, France with 76% of Hafnium, Finland with 38% of nickel, and Spain with 99% of strontium.

However, recent events like the Ukraine war and global pandemic COVID-19 have highlighted the vulnerability of the EU in regards to metals supply [118], [119]. The supply chain disruption worldwide has forced many companies and industries to cease activities, which has had a significant economic impact for various sectors, such as the automotive industry [120], [121]. To avoid similar future situations in European industries, the European Parliament Research Service (EPRS) developed a list with different goals in order to reduce the current 75% dependency rate the EU has on imports [122]. These actions are collected under the Critical Raw Materials Act. These acts are developed by the European Commission through the regulation of the European Parliament and Council. It is aimed at establishing a framework to ensure a secure and sustainable supply of critical raw materials [123]. In Chapter 5, entitled ‘Sustainability’, section 1, article 25 relates to circularity, and aims to regulate the fostering of recyclability for each Member State. The following measures are collected below:

- Setting benchmarks by 2030 for domestic capacities: setting benchmarks for extraction, processing, recycling, and annual consumption from a single third country.
- Creating secure and resilient supply chains: reducing the administrative burden and also developing national programs for exploring geological resources.
- Supply risk preparedness and mitigation: creating a critical raw material supply chain monitoring and stress-testing.
- Improving sustainability and circularity of critical raw materials on the EU market: setting requirements on recyclability and recycled content. Also establishing rules for the environmental footprint.
- Diversifying the Union's imports of raw materials: promoting the international trade to support global production and ensuring the diversification of supply.

2.9. Satisfying demand through enhanced and sustainable primary production

In order to meet demand, the mining industry faces the need for more extensive mining, as mandated by the Critical Raw Materials Act. However, the industry is currently grappling with various challenging trends that are reshaping its future [27]. Scarcity of resources for certain metals is pushing mining operations toward more remote and deeper locations [37], but this shift brings additional challenges, including declining ore grades and associated social and environmental issues. As a result, the mining industry in the 21st century aims to establish itself as 'sustainable,' striving for technological, economic, social, and environmental viability [28].

A stable supply of raw materials can be secured by resorting to domestic production. However, this is not without challenges, as opposition to the opening of new mines due to concerns over the potential social and environmental consequences act as a major barrier [124], [125]. This is crucial because the growing daily consumption of metals and the subsequent extraction of minerals, indicate that the current state of the industry is far from being sustainable [126]. Furthermore, new mining projects often face significant social pressure as environmental preservation is often preferred over the economic gains that come from the exploitation of soil [127].

Another alternative to enhance primary production is through the reopening of abandoned mines. The long mining tradition has left many abandoned facilities and discarded materials, such as tailings, which are a source of concern. The concentration in abandoned tailings could be higher than in some mines, making them more profitable and viable to extract. In this respect, it could be a solution to avoid the environmental impacts of tailings. Tailings can contain certain elements whose mobility and dispersion may pose an environmental hazard for soils, water, ecosystems, and people [128], [129].

Several trends have been identified to be addressed in the coming years within the mining industry. These include concerns regarding contributions to climate change due to emissions into the atmosphere, as well as the high risk of investment [37]. As a result, some authors have outlined several recommendations that the mining industry should implement in the coming years [126]:

- Social revolution: Acceptance of mining by society and avoiding the concept of NIMBY (Not In My Back Yard). This concept relies on the opposition of people to the implementation of any activity, mining in this case, in a place located next to the neighborhood. Conversely, the communities that do not agree with this implementation recognize the need for this activity and support these projects in other areas.
- Energy revolution: The energy required to extract minerals is increasing due to the ore grade decline. As a consequence, more CO_2 is sent to the atmosphere and therefore, more contamination is being generated.
- Environmental revolution: In the future, mining should be discreet, hidden, and environmentally compatible, to the extent that its presence goes unnoticed. Once closed, there should be no indication that a mine ever existed.
- Education revolution: Education for mining professionals must be improved to involve more technical aspects of the mining industry, such as processes during beneficiation.
- Technology revolution: Innovation is the key for the future of this industry. To achieve this, more efficient machines and substantial investment is vital for any advancement to be achieved.

2.10. Satisfying demand through the recovery of raw materials from waste

One potential solution to preserve the mineral wealth is through recycling, as minerals are limited resources in the Earth's crust. Recycling has been demonstrated to benefit the planet by reducing pollution, conserving resources and energy, and alleviating the strain on landfill space [130], [131]. In that respect, there have been several projects and programs encouraging people to recycle globally [132]. However, although the recycling ratio has improved, these initiatives have failed to make a meaningful impact on the results [133]. An additional solution might center around the concept of urban mining, capitalizing on the vast reservoir of metals concealed within diverse EEE residing in landfills. Exploring the potential for metal recovery from landfills becomes particularly interesting due to the possibility of higher metal concentrations compared to conventional mining sources.

The Joint Research Centre (JRC) published a report in October 2018 outlining recycling indicators based on European Union (EU) flows and material systems analysis data [134]. Since recycling rates can be estimated at different points in the recycling chain, this report provides a differentiation between the rates. The first one is the end-of-life recycling input rate (EOL-RIR), which reflects the total material input into the production system that comes from recycling of post-consumer scrap. The second one is the end-of-life recycling rate (EOL-RR), which reflects the share of a material in waste flows that is actually recycled [134].

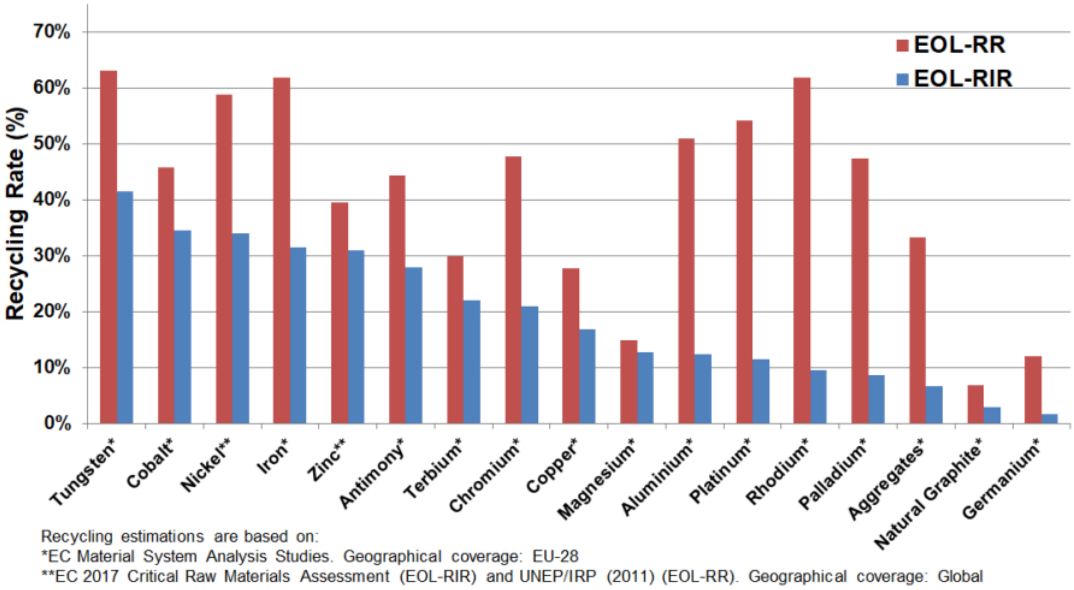


Figure 2-7. Percentages for some metals for EOL-RR and EOL-RIR [134].

In the case of the EU-28, Figure 2-7 illustrates that even though numerous materials found in end-of-life products have an EOL-RR exceeding 40 or 50%, recycling typically makes only a modest contribution to the overall demand for these materials (EOL-RIR). The gap observed in certain metals reflects that, while the recycling processes in Europe exhibit high efficiency in recovering materials from end-of-life products, this does not always correspond to a proportional increase in resource security [134].

Due to the low recycling ratio and the depletion of mineral resources, the concept of the Circular Economy (CE) is being promoted on a global scale. CE is a model of production and consumption, trying to extend the life cycle of products. To that purpose, materials are reused, recycled, repaired and refurbished. In this way, this concept allows the use of waste from one sector and using it as a raw material for another sector, with the aim of reducing the waste to a minimum [135].

Particularly for waste of electric and electronic equipment (WEEEs), there are several directives trying to promote CE in Europe by means of regulating WEEE flows and trying to achieve higher collection rates (35%) [136]. In this region, the first Directive related to electrical and electronic equipment (EEE) was approved in 2002 (Directive 2002/96/CE), recognizing the responsibility of producers once the product becomes a waste. In 2012, the Directive2012/19/EU entered into force to try to reduce the environmental impact of WEEE acting through all the different stakeholders involved. Among all the stakeholders, producers have the main responsibility as they should finance at least the collection from collection facilities and the treatment, recovery and disposal of WEEE.

The quantity of WEEE generated has increased considerably in the past few decades due to the rise of new generations of devices and technologies [137]. For instance, 1.5 billion smartphones were sold in 2017 and almost 140 million tablets in 2018 [138], [139]. According to a report of the United Nations Environment Program (UNEP), the world's production of e-waste in 2019 was 50 million tons, 90% of which ends up illegally traded or dumped [140]. The amount of this value is expected to increase and it could reach 120 million tons of e-waste in 2050 [141]. The Global E-waste Monitor Report in 2020 published that 53.6 million metric tons of e-waste was generated in the world in 2019, and only 18% was recycled through the correct channels. Europe was highlighted as being the second largest generator of WEEE per inhabitant with an average of 16.6 kg/inh [142].

Comparing the amount of e-waste generated and recycling data, the problem becomes clear. For this reason, increasing the amount of recycled EEE is one of the key points on which to focus in order to reduce the negative impact that our society has on the environment [143]. The high volume of e-waste poses significant environmental challenges due to its toxic element content and complex designs, making it difficult and expensive to disassemble [125].

The problem is not only the WEEE generated, but also the process carried out to treat them when they are disposed of. There is a large amount of WEEE whose fate is unknown and a portion of this is likely to enter the so-called informal sector [144]. In this way, the collection of e-waste as well as the extraction of valuable metals are carried out without any environmental and health protection against the potential burdens related to the hazardous substances contained in WEEE [145]. During this treatment, there is a risk that toxic emissions could be released into to the atmosphere, potentially posing serious threats for both environment and human health [146]. Currently, although the techniques used in the separation of glass, ferrous and non-ferrous and plastics are operational, they are not optimal and thus, the future for the separation lies in technical advances [147]. For instance, smartphones are treated using pyro-metallurgic processes which can recover copper, gold and PGMs. However, this will result in the loss of gallium and indium tantalum as well as other scarcer metals, which are concentrated in the slags [148]. However, new developments are taking place in an attempt to recover the largest amount of materials as possible, i.e., using hydrometallurgy to recover minor elements [149] or hydrogenation of magnets to recover REE without dismantling hard discs [150]. Therefore, it can be assumed that various recovery technologies are now being adopted, and significant progress is predicted in the coming years by companies that must adhere to environmental standards and regulations. These companies are focusing more on green technologies across their entire supply chain [151].

There are several barriers that can hinder the adoption and implementation of WEEE management. These barriers include: government policies, consumer attitudes, technological gaps, stakeholders role, globalization and economic consideration between the formal and informal sectors [152]. Furthermore, driving this mindset is a prevailing lack of consensus regarding the adverse impact of current human consumption and production methods on environmental well-being, social equality, and long-term economic stability [153]–[155], [156].

2.11. Conclusions

This chapter includes a literature review conducted to provide an overview of the mining industry, spanning from its inception to the present day. The aim is to gather important aspects of this industry to enhance the understanding and necessity of this thesis. Various topics have been addressed, including the history and evolution of mining, the challenge of declining ore grades, environmental and social impacts, and raw material requirements. By exploring these aspects, the context and significance of this industry has become apparent.

The following is a synopsis of the core arguments outlined in this chapter and will serve in the development of this thesis:

- The modern mining industry has undergone significant transformations driven by political and social shifts. The demand for metals is on a relentless upward trajectory, fueled by advancements in technology and society's evolving needs.
- Mineral reserves are generally on the rise. While this may influence metal prices, the relationship is not direct. Market dynamics, political developments, and various events can exert significant influence on the volatility of these prices, irrespective of the available reserves and associated production costs.
- A global decrease in ore grade is becoming evident for many essential minerals such as copper. This will entail a significant increase in production costs, which could jeopardize mining operations.
- The mining industry is associated with many environment issues - water, land, and noise for instance. Mine preparation often involves deforestation and the extensive use of water for mineral washing. Additionally, as ore grades decline, the energy required for mineral extraction increases. This industry heavily depends on fossil fuels, resulting in increased pollution emissions.
- The transition towards sustainability in the mining industry is complex, as numerous factors are at play. However, certain solutions can be pursued, such as enhancing technology for greater efficiency and integrating renewable energy sources to power operations.
- The energy transition is demanding a significant quantity of metals. An illustrative example is the use of 124 kg of neodymium per MW in wind turbines. Europe aims to achieve carbon neutrality by 2050 through the establishment of numerous solar power plants, wind farms or the EV. Consequently, if these expectations are fulfilled, the demand for raw materials in this sector could become critical, particularly due to the reliance on specific metals.
- Another sector that requires a large number of metals is the electric and electronic equipment industry. Although the quantity of metals embodied in each device is relatively small, the cumulative total becomes significant due to the vast number of devices present worldwide.
- Increasing demand requires increased production, but the availability of metals is limited, with declining ore grades. The COVID-19 pandemic and

the Ukraine conflict have exposed vulnerabilities in countries and industries dependent on foreign sources for metals, disrupting the raw material supply chain and causing production stoppages in various global industries. For instance, the European Commission has identified 34 materials at risk of supply shortages and suggested initiatives to prevent future bottlenecks.

- Enhanced and sustainable mining is proposed as a solution. Promoting increased domestic mineral production is crucial to reduce reliance on raw materials from third countries. However, opposition to the opening of new mines, driven by concerns over potential social and environmental consequences, presents a significant barrier.
- Another extraction source is tailings. With ore grades in active mines declining, the concentration of tailings in abandoned mines may be comparable. Therefore, extracting minerals from tailings could prove more economically viable than from currently active mines. Many abandoned mining facilities and discarded materials, like tailings, exist due to a long mining tradition. However, these materials have adverse environmental effects as they often contain hazardous elements that can harm water, soils, ecosystems, and people if dispersed.
- Recycling offers a practical solution since millions of metals from electronic devices and the automotive industry become discarded and lost. Currently, the costly and challenging process of recovering metals from secondary sources discourages such initiatives. However, the growing demand for these elements for the green transition, electronics and other industries, coupled with potential supply shortages due to scarcity and the demanding extraction process, may soon render secondary resource recovery economically viable.

Building upon the historical context and the framework of requirements discussed in this chapter, the subsequent chapter will delve further into the methodology used to analyze energy requirements as a function of ore grade decline and to physically assess raw material contents in WEEE. It will outline the applied methodology and procedures, as well as the software required to carry out the simulations.

Chapter 3. Methodological framework and procedure

3.1. Introduction to the chapter

This chapter will focus on explaining the methodology employed in this thesis. It will begin by outlining the primary objective, followed by a discussion of prior research, highlighting the key distinctions between those studies and the present work. Additionally, the thesis's novelty will be elucidated, with a specific focus on the calculation methods employed to determine energy consumption at each stage of the beneficiation process.

Furthermore, this chapter will introduce the concept of the ore grade limit and its implications when selecting a higher or lower concentration value. Lastly, the specialized software utilized in this thesis, known as HSC Chemistry, will be introduced. This software enjoys global recognition for its efficiency in calculating the beneficiation stages for various minerals.

3.2. State of art and aim of the work

As discussed in the previous chapter, minerals have grown in importance in the 21st century, driving both the clean and digital transformations. This heightened significance leads to the extraction of substantial quantities each year, emphasizing their essential role in modern society. However, this trend also accelerates the depletion of mines, increasing the energy intensity in extraction processes. Consequently, operational costs and increased environmental impacts are expected to rise.

One important objective of this thesis is to determine the evolution of production costs when the ore grade in mines decreases. As we anticipated in the previous chapter, these costs can jeopardize mining activities while also making the recovery of raw materials from tailings or waste from electrical and electronic devices, for example, more competitive.

This work is based on previous theses of this doctoral student's research group, which are briefly described below.

3.2.1. Background

The number of minerals and elements that can be extracted from Earth is limited due to their availability in the crust. As such, the evolution of technology is triggering a demand for certain materials, which are considered critical by many economies, such as REE, gallium or indium. These elements are, in many cases, considerably scarce in the Earth’s crust or have mining and beneficiation processes that require large amounts of energy. Therefore, the criticality of a resource means, according to van Oers et al. [157], that it is scarce and, at the same time, essential for today’s society.

That said, there is no global criteria to evaluate the criticality of mineral commodities. However, through the “Exergoecology” concept, Valero et al. [158] proposed the use of the Second Law of Thermodynamics, particularly exergy analysis, to evaluate mineral resources. To calculate the exergy of any resource, it is necessary to define a reference state, which must be determined by the surrounding environment and can be similar to that of a depleted planet.

Physical hydronomics and physical geonomics are two fields of investigation within exergoecology [158], [159]. On one hand, the former focuses on the exergy degradation of water, while the latter concentrates on mineral resources, emphasizing the importance of mineral concentration in their evaluation. Going deeper into the study of mineral resources, a model of the Earth's continental crust was developed. This model includes the composition and average concentration of the most abundant minerals on Earth, providing the basis for the concept of a depleted state known as Thanatia [160], [161]. Once this state is defined, the thermodynamic characterization of the crust was calculated, requiring data from the 300 minerals analyzed, including Gibbs free energy and entropy [161].

Thanatia represents a state of the Earth where all mineral resources have been extracted and dispersed, and all fossil fuels have been burned [162]. Understanding this depleted state can be a valuable tool. If we know our current position and the rate at which we are approaching depletion, we can determine the best strategies to slow it down.

In this regard, the Hubbert peak model can be applied. This omodel accurately predicted the point at which oil production would peak and subsequently decline [163]. It was also applied to forecast similar data for other fossil fuels such as natural gas and coal. However, applying this model to non-energy mineral resources presents challenges because it involves not only production but also ore grade. This challenge can be resolved using exergy, as this variable includes both composition and concentration [164].

Exergy also allows to physically assess the degradation of the resources involved in a specific process. In this respect, the well-known life cycle assessment methodology, which accounts for the resources used in a given process from cradle to gate or even to grave is relatively straightforward. Initially, it takes into account the energy and materials required for resource extraction. Then, at the end of a product's life, it can either be recycled, ideally reintegrated into the manufacturing process, or sent to landfills. It is at this point, where traditional assessments encounter limitations, attempting to account for them through factors such as energy and materials, impacts on reserves, and current consumption. This challenge can be partially addressed with the concept of 'grave to cradle' [165] through the so-called 'exergy replacement costs' (ERC) [166]. This concept evaluates, in exergy units, the amount of energy required to restore dispersed materials in Thanatia to their original state in the mines. Furthermore, the exergy replacement cost allows for the calculation of the impact of abiotic resources.

3.2.2. Exergy replacement cost

The term 'replacement cost' was initially defined by Botero, and it is determined by multiplying the exergy of a substance by the unit exergy cost [167]. The latter is calculated as the useful energy required to obtain a specific mineral from the mine to its refinement, divided by the minimum exergy needed to perform the same process. Using this methodology, Botero computed costs for various substances. However, it remained challenging to understand how these costs would vary over time and with the reduction of ore grade. This knowledge was essential because the energy required for mineral extraction depends on two parameters: available technology and the ore grade of the exploited deposit.

These effects were analyzed in Dominguez's thesis [168], along with the redefinition of exergy replacement costs. She investigated whether technology had been effective in addressing the issues arising from the reduction of ore grade. The primary finding of her thesis was that costs generally increased over time, indicating that the predominant factor was not technology but concentration. Consequently, new values for exergy unit costs and exergy replacement costs were calculated.

The exergy costs from grave to cradle have been defined as 'Exergy Replacement Costs.' These costs can be regarded as a natural benefit bestowed by nature. Additionally, they represent cost savings since this energy is not needed for mineral extraction since minerals are concentrated in mines rather than dispersed. The process for calculating exergy replacement costs is outlined below.

Equation (3-1) can be used to calculate the exergy required to separate elements, which will be needed to calculate the ERC.

$$b_{ci} = -RT_0\left[lnx_i\frac{(1-x_i)}{x_i}\ln(1-x_i)\right] \tag{3-1}$$

Being b_{ci} the concentration exergy needed to separate an element from a substance. R is the universal gas constant (8.314 kJ/kmol K), T_0 is the temperature of reference, while x_i is the concentration of the given mineral measured in grams of mineral per gram of ore.

The difference between the concentration exergy and the ore grade of the mine is called “Replacement exergy” and it is possible to calculate it through Equation (3-2).

$$\Delta b_{ci} = b_{ci\,(x=x_c)} - b_{ci\,(x=x_m)} \tag{3-2}$$

Being Δb_{ci} the “Replacement exergy”, x_c the concentration of a certain mineral in Thanatia and x_m the ore grade of a certain mineral in a mine. Additionally, exergies must be multiplied by a K factor which is constant. This factor is defined as the ratio between the total exergy required to extract a mineral from a mine and the minimum exergy to carry out the same process. Equation (3-3) summarizes how can it be calculated.

$$K = \frac{E_{Real\_process}}{\Delta b_{mineral}} \tag{3-3}$$

With all the data obtained, it is possible to calculate the ERC through Equation (3-4).

$$ERC = K \cdot \Delta b_{ci} \tag{3-4}$$

The calculation of ERC was calculated by studying the behavior of specific metals over a certain period of time, utilizing available data for those metals. Valero et al. [166] studied the energy consumption as a function of the ore grade for different commodities. In the study, they found restrictions due to the lack of empirical data in the bibliography, and therefore, the authors proposed the following general expression for the exponential curve applied to estimate the energy consumption as a function of the ore grade (see Equation (3-5)):

$$E_{(X_m)} = A \cdot X_m^{-0.5} \qquad (3\text{-}5)$$

Where $E_{(Xm)}$ is the energy for the concentration and extraction of minerals at the ore grade (X_m), and the factor A is determined for each mineral with empirical data from existing mines. With this equation, it is possible to have a first assessment of $E_{Real\_process}$ in Equation (3-3) and therefore of K, when the concentration reaches that of Thanatia.

The concept of exergy replacement cost serves as an indicator of how humanity is degrading its mineral capital. This constituted the central focus of Calvo's thesis [169]. Through exergy analysis, it becomes evident that fossil fuels and non-industrial minerals carry greater relative significance. Consequently, exergy emerges as a powerful tool for resource management, with exergy replacement costs offering substantial utility in enhancing resource management practices. One of the primary findings of her thesis was the high dependence of European countries on scarce minerals, while Latin-American countries primarily export these types of substances.

3.2.3. The concept of thermodynamic rarity

In addition to assessing the degradation of mineral wealth through ERC, it is crucial to consider also the 'grave to gate' process, which can be rigorously accounted for through the embodied exergy. This is defined as an actual cost within the beneficiation process, encompassing activities such as ore handling, extraction, concentration, and refining. The combination of Exergy Replacement Costs (ERC) and embodied exergy is referred to as "thermodynamic rarity" ($TheRy$ and it is calculated as shown in Equation (3-6).

$$TheRy = ERC_i(grave - cradle) + Embodied\ exergy_i(cradle - gate) \qquad (3\text{-}6)$$

Thermodynamic rarity serves as an indicator of the physical scarcity of minerals. As illustrated in Figure 3-1, extraction costs increase exponentially as ore grades decrease. Therefore, higher concentrations result in lower embodied exergy, as represented in the green area of the figure. Conversely, as concentrations decrease and embodied exergy increases, we approach a point where it could become feasible to extract minerals from landfills (yellow area). Once mines are depleted, we reach a state known as Thanatia. At this point, there are no replacement costs, while the embodied exergy reaches its maximum.

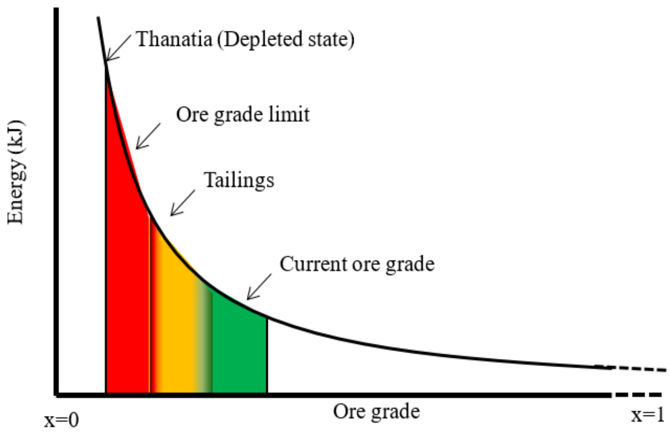


Figure 3-1. Energy requirement from the beneficiation process of a certain mineral when the ore grade decreases [170].

If technology remains unchanged, the thermodynamic rarity of a mineral will remain constant over time, as it depends on the initial and final states, Thanatia, and the quality of the resource. On the other hand, if there are improvements in the beneficiation process, the thermodynamic rarity will decrease due to lower exergy extraction costs. It can be assumed that technology efficiency will improve in the coming years and more efficient units and devices with less metal content will be developed [151].

Table 3-1 shows the thermodynamic rarity values calculated by Valero et al. [170] and updated later by Calvo [169] for several metals, considering state of the art technology.

Table 3-1. Thermodynamic rarity values of different metals [GJ/t] [169].

Element	Embodied Exergy	ERC	Thermodynamic Rarity
Aluminum (Al)	54	627	682
Antimony (Sb)	13	474	488
Arsenic (As)	28	400	428
Barite (Ba)	1	38	39
Beryllium (Be)	457	253	710
Bismuth (Bi)	56	489	546
Cadmium (Cd)	542	5,898	6,441
Cerium (Ce)	523	97	620
Chromium (Cr)	36	5	41
Cobalt (Co)	138	10,872	11,010
Copper (Cu)	57	292	348
Fluorite (F)	1	183	184
Gadolinium (Gd)	3,607	478	4,085
Gallium (Ga)	610,000	144,828	754,828
Germanium (Ge)	498	23,749	24,247
Gold (Au)	110,057	553,250	663,307
Hafnium (Hf)	11,183	21,814	32,997
Indium (In)	3,320	360,598	363,917
Iron (Fe)	14	18	32
Lanthanum (La)	297	39	336
Lead (Pb)	4	37	41
Lithium (Li)	433	546	978
Manganese (Mn)	58	16	73
Mercury (Hg)	409	28,298	28,707
Molybdenum (Mo)	148	908	1,056
Neodymium (Nd)	592	78	670
Nickel (Ni)	115	761	877
Niobium (Nb)	360	4,422	4,782
Palladium (Pd)	583,333	8,983,377	9,566,710
PGMs (average)	175,000	2,695,013	2,870,013
Platinum (Pt)	291,667	4,491,688	4,783,355

Potassium (K)	2	665	667
Praseodymium (Pr)	296	577	873
REE	384	348	733
Rhenium (Re)	156	102,931	103,087
Selenium (Se)	589,405	2,235,699	2,825,104
Silicon (Si)	77	1	77
Silver (Ag)	1,566	7,371	8,938
Sodium (Na)	41	17	58
Strontium (Sr)	72	4	76
Tantalum (Ta)	3,091	482,828	485,919
Tellurium (Te)	589,405	2,235,699	2,825,104
Thallium (Tl)	4,337	43,453	47,790
Tin (Sn)	27	426	453
Titanium (Ti)	258	9	266
Uranium (U)	189	901	1,090
Vanadium (Va)	517	1,055	1,572
Wolfram (W)	594	7,429	8,023
Yttrium (Y)	1,198	159	1,357
Zinc (Zn)	56	1,627	1,683
Zirconium (Zr)	1,372	654	2,026

Despite the limitations of the method, as described in the following section, the thermodynamic rarity values in Table 3-1 serve as an indicator of the physical quality of resources and enable their classification based on their scarcity in the Earth's crust and the energy intensity required for their extraction. Hence, this thesis will utilize these values to ascertain the physical wealth contained within the metals of WEEE, as elaborated in Chapter 7.

3.2.4. Update and new methods to calculate ERC

As it was previously mentioned, ERC was calculated with the average concentration in mines for every mineral. Despite this data coming from a literature review, the reference was published more than 20 years ago, in 2003 [171], [172]. This means that the average concentration in mines has not been updated to current values, which are likely to be lower according to some authors [47]. According to this research, it is highly likely that the values obtained using similar methods today would be different, since the concentration for some minerals has decreased since the early 2000’s.

The concentration is essential for the calculation of the ERC, since this method considers the geological situation of a particular mineral. Nevertheless, the individual consideration of mineral processing and the various methods required to extract and refine minerals into metals was not taken into account. This is an important point to highlight from a metallurgical perspective, as the effort required to refine Platinum Group Metals (PGMs) is not the same as that needed for lead, for instance. This idea is also reflected in the comminution process or in the concentration stage, where concentrated minerals would require less energy to obtain the desired concentration.

Thus, the estimation conducted using this methodology does not account for technological advancements. Due to the inherent uncertainty associated with such advancements, it is challenging to ascertain the specific nature or timing of their materialization.

In this respect, the software HSC Chemistry (which will be explained at the end of this chapter) has made it possible to simulate the extraction of certain elements and analyze the energy behavior as ore grades decrease. This not only allows for more accurate calculations of thermodynamic rarity but also enables the simulation of the expected environmental impact for low ore grades. This formed the basis of Palacio's thesis, in which he simulated the extraction processes of three metals: gold, iron, and copper [173]. One of his key findings was a significant increase in thermodynamic rarity. When comparing these values with previously calculated ERCs, he found them to be two orders of magnitude higher, suggesting that we may be in a more challenging situation than previously believed.

3.3. New perspective of metal extraction

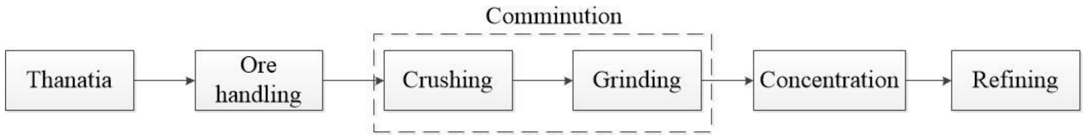
The research conducted in this study builds upon prior works, employing a consistent methodology to analyze the depletion of mineral deposits with a shared objective. Despite the presence of the thermodynamic rarity approach in this and Palacio's thesis [173], there are certain variations that are worth highlighting to fully comprehend the results obtained and the reasoning behind their incorporation in this study.

The calculations followed in Palacio's thesis are very similar as those applied in this study. Energy cost associated to the extraction of minerals in different stages of the beneficiation process were calculated. In the comminution stage, not only was a circuit design been formulated, but also a calculation of the energy needed in every unit. Likewise, during the flotation stage, the number of units needed to achieve a specific concentration at the end of the process was carried out. Since the future of mines and their behaviors are assessed, these calculations were also carried out for various ore grades.

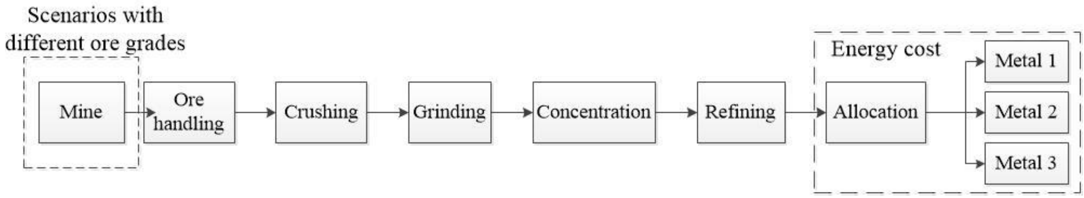
There are two main differences in the methodology applied between the thesis of Palacios [173] and this work, and they are stated below:

1. Different reference state
2. Extraction of minerals as by-products

In previous works, the reference used was Thanatia. As previously explained, Thanatia represents a hypothetical reference state where minerals are completely dispersed. In this regard, the metals are uniformly distributed or dispersed throughout the crust. Therefore, the ore grade used in Palacio's work was set at Thanatia's concentration. The calculation process is depicted in Figure 3-2a, which outlines the steps followed in his study. Starting from a very low initial ore grade, the values are gradually increased until reaching the average values currently found in mines. This directly affects the amount needed to recover minerals. Since the ore grade is very low, a large amount of rock is needed in order to recover an adequate amount of metal in its pure form.



(a)



(b)

Figure 3-2. Comparison between the different processes. On the top is defined the process that Palacios applied in his thesis, with Thanatia as a starting point. On the bottom, it is the process applied in this thesis, applying current ore grades at the beginning and then reducing it until reaching low ore grades

In contrast, the calculation procedure employed in this study differs. As illustrated in Figure 3-2b the initial ore grade is derived from a standard modern-day mine. Using this as a starting point, the ore grade is gradually reduced until it reaches very low values, demonstrating the decreasing trend in ore grade over time. However, Thanatia does not serve as the final source of recoverable minerals. Instead, an ore grade is sought and calculated to determine the energy cost associated with extracting minerals from specific concentrations. The primary advantage of this distinct calculation method is that it aids in assessing the feasibility and energy requirements of extracting minerals from various ore grades. Furthermore, while Thanatia is a hypothetical state from which no minerals can be realistically recovered, this study addresses real situations that could potentially arise in the future.

Another distinction in this study is its basis on the number of different metals extracted. While Palacios analyzed the extraction of individual metals such as iron, gold, and copper [174]–[176], this work centers on the extraction of both primary and companion metals. This approach is preferred because certain groups of metals naturally occur together and can even be extracted from the same mineral, suggesting that real mining operations are not designed solely for extracting a single metal. Extracting only one metal would not be economically viable. Instead, mines are designed to extract multiple metals, contingent on the ore grade of the metals found in the deposits. This approach facilitates a more efficient and cost-effective extraction process.

Consequently, Palacios analyzed the energy cost of extracting a single metal, whereas in this case, the energy cost has been apportioned among the extracted metals. This distinction is substantial and critical, as cost allocation is not fixed but can vary depending on various factors and interests.

3.4. Allocation

Mines are not solely designed for the extraction of a single metal, but rather for the extraction of multiple metals to ensure the economic viability of the deposit. When extracting various minerals to produce multiple metals from the same deposit, the energy cost of extraction must be allocated among all the metals obtained. However, there is no consensus regarding this allocation, as it depends on several factors, such as metal production, mine feasibility, and metal abundance. Nevertheless, this allocation is crucial when assessing minerals, as the final values could vary significantly depending on the chosen cost allocation.

Accordingly, different cost allocations have been reviewed in this thesis to select the most accurate. Hence, this analysis will compare different types of cost allocation systems, using metal market prices, data from the Ecoinvent database, and through the thermodynamic rarity indicator explained before.

The initial allocation is determined using the average metal prices from 2010 to 2020, in addition to the production data, as depicted in Equation (3-7).

$$Allocation = \frac{P_i \ x \ M_i}{\Sigma_{i=1}^{n} \ (P_i \ x \ M_i)} \tag{3-7}$$

In this allocation, P_i represents the market price, and M_i represents the mine extraction for each metal. This allocation is computed by multiplying the annual production of each metal by the average price mentioned. Subsequently, the obtained result is divided by the sum of the productions of all extracted metals, yielding the share of each of them. Depending on the chosen year, these percentages may vary, as metal prices can be highly volatile.

Another option for cost allocation is to obtain values from bibliography, in this case from Ecoinvent database [177]. This allocation is based on the energy applied in the beneficiation process, as well as the metal produced.

The last cost allocation applied has been undertaken considering the thermodynamic rarity values of these metals, as explained in section 3.2.3 and reported in Table 3-1 [112]. In order to obtain the allocation factor in this case, it is necessary to multiply the annual production of every metal extracted by their thermodynamic rarity value.

One could assume that a price-based approach would also allocate more weight to scarcer materials. However, price is volatile and depends on many factors alien to the physical reality of the material itself, and it cannot be considered as a universal numeraire. On the other hand, using a thermodynamic rarity approach, the weight of every material is strictly based on physical aspects of the resource and is therefore stable and universal. Moreover, as well as the price-based approach, it reflects the social perception of "value". Therefore, thermodynamic rarity allows assigning numerical values to measure the availability of scarcer minerals such as platinum, niobium or gold compared to other minerals with higher availability such as silicon, iron or lead.

3.5. Limit of extraction

No consensus has been reached regarding the minimum value of ore grade required for mineral extraction analysis. As future assessments of mine depletion will rely on this value, this issue could be crucial for such calculations. However, many authors approach this situation from different perspectives, as discussed below.

Rotzer et al. [53], West [55], and Norgate et al. [178] have conducted studies to determine the limit of ore grade required for mineral extraction. West argues for a scenario without restrictions on extraction in the future, as the depletion of mines can be mitigated through dilution [55]. Emphasis is instead placed on the importance of technological advancements to ensure economic extraction. Conversely, Rotzer et al. suggests that the challenge lies in the cost implications associated with very low ore grades, as the energy requirements and in turn, the price, would increase [53].

On the other hand, Prior et al.[179], Dones et al.[180], and Norgate et al. [181] have developed various models to identify the minimum ore grade for extracting metals. Some findings suggest a limit of $5x10^{-5}$ wt-% as the ore grade threshold [182]. This threshold is lower than what production costs could exceed the value of the ore, if the most advanced currently available technologies are considered [183]. Although mines with very low ore grades close to 0 wt-% exist, they are not economically viable [179]. Moreover, the same authors demonstrate that lower concentrations result in reduced recovery yields [184], which would require longer processing times as the ore grade decreases [179]–[181].

This study has been conducted using a model that sets an extraction limit. This choice was made in response to the uncertainty regarding potential future technological advancements.

To analyze the specific energy required for concentrating depleted mines, we have examined two extraction limits. Firstly, the Ultimate Recoverable Resources (URR) with a concentration of $5x10^{-5}$ wt-%. This concentration was proposed by Sverdrup et al. [182] and is based on maximum production rates, following the Hubbert peak model, which is a concept that predicts the point at which the production of a finite resource, such as oil, will reach its maximum point and begin to decline. Secondly, we introduce an ore grade limit called the Limit of Recovery (LOR). The LOR is determined by the energy needed to extract one ton of PGMs from tailings, which serves as the maximum available energy for extracting any metal. PGMs have been chosen because they have the lowest concentration among metals, even lower than gold. This decision was made considering the concentration of PGMs in tailings, sourced from the literature at $2.4x10^{-6}$ wt-% [185]. Subsequent chapters will demonstrate that while this concentration is extremely low, it is technologically feasible but not economically viable due to the high extraction costs.

3.6. Technology applied and model explanation

It is expected that technology continues to develop in the coming years, which would allow the mining industry to continue improving its processes. However, it should be noted that this is a hypothetical situation since the future development of technology cannot be confirmed with certainty. Several variables can potentially impact both the investigation and the manufacturing of the expected technology.

The best available technology has been applied for every simulation in this study. Applying this approach, the extraction of both lead and zinc from the same mineral has been analyzed, with the separation occurring during the flotation process [186], [187]. Moreover, tantalum and niobium are separated through metallurgy processes [188], [189], while nickel, cobalt and PGMs are extracted as by-products from nickel sulfide ores [185], [190]. Therefore, if there are improvements in the technolocy used for extraction, it is likely that this could affect the final results obtained for the energy extraction. Nevertheless, the aim of the work is calculating an estimation of the behavior of a particular mine to understand the order of magnitude that will be needed in the future.

The technology used during the beneficiation process is applied in four main stages: comminution, flotation, refining and ore handling, all of which are briefly explained next.

3.6.1. Ore handling

Ore handling considers the processes of transportation and management involved in moving the extracted ore from the deposit location to the processing facilities. This includes activities like storage, crushing and washing the ore on route or during different stages through the beneficiation process [188]. Even though ore handling does not involve the treatment of the mineral itself, it plays a crucial role in mining operations with regards to minimizing costs. When a mineral is extracted from a mine, large quantities of rock need to be transported from the mine to the facilities to process the ore. The transportation is primarily carried out by trucks, and to a lesser extent, by conveyors. A number of factors need to been considered in the transportation process such as considerable distances between locations, the vast quantities of rock that must be moved, and the large volume of energy required [189], [191]. The topic of transportation is therefore carefully analyzed, and in some cases can result in being the most expensive element during the beneficiation process of minerals.

Additionally, the term ‘store’ refers to the ore that must be kept in the deposit, either short or long term, until it is required to be transported to the processing facilities for further handling. There may also be a need for a crushing machine at the mining site to aid in the transportation of small particles. Additionally, ore washing is necessary to remove impurities adhering to the minerals [188].

3.6.2. Comminution process

Minerals have different chemical and physical properties that influence the power demand in the units to reduce their particle size. The comminution process is carried out through different stages, such as crushing, grinding, and re-grinding. These stages are composed of several units which aim to reduce the particle size, obtain the correspondent size, and to send the feed to the flotation process [162], [192]. For a better understanding of the process in the upcoming chapters, these units are defined as follows [191]:

- Jaw crusher: It is the first unit where the rock is sent. The size of the rock in this unit can be very large (up to 1 m) and as a consequence, the reduction ratio is also the highest. Jaw crushers are also called impactors.
- Cone crusher: This unit is also a part of the impactors. It processes rocks ranging from 100 mm in size and can reduce them to as small as 32 mm.
- SAG mill: It is defined as a Semi-Autogenous unit, which is often included to enhance the circuit's capacity. The reduction in particle size in this unit typically ranges from 10 mm to 1 mm.
- Ball mill: This unit typically serves as the final stage of the circuit. It is used to achieve fine particle sizes, down to 35 µm.

To calculate the energy required in each mill during the comminution process, the Bond's Work Equation is applied (refer to Equation (3-8)). [193].

$$W = 10\, W_i \left(\frac{1}{\sqrt{P_{80}}} - \frac{1}{\sqrt{F_{80}}} \right) EF_x \qquad (3\text{-}8)$$

Where P_{80} is the diameter in microns through which 80% of the product passes, F_{80} is defined as the size through the 80% which 80% of the feed passes [189], and EF_X being the efficiency factor.

The reduction ratio (P80 and F80) is one of the main factors in the equation. The units in the comminution process can treat a wide range of reduction ratios, which were selected after the literature review [63], which considered both the feed introduced and other factors such as the number of units.

Equation (3-8) depends on the Work Index (W_i), a parameter expressing a material's resistance to crushing or grinding, denoting the energy (kWh/t) required to comminute one ton of material [194]. The selection of W_i significantly influences specific energy calculations. For instance, the Bond index for copper-zinc ore can vary from 5 to 14 kWh/t, resulting in nearly threefold differences in Equation (3-8) outcomes and affecting production costs at this stage. Given that extracted rocks consist of multiple minerals, incorporating the average Bond Work Index of all minerals present in a rock into Equation (3-8) is essential for achieving the most precise results.

In situations where ore grades are exceptionally low, the comminution stage becomes the primary energy consumer. Therefore, the Bond Index plays a crucial role in determining the energy requirements during this stage. The choice of Bond Index value should accurately represent the ore being processed, and there is a broad range of applicable values, typically ranging from 2 kWh/t to 24 kWh/t, depending on the mineral composition of the mine's rock [195]. Given the limited information on mine rock composition and the theoretical nature of model development, a simplified W_i value within the range identified in the literature review is commonly chosen to align with the ore's characteristics.

Table 3-2. Bond Work Index values for some minerals [194].

Mineral	kWh/t	Mineral	kWh/t
Alumina	7 - 34	Copper (Zn ore)	5 - 14
Barite	4 - 9	Dolomite	6 – 25
Basalt	18	Ferro – Chrome	3 – 77
Bauxite	1 - 31	Ferro – magnesium	6 – 9
Chrome ore	7 - 17	Gold ore	3 – 42
Coal	13 - 18	Granite	10 -11
Coke	29 - 40	Gravel	11 – 27
Copper (Ni ore)	13 - 18	Iron ore	4 – 31
Copper ore	4 - 30	Siderite	9 – 14

Apart from the Work Bond Index, the efficiency factors must be named and briefly explained. These factors are an adjustment of the power calculated by applying different efficiency factors dependent on the size of the mill, such as the size of the feed, and the type of grinding circuit [196], [197]. These factors are significant since they could represent an increase of up to 20% of the specific energy calculated for a regular particle size [198], and this could be even greater if the particle size is particularly small. Thus, the size of the particle plays a crucial role. Smaller particles necessitate higher energy input for achieving the desired outcome, leading to reduced efficiency. In other words, the smaller the particle required, the greater the volume of energy needed. In this regard, depending on the parameters applied in every mill, the final result will be multiplied by different factors sourced from a literature review [198]. The specific energy calculated in every mill will be chosen according to the reduction ratio which follow the parameters found in the literature review [47], expecting to obtain values with the same order of magnitude [191].

3.6.3. Flotation process

The flotation process is a concentration technique consisting of physically separating particles based on differences in the ability of their air bubbles in selecting specific mineral surfaces [199]. The flotation circuit is primarily composed of three main units: roughers, cleaners and scavengers [200]. Different elements must be considered when a flotation circuit is designed. You can find their definition below:

- Flotation rate: it is the efficiency at which a specific mineral rises to the surface of the flotation cell.
- Particle size recovery: it is the size of the particle required to be introduced into the flotation cell for the bubbles to attach to the desired mineral.
- Airflow: it refers to the volume of air introduced into the flotation cell with the purpose of generating bubbles that attach to the particles.
- Pulp density: this term refers to the concentration of solid particles.
- Feed rate: it is the amount of material introduced in the flotation cell.
- Volume cell: it is the size of the flotation cell, measured in m^3.
- Residence time: it is the time needed in the flotation cell to concentrate the mineral to the desired values.

Since the elements are interconnected, when one is modified, it has a direct effect on the rest. Therefore, it is not possible to analyze a single modified element in isolation [201]. Additionally, it is not possible to separate some minerals when entering the flotation process because their properties are interlinked with the rest of the minerals. However, by adding additives or reagents, some minerals can react, changing the hydrophobic/hydrophilic property and therefore allowing their separation from the unwanted minerals [199]. This is illustrated in Figure 3-3.

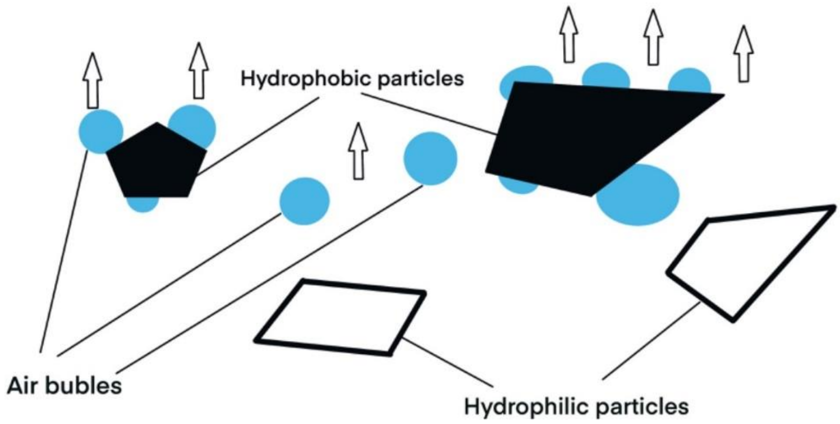


Figure 3-3. Illustration about the explanation of the hydrophobic and hydrophilic particles in a flotation cell.

When all parameters are obtained, either from the literature review or calculated from laboratory data, and the reagents are selected, a flotation circuit must be calculated. To that end, selecting the size and number of cells for each stage of the flotation process will be made by different calculations. Firstly, the cell volume is formulated and can be calculated with the Equation (3-9).

$$V_f = \frac{Q \cdot T_R \cdot S}{60 \cdot C_a} \tag{3-9}$$

Where V_f is the total flotation volume required [m^3], Q is feed flow rate [m^3/h], T_R is the flotation retention time [min], S is the scale factor (between 1 and 2,6), and C_a is the Aeration factor to account for air in pulp (0,85 unless other value is specified).

Once the volume cell is calculated, it is necessary to select the number of cells per bank. Since each model requires different specifications, this parameter will be chosen from the unit flotation provider, in accordance with the circuit configuration being modeled. The final calculation will then be determined by the bank arrangement selection, which is affected by the maximum number of flotation cells allowed by the chosen model [191].

3.6.4. Metallurgical process

While comminution and flotation processes are designed to concentrate the mineral by a physical separation, the metallurgy process focuses on the concentration of the mineral by separating its chemical components [202]. Metallurgical processing requires an organized and coordinated arrangement of unit operations designed to provide physical and chemical changes to purify certain raw materials ensuring they are ready for use in the industry [203]. The metallurgical process, also known as the refining process, is the final step in the beneficiation process of a mineral. After this stage, a specific concentration of the desired metal is expected to be revealed allowing it to then be sent to the industry to be manufactured for various devices. It is composed of three main processes, which can be applied individually or through a combination of all three, depending on the metal being recovered. These processes are pyrometallurgy, hydrometallurgy and electrometallurgy [202].

Pyrometallurgy is based on the chemical separation and refining of a certain mineral occurring at high temperatures. Included in this process is the use of various methods, such as calcination, roasting, smelting, and refining. The principle applied in pyrometallurgy comes from the Ellingham’s diagram, used to determine the conditions in separating the metal. There are many advantages of using this process [204]:

- The reaction rate is accelerated and therefore, more metal production can be carried out.
- It is considered less expensive in comparison to other metal extraction processes.
- It can process high volumes of feed.
- There are reactions that cannot be carried out in the presence of water, so pyrometallurgy must be applied.

Despite its many advantages, there are some disadvantages, such as the high amount of emissions that are sent to the atmosphere. Hydrometallurgy aims to produce pure metals by the reaction of reagents and minerals in aqueous and organic solution. The metallurgy process is typically carried out in several steps, including the preparation of the ore for leaching, the leaching process itself, the separation of leach liquor, and the recovery of metals from the liquor. Although a metal can be recovered directly from the hydrometallurgy process, it usually requires an extra step involving pyrometallurgy to yield the metal. The main advantages are collected below [199], [205].

- It is applied for complex ores.
- It is possible to recover valuable products thanks to the control it offers to the operation.
- Process is carried out at room temperature.
- The reagent can be recirculated to introduce it to the process again.

However, it must be mentioned that the main disadvantage of this process is not only the high cost of the chemicals used, but also the volume of water required along with the disposal of effluents that can contaminate the environment.

Finally, the last process is called electrometallurgy which is an important branch of metallurgy. This involves the utilization of electrical energy for extracting metals from leach liquors and refining metals obtained through pyrometallurgy and hydrometallurgy processes. In this process, an electric current is applied to an electrolytic cell composed of a solution of metal ions. In this way, chemical reactions occur in the electrolytic cell, leading to the separation and deposition of the desired metal. There are two main processes in electrometallurgy [206]:

Electrowinning: An electrolytic extraction method in which cathodic reduction is carried out and used to deposit the desired metal from the electrolyte that is obtained from a leaching step.

Electrorefining: This process is applied for refining a metal in an electrolytic cell. In this case, the impure metal is used as the anode, while the refined metal is deposited on the cathode.

3.7. Software applied

To conduct the simulation of various beneficiation processes for the analyzed metals (Pb, Zn, Nb, Ta, Ni, Co, PGMs), the software Outotec HSC Chemistry was utilized. This software was developed by the Finnish company Outotec, which focuses on delivering sustainable technology and services across various chemical industries. The acronym HSC stands for Helsinki Software Chemical, and it finds application in several industries, including mining, metallurgy, chemical engineering, and materials science. This software offers an extensive range of advanced tools for performing thermodynamic and mineral processing calculations, as well as for developing processes through modeling and simulation, designing flowsheets, and estimating the environmental impact through life cycle assessment (LCA). Outotec has also created its own flowsheets and calculations for research purposes [207].

The software is composed of twenty-four modules to carry out the entire simulation for the beneficiation process as illustrated Figure 3-4, not every module has been used for this thesis, only those that are relevant for the design and calculation of the energy for the units of the process. Among these tools, it is possible to plot Ellingham's diagrams, stability phase diagrams, equilibrium compositions, simulation, etc. More information as well as screenshots of the different modules can be found in Annex 1 included at the end of the document.

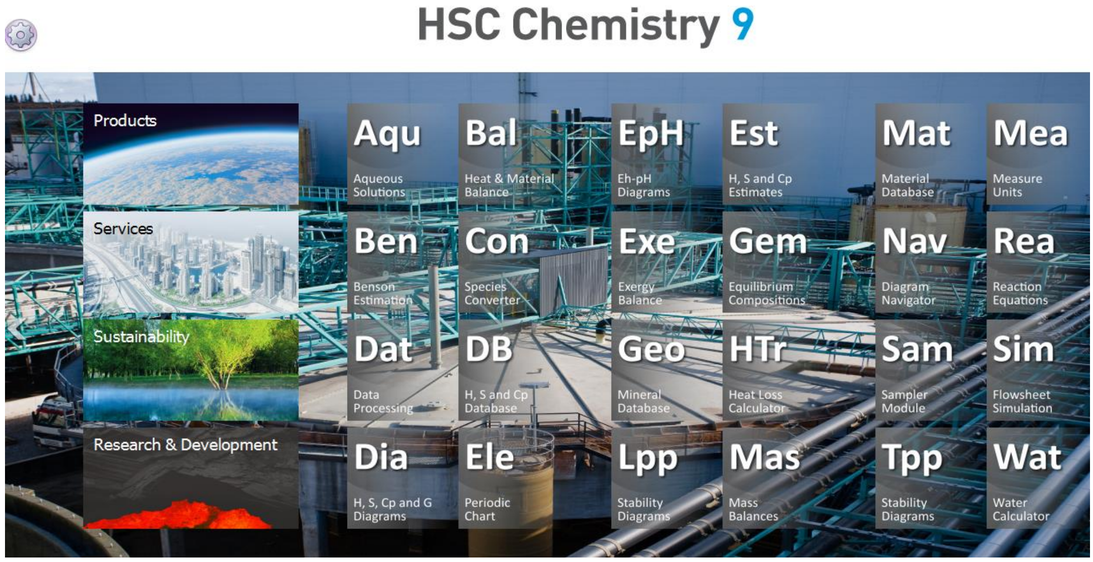


Figure 3-4. Modules available in the software utilized for the differentsimulations in the thesis.

3.8. Conclusions

This chapter has discussed the background of this work by conducting a review of previous works that formed the foundations of this thesis. Furthermore, the methodology and the concepts necessary to address the thesis objectives have been explained, namely:

- Previous studies related to this thesis have been reviewed, providing a foundational context for the current research.
- The concept of Thermodynamic rarity has been explained, which will be used in this thesis as a tool for conducting cost allocation as well as for assessing the physical value of metals contained in WEEE.
- A comparative analysis of this work and previous thesis has been conducted, elucidating the distinctions between these prior works and the present study.
- The novelty of this work centers on the methodology for calculating the energy required to extract metals as ore grades decline. This methodology diverges from its predecessor from Palacios [173] in two primary aspects: 1) The reference state – Given that mineral extraction from Thanatia is unfeasible, a specific ore grade has been selected as the minimum concentration for mineral recovery. 2) Real mining operations are engineered to extract multiple minerals. Consequently, this study considers mineral extraction with a primary metal recovery focus, while others are obtained as by-products.
- To be economically viable, mines are designed to extract more than one metal with the same effort. Therefore, the energy applied to extract these metals

must be allocated. This is essential when assessing a mine since the viability of extracting a metal can depend on the allocation procedure applied. There are different allocations, such as metal price, mass, or thermodynamic rarity, which will be used in this thesis.

- Ore grades in mines are continuously decreasing even though minerals are still being extracted. However, there will come a point when extraction is no longer economically viable due to low mineral concentration; this point is known as the cut-off grade. Two cut-off grades have been analzyed: the Limit of Recovery (LOR) and the Ultimate Recoverable Resources (URR). The LOR has been calculated using the maximum energy required to extract PGMs (as PGMs contain the lowest concentration of all metals), while the URR is set at 5x10-5 wt-% and has been sourced from the literature.
- The main processes applied during the thesis have also been explained, such as ore handling, comminution, flotation, and refining.
- While ore handling may not be considered a treatment process, it holds significant importance in terms of energy consumption. This is primarily due to the extensive transportation required to move the ore from the mining site to the processing location where the mineral is treated.
- The energy related to the comminution process is determined by the Work index. This index could vary depending on the rock composition of the mine. Then, depending on the figure chosen, the energy cost in this process can be acutely affected.
- The metallurgy process is examined in relation to the final stage of the beneficiation process. Moreover, chemical reactions as well as chemical processes carried out in this work have been simulated in the software.
- The software used during the analysis of extraction of every metal has been explained. It is called Outotec HSC Chemistry. It is used worldwide to calculate metallurgy processes and thermodynamic and thermochemical calculations.

With this information, it is possible to analyze the extraction of metals individually. This will be explained in the next chapter, which will focus on the assessment of extracting lead and zinc, including their energy costs when the ore grade declines.

Chapter 4. Assessment of the energy requirements in the beneficiation process. The case of lead and zinc

4.1. Introduction to the chapter

The aim of this chapter is to analyze the energy required to concentrate lead and zinc from a particular mine, considering a reduction in ore grade. It has been developed using the methodology outlined in the previous chapter, and it encompasses the calculation of energy consumption at every stage of the beneficiation process, while simulating the process in HSC Chemistry. It begins with a general overview of the current state of both lead and zinc, identifying countries with the largest reserves and production potential. Additionally, various applications and current statistics for these metals are discussed. Subsequently, an explanation is provided to understand the simulated model and how the data has been formulated. Finally, the results generated by the software are compared with those of other authors to identify any discrepancies or variations. This chapter corresponds to the information presented in **Paper I**.

4.2. General overview for lead and zinc

4.2.1. Lead

Lead (Pb) was discovered more than 5000 years ago. Its use has been essential for the development of civilization, and has historically been used to create ornaments and statues for the ornamentation of castles and cathedrals [208]. Nowadays, due to its specific properties, Pb is the fifth most used metal [209]. It is found in many different applications such as in storage batteries, electric cables sheathing, construction, tanks, and ammunition [208].

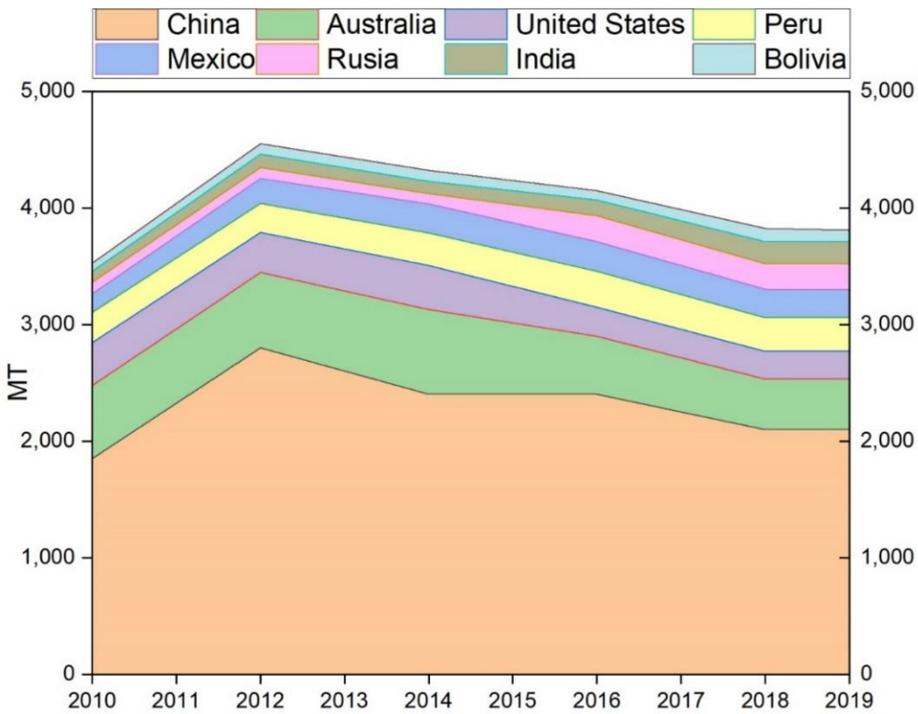


Figure 4-1. World Pb production by country in the last 10 years [Mton] [31], [210].

Pb is particularly essential in energy storage, as the most common batteries are lead-acid [211], and are widely used in the automotive industry [212]. According to the International Lead & Zinc Study Group, the demand for Pb rose by 2.7% in 2018 due to the increase in demand from China (3.4%) and United States (3.1%) [213]. In the coming years, it is expected that demand will increase at a rate of 4.2%, with Australia experiencing the most significant growth [213]. Figure 4-1 shows the trend in Pb production over the last decade, where China emerges as the leading producer when compared to other prominent producers. That said, Australia may play a major role as it currently contains the highest reserves of Pb in the world, with more than 24,000 Mton [31]. China is the next country in terms of Pb reserves, following Australia, with more than 18,000 Mton and is already producing more than 2,000 Mton per year [31].

4.2.2. Zinc

Despite its widely common use during Roman times, zinc (Zn) was not recognized as a single metallic element until the 16th century. It was first called *zinckum* and eventually Zn in 1743 [208]. Zn metal is the fourth most used metal, with extensive applications such as in galvanization, alloys (especially brass), and even Zn sulfide for electroluminescence photoconductivity [208]. Despite Zn naturally occurring with Pb, it is extracted as a by-product of it. The beneficiation process carried out to extract Pb, facilitates the separation of Zn.

Zn mine production rose by 1.1% in 2017, and further increased to 5.1% in 2018 [213]. This increase was due to Dugald River Mine's opening in late 2017 in Australia and the Castellanos Mine opening in late 2017 in Cuba. Figure 4-2 shows Zn production in the last decade, showing that after a small peak in 2012, production is increasing again. This data could confirm the future trend for Zn published by Mohr et al. [214], suggesting that the peak production from Zn mines, is estimated to occur in 2031. Therefore, it is expected to see a significant increase in the coming decades according to various authors [182], [214]. This suggests that in that particular timeframe, almost 100% of Zn should be obtained from secondary resources (currently standing at 15% [215]).

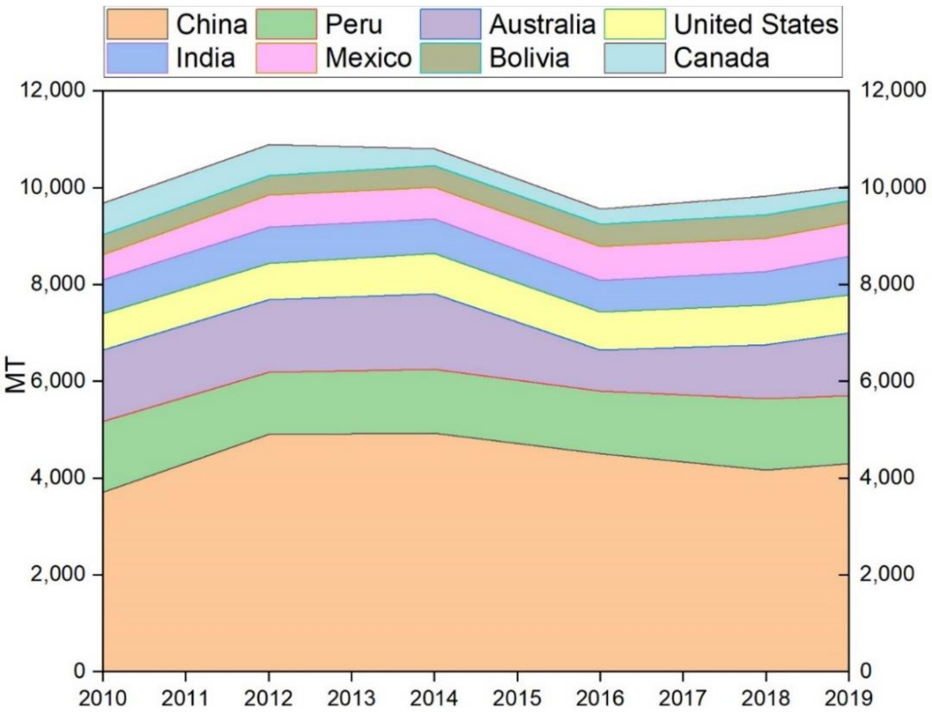


Figure 4-2. WorldZn production by country in the last 10 years [Mton] [216].

4.3. Explanation of the model

With a methodology based on previous studies [174]–[176], the specific energy required for concentrating Pb and its by-product, Zn, will be evaluated. Pb bearing minerals include galena, anglesite, boulangerite, and cerussite, while Zn is typically found in conjunction with sphalerite, smithsonite, and hemimorphite [217]. Deciding to focus on these two metals in conjunction is due to their combined occurrence in nature of galena and sphalerite (minerals with the highest concentration of Pb and Zn, respectively) [218] and hence their geological distribution is similar [219]. For the analysis of the metals, models in HSC software have been carried out for all metals to estimate the energy required for their processing.

Figure 4-3 shows the general flowchart for the mining, flotation, and refining of Pb and Zn. It has been compiled following guidelines obtained from the following technical reports: Prairie Creek mine in Canada [186] with a capacity converter of 87 tons per hour [tph], Platosa Silver-Lead-Zinc in Mexico [193] with a capacity converter of 83 tph, and Ying property mine in China [187], with a capacity converter of 74 tph. Additionally, the essential data required to develop the flowsheet has been obtained from specialized mineral processing books [191], [188], [189]. Likewise, specific details for every process for the particular metals analyzed in this study have been sourced from different references [189], [220].

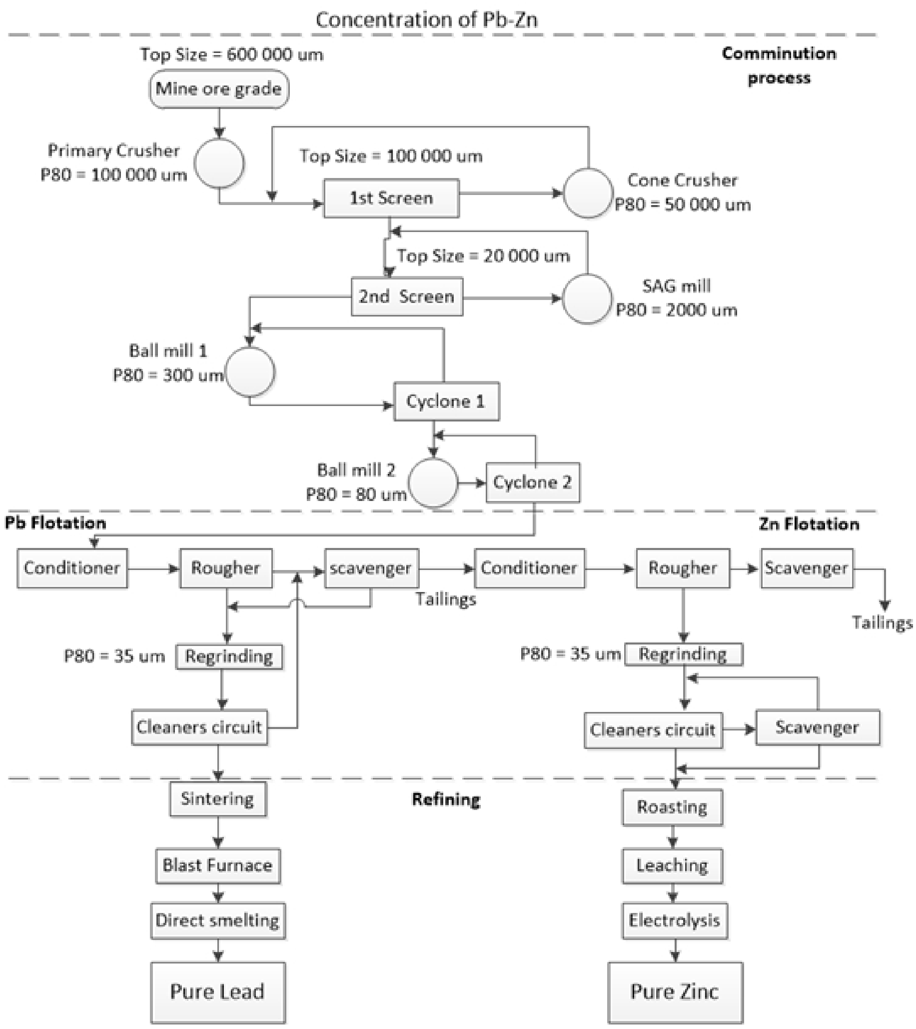


Figure 4-3. Flowsheet of the Pb-Zn beneficiation process.

It is important to identify the most appropriate mineral for extracting Pb and Zn. For this reason, the Pb and Zn bearing minerals chosen are galena and sphalerite, respectively, due to their abundance in standard mines [200]. The initial starting point will be a typical concentration of Pb and Zn commonly found in mining operations: 4-8 wt-% for Pb [221] and 2-5 wt-% for Zn [220]. Using this data, different scenarios will then be posed, all with a lower concentration, which will simulate the expected future state of mines. Therefore, for the purposes of this study, 12 scenarios will be simulated which represent a linear decrease in concentration. It should also be stated from the outset that no two mines are the same and therefore, the results obtained from each mine will have variations. However, the results obtained from a generic mine can be used as a proxy for the rest, as the results show an estimation of the specific concentration energy when the ore grade decreases. In this study, Ying property minerals have been chosen as a starting point for the simulation in HSC [187].

Since ore grade values are expected to decrease significantly to very low levels, it will be necessary to introduce an increased amount of feed in order to correctly extract metals from the chosen minerals. Therefore, the feed introduced in the simulation will not follow the values found in the literature review for Pb / Zn mines, so an alternative method is sought to concentrate these metals even when the ore grades are exceptionally low. In this way, it has been decided to introduce 800 tph and 600 mm as a top size, as recommended in the literature review [222].

As illustrated in Figure 4-3, the comminution process is common in both, Pb and Zn. In that regard, this process encompasses three different stages: crushing, grinding and regrinding.

The comminution process begins with an introduction of the feed in the crushing stage. A primary crusher is applied, processing 80% of the product (F80) with a configuration of a top size of 219 mm. It is then needed to configure the particle size output (P80), which has been set at 50 mm. All the configurations are illustrated in Table 4-1.

Table 4-1. Details of comminution process for the extraction of Pb and Zn.

	Primary crusher	Cone crusher	SAG mill	Ball mill 1	Ball mill 2	Re-grinding	
						Pb	Zn
Feed [tph]	800	512	578	1,569	1,406	474	250
P80 [μm]	100,000	50,000	2,000	300	80	35	35
F80 [μm]	245,631	219,277	38,163	3,164	138	50	48

During the comminution process, the addition of screens has been deemed necessary in order to filter the particle size. Then, particles larger than the screen are recirculated back to the crushing stage, where a cone crusher is employed to further reduce their size below that of the primary crusher. The stream recirculated from the second screen is then sent to a SAG mill as these units are designed to obtain small values with a high reduction ratio. Lastly, two Ball Mills are incorporated into the process, each equipped with an individual cyclone. This addition is intended to reduce the particle size of the material, making it suitable for further processing in the concentration stage.

Equation (3-8) has been used to calculate the theoretical power draw for the different units during the comminution stage. Some parameters, such as the feed passing size (F80) and the product passing size (P80) have been obtained from the simulation developed in HSC. The introduced Work Index is the same for both minerals since they originate from the same mine and undergo comminution together. Additionally, their Work Index values are very closely aligned, with any differences in the final results being negligible and indistinguishable. Therefore, a *Wi* value of 11 kWh/t has been selected [194]. Furthermore, as previously stated, differing efficiencies must be added in line with the Rowland Efficiency factors, which have been obtained from the literature review [198].

Once the *W* values have been calculated, units of mills are selected from catalogues provided by manufacturers. Consequently, the unit selected will always be the one capable of operating with the required power, thereby determining the number of units to be employed accordingly. Further referencing of the literature review allows for the selection of the appropriate units according to the parameters established [223].

The comminution process is not configured to concentrate the minerals, but to firstly reduce the particle size so they can then be concentrated in further stages. Consequently, the flotation process has been chosen to assist with the concentration of both minerals. Table 4-2 shows the concentration during various steps in the beneficiation process illustrating the concentration of the minerals remaining unchanged between the mined ore and the stage prior to the flotation process. However, these values change due to the last stages of the beneficiation process as their aim is to concentrate the metals further by eliminating impurities. Sulfide metals are the main resources to produce Pb and Zn because they are separated from the remaining minerals in the flotation stage [224]. Moreover, a significant situation has arisen between the two metals being studied, as the tailings from the initial flotation unit serve as the feed for a subsequent flotation circuit specifically designed for Zn extraction [225]. Thus, the separation between these two metals can be carried out easily (see Figure 4-4).

Table 4-2. Concentration in different steps along the Pb-Zn beneficiation process [wt-%] [220], [221].

	In mined ore	After flotation	After smelting & converting
Pb	2-4	40-50	99,99
Zn	5-8	50-60	99,99

Additionally, the flotation process for both metals follows a similar pattern, as they are composed of a rougher circuit followed by several cleaners and a retreat circuit [226]. Additives are needed to force the required minerals to float and eliminate any impurities through the tailings [209], [227]. While the overall process for both minerals is similar, the specific parameters such as volume, number of cells, and kinetics are obtained from manufacturers data [181], [219] and institutions specializing in flotation cells [228]. The power required for the flotation process has been taken from the software directly which has an impact on the regrinding stage which aims to reduce the particle size up to 35 μm. Additionally, there are tailings that are then recirculated in an attempt to recover as much mineral as possible. After the re-cleaners, a concentration for Pb and Zn of 45 wt-% and 52 wt-%, respectively is expected to be obtained from the results [197].

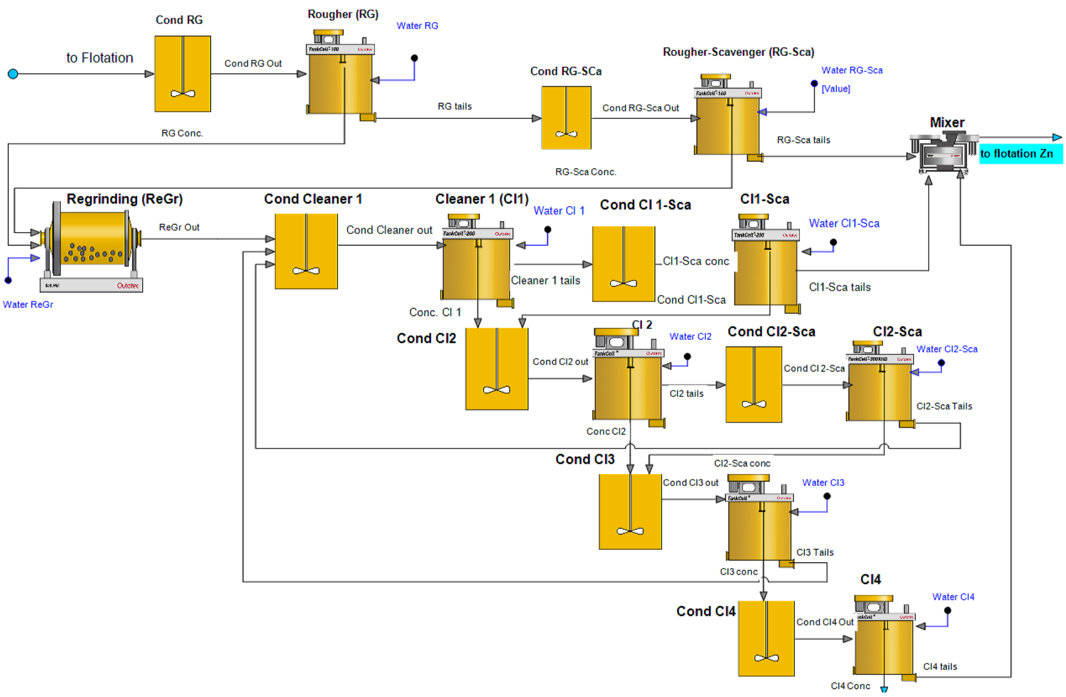


Figure 4-4. Flowsheet for the flotation process for Pb and Zn. Illustration of the separation of Pb and Zn during this stage.

The process ends with the refining stage. When the feed reaches the desired concentration, pyrometallurgy will be used to extract pure Pb, while hydrometallurgy and an electrolytic process will be employed to obtain pure Zn [197]. Pyrometallurgy consists of sintering and a blast furnace [229].

4.4. Results

As was previously explained, the comminution process is common for both minerals. Hence, in this section, the results obtained from modelling through HSC software and the specific energy required for every unit for the comminution process will be shown. Subsequently, the section will be divided to explain the flotation and refining process for every metal, highlighting the values obtained.

4.4.1. Comminution process

Table 4-3 has been formulated to summarize the values obtained for the power demand and the energy required for the comminution process.

Table 4-3. Power demand and energy required for comminution process for Pb and Zn.

Equipment	Power demand [MW]	Specific energy [kWh/t-rock]
Primary crusher	0.60	0.75
Cone crusher	0.45	0.88
SAG mill	4.20	7.27
Ball mill 1	17.80	11.40
Ball mill 2	17.80	12.72
Re-grinding Pb	5.96	12.57
Re-grinding Zn	2.7	10.80

From this, it is possible to identify the units that require more power. The Primary crusher and Cone crusher requires less power and less specific energy due to its heightened efficiency caused by the smaller particle size required at the end of these machines. On the other side, it is important to emphasize the significance of the Ball mills in the process, as the energy required increased by nearly two orders of magnitude in comparison with the previous units. These values have been cross referenced with other authors [230], [231], who obtained similar results, remaining the same for the order of magnitude.

4.4.2. Flotation process

The flotation process has been designed in accordance with the literature review, utilizing roughers, cleaners and scavengers [200]. The aim of this process is to increase the concentration of the desired mineral in the pulp for later transferal to the metallurgy process. It begins with the average concentration found in mines, and then, various scenarios will be created by reducing the concentration gradually. As such, additional flotation units will be required to attain the desired concentration before sending the pulp for further refining.

The first scenario is created using a typical value found in mines of 2.83 wt-% and 6.29 wt-%[186] for Pb and Zn, respectively. These values must be then increased to 45 wt-% for Pb and 52 wt-% for Zn [197], as these are typical concentrations used when transferring minerals to the metallurgy process. In order to increase the concentration, the feed containing both minerals is introduced to a rougher in order to begin the separation. Due to their froth properties, galena floats in the surface while sphalerite is vacated through the tailings. This starts a new flotation process.

The concentration stream from the rougher, containing the galena, is then passed through different cleaners and scavengers until the desired concentration is reached. The regrinding process occurs in between to guarantee the absence of particles higher than 35 µm. It should be noted here that the tailings from the flotation units are directed to the Zn flotation process in an attempt to recover the entire mineral. Once all the sphalerite feed has entered the flotation process, it is sent through a new rougher unit, then through a regrinding process and finally through flotation units. The concentration that has been obtained from this is to then be sent through the metallurgy process.

More scenarios are created in order to simulate the evolution of mines to discover how the specific energy for concentration of each metal increases when the ore grade decreases. This information will show the number of flotation units needed to obtain the same value. Table 4-4 has been formulated to examine how the specific energy for concentration increases across the different scenarios created. It is worth noting that the last scenario created (12) contains a particularly high value of specific energy for concentration due to the low concentration level at the beginning of the process. It must be further noted that the flotation process for each mineral has been designed according to parameters sourced from the literature review such as recovery ratio, residence time, and volume of cell [186], [187], [200], [225], [232], [233].

Table 4-4. Variation of the specific energy for concentration in flotation for Pb and Zn.

GJ/t-ore	Pb	Zn
Scenario 1 (con. in mine)	0.03	0.06
Scenario 4	1.15	2.09
Scenario 8	84.13	175.22
Scenario 12	5,234.92	21,197.42

4.4.3. Metallurgy

The process of mineral refining serves as the ultimate stage in achieving pure metal from the ore, and it holds significant importance as a critical step conducted prior to industrial utilization [234]. In this case, the metals studied are not in their purest form, so further processes are required to obtain bullions from each of them. Hence, it has been decided to apply pyrometallurgy due to the advantages of this process, like the high velocity of the reactions and the large production yield. Furthermore, it is the most widely used process to obtain pure Pb [235].

Regarding the Zn refining process, the most common methods for obtaining bullion are ISF (Imperial Smelting Furnace) and electrolytic processes [197]. Although ISF experienced significant growth at the end of the 1990's, the electrolytic process remains the most commonly used since 1970 and is expected to continue with an addition of 86 plants, 76 more than ISF in second place [197].

4.4.3.1 *Lead*

There are various methods available for treating Pb, with the historically most common approach being primary production, which involves a two-stage process [196]. Secondary Pb production is derived from scrap and acid batteries due to their high proportion of Pb [227]. On the other hand, there is an alternative process to the two-stage process: the so-called 'direct smelting'. Direct smelting possesses some advantages such as its greater efficiency in terms of energy consumption and its ability to obtain a high percentage of Pb in the slag [196].

To proceed with the study of this metal, direct smelting will be used, as it is the most efficient and simplest process in obtaining Pb [229]. There are several direct smelting processes (Isasmelt, Kivcet, QSL, Outokumpu) which all hold a different heat input, design, and process control [229], [232]. For this reason, it has been decided to proceed with the QSL process due to the advantages it offers in comparison with other processes. As the smelting process can be carried out in a single step, the emissions are lower and the range of feed is very wide [229].

Figure 4-5 demonstrates the process applied to obtain the Pb bullion. As shown, a sintering machine and a blast furnace carry out the process. Although it is not necessary to introduce the sintering unit, water remains in the pulp, so the feed is introduced in the sintering, obtaining dry feed in the output. With the feed dried, it is ready to feed the blast furnace, as well as the different components needed to proceed with the chemical reactions. Coke is introduced in the blast furnace as a fuel, limestone is introduced to react with the pulp and the fuel and air are introduced to control the temperature of the blast furnace [229], [232].

The outputs from the blast furnace are determined by the chemical reactions produced in it. The Pb bullion obtained from the blast furnace typically consists of more than 99% Pb, while the matte primarily comprises sulfide compounds. Furthermore, speiss (mixture of metal sulfides) is compounded by oxides and the slag is compounded by various metal oxides, including a small percentage of Pb.

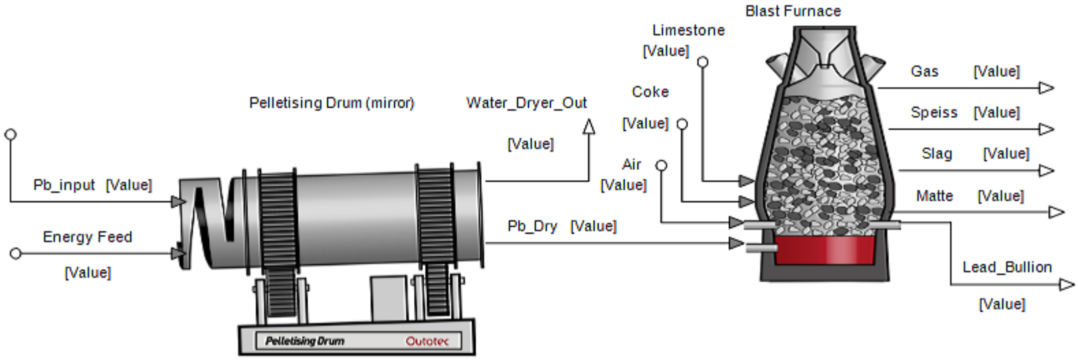


Figure 4-5. Pb refining process carried out through direct smelting.

4.4.3.2 *Zinc*

As previously mentioned, in order to obtain pure Zn, the electrolytic process will be undertaken, which is shown in Figure 4-6. For the purposes of this study, the process has been simplified, including only the most important steps in this stage. This process involves an initial step of roasting, aimed at eliminating the sulfur and converting the Zn mineralization to Zn oxide [197]. The next steps are the leaching stages. Then, electrolysis is applied followed by melting the obtained material to obtain pure Zn [197].

Feed contains high amounts of sulfurs and sulfides and must be converted into oxides to eliminate the impurities from the pulp to prepare it for the following steps [225], [232]. The major impurities in this portion of the roasting process are Cu, Pb, Si, Ca, Na and K [236]. The roasting process is carried out by a roasting furnace, where natural gas is introduced to cause a reaction with the pulp and eliminate sulfurs. The temperature during the process is regulated by the controlled introduction of oxygen. This is undertaken to prevent the temperature from exceeding 960ºC, as higher temperatures can Pb to the formation of molten phases [236].

Once the feed is almost free of sulfides, it is sent to the leaching unit so it can dissolve the Zn as carefully as possible to create a solution suitable for future processes [193], [237]. Apart from other leaching agents, Zn oxide is usually leached by sulfuric acid due to its chemical properties and its low cost. The leaching rate is set according to variables such as temperature, time, pH and particle size [235], [238]. Leaching is carried out in two steps. The primary leaching involves the dissolution of Zn sulfate and a sizable amount of Zn oxide through neutral leaching. In the secondary leaching step, efforts are made to eliminate Zn ferrites, although leaching the ferrite component can be challenging due to its inherent difficulty to dissolve [204], [237].

In order to reach the desired refining stage, the feed is introduced in the electrowinning unit, where Zn ions are discharged from a Zn sulfate solution with an open electrolytic cell [197]. It is important to note that gas treatment is implemented throughout the refining process, however this step is omitted from the final results due to its marginal impact.

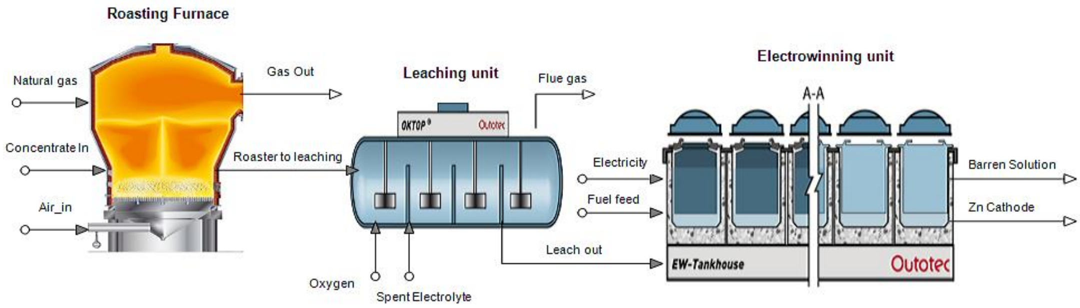


Figure 4-6. Zn refining process.

4.4.4. Considerations for the simulation and calculation

Mines are typically designed to extract multiple metals simultaneously. Consequently, the effort required to extract one metal may be the same if more metals are extracted as by-products. Therefore, utilizing the same beneficiation process, two metals can be acquired. Then, it becomes necessary to allocate energy costs in order to determine the amount of energy dedicated to each metal. In the case of this work, comminution process is similar across both metals, Pb and Zn. The energy allocation cannot be the same due to their distinct properties and the variation in concentration at the initial stage of the process. In this way, according to the Ecoinvent Database energy consumption, the percentage assigned to Pb and Zn is 37.4% and 62.6%, respectively [170].

The results obtained show that the specific energy for concentration is higher for Zn than for Pb. This could be explained by the cost allocation applied during the comminution process, which can reach more than 90% of the total value in low concentrations. These values could change however, if the cost allocation were different, thereby reducing the figure obtained. Different studies have revealed [181], [239] that the specific energy required to extract Zn would decrease when the energy efficiency improves.

Additionally, other parameters are needed to complete the simulation. For example, in the blast furnace (included in the refining process), a value of 31.4 MJ/l [240] has been considered as the High Heating Value (HHV) for carbon. In the case of the ore handling, it has been taken from the literature review, while the refining process for both metals has been compared with other studies and reports [177], [207]. The results obtained from this comparison show small differences compared to the existing literature, but they remain within the same order of magnitude.

4.5. Total energy requirements as a function of ore grade

As it has been explained already, ore grades are expected to decrease in the future as mines become depleted through increased extraction. In order to simulate the future behavior of a mine, different scenarios were created, reducing the concentration in mines to estimate the assumed energy consumption.

Figure 4-7 and Figure 4-8 illustrate the results obtained for Pb and Zn, respectively. What is observed is that energy increases exponentially when the ore grade of the mine decreases. This can be explained by analyzing the comminution and flotation processes. The comminution process is applied to reduce the particle size with a specific concentration. Therefore, as ore grade declines, the specific comminution energy increases since less desired minerals are contained in the processed rock.

In contrast, the flotation process becomes more complex as additional roughers, cleaners, and scavengers are required to concentrate the mineral to typical values before sending it to the metallurgical process. With this concentration, flotation units require a high amount of specific energy since the concentration values contain a very low ore grade (close to 10^{-5} wt-%). Despite the increase in specific energy for the comminution and flotation processes, the refining process maintains a consistent energy requirement without major changes. This occurs because the feed that arrives at the refining process has the same properties at the end of the flotation process and no alternative process exists at this stage.

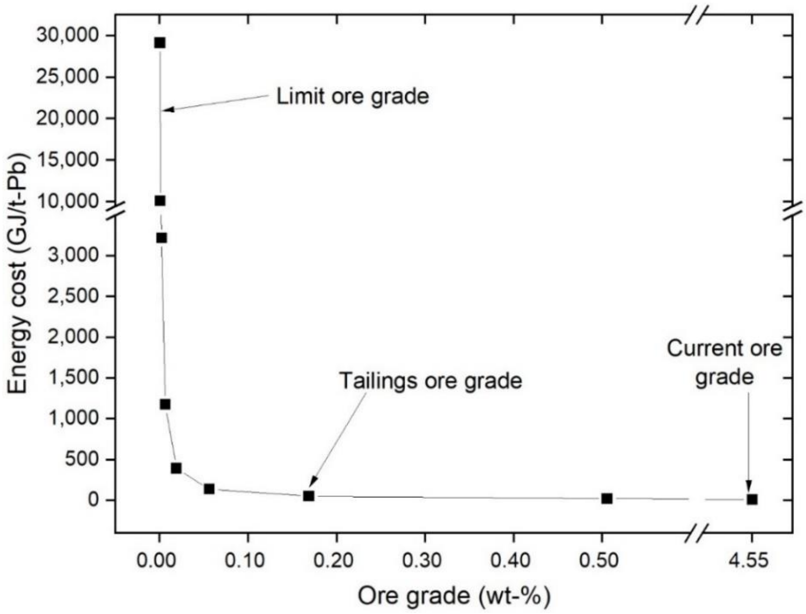


Figure 4-7. Specific energy for concentration for Pb when the ore grade is reduced [GJ/t-Pb].

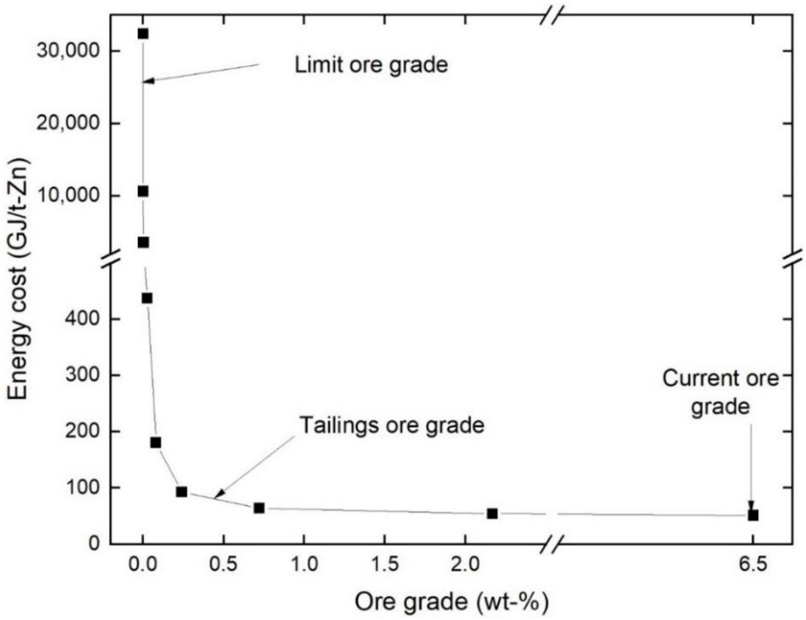


Figure 4-8. Specific energy for concentration for Zn when the ore grade is reduced [GJ/t-Zn].

Three separate points of reference have been calculated to estimate the energy requirements for both metals. The first is the current ore grade. Current ore grade can be used as a baseline for the models, since it has been calculated with real data obtained from the literature review. Using this as a starting point, the ore grade will be gradually decreased and the specific energy, increased. The second point is the discarding of the ore grade that is contained in the tailings. This means that a valuable percentage of desired mineral exist in the discarded tailings. It is crucial to determine the specific energy at that specific point in order to facilitate further calculations and analysis. The final point analyzed is the ore grade limit, set up at 0.5 g/t.

With the simulations carried out, the specific energy for concentration calculated in the beneficiation process for Pb is 10.85 GJ/t-Pb, while for Zn, it is 50.90 GJ/t-Zn. According to the data obtained in this study, these values would increase exponentially when the ore grade decreases. Table 4-5 attempts to put into context these results, comparing the specific energy obtained and the tons of oil equivalent (toe) with meaningful concentrations to better understand the order of magnitude that could be reached.

Table 4-5. Comparison of the specific energy obtained in the simulation of the extraction of Pb and Zn.

	Pb			Zn		
Ore grade	Wt-%	GJ/t-Pb	toe/t-Pb	Wt-%	GJ/t-Zn	toe/t-Zn
Current ore grade	Sce. 1 (4.55)	10.85	0.259	Sce. 1 (6.5)	50.90	1.22
Tailings ore grade	Sce. 3 (0,17)	23.21	0.55	Sce. 4 (0.24)	93	2.22
Limit ore grade	Sce. 8 (0.005)	3,220	76.91	Sce 8 (0.005)	3,579	85.5

The first scenario has been chosen as it represents a typical concentration found in mines, which is the starting point of this study. In this case, obtaining a ton of Pb and Zn requires 0.259 toe and 1.22 toe, respectively. Scenario 3 for Pb and Scenario 4 for Zn represent a concentration that is in the same order of magnitude found in tailings [187]. From this, it is clear that obtaining a ton of Pb from tailings would require 0.55 toe, which is more than twice needed currently. On the other hand, a ton of Zn would require 2.22 toe, which would require an increase of more than 80% of the energy needed from the first scenario.

Scenario 8 is the final comparison since the concentration analyzed for both metals slightly passes the limit chosen in this model [182], which affirms that it is not economically feasible to extract any metal from that concentration. At this point, the energy required to extract a ton of Pb would increase to almost 77 toe, while 85.5 toe would be needed to obtain a ton of Zn. In other words, the energy to obtain Pb would increase almost 300 times in comparison with the first scenario, while Zn would increase more than 70 times.

4.6. Cost assessment as a function of ore grade

Further analysis has been carried out, focusing on the price of the commodities and the expected value Pb and Zn could reach in the future. Even if commodity prices are generated in the market affected by different factors, these should at least cover all associated costs, including energy, water and chemicals used to obtain the refined metal, and leave a profit margin for investors. Additional costs are related to investment, operations and maintenance costs, and royalties.

According to the calculations in this study, the energy requirements of typical ore grades currently found in mines (4.55 wt%) is approximately 10.85 GJ/ton. We can now transform this energy into monetary prices. To that end, it will be considered that such energy is in the form of electricity. Additionally, there are different types of energy involved in the process, such as diesel for waste rock transport and natural gas, etc. Yet by considering that energy is paid at the electricity price, it provides us with an upper bound. Certainly, this exercise primarily intends to provide orders of magnitude because uncertainties are significantly high. The electricity price chosen is that of the US in 2020 due to the importance of this country in the mining industry of Pb: 0.111 $/kWh [241].

With these values, we can estimate the energy costs associated with an average Pb deposit: 335 $/t-Pb (metal). Considering the 2020 Pb prices (2,095$/t) [242], energy costs contribute to about 16% of the price. Therefore, investment, O&M, royalties, profit, etc. would amount to 1,760 $/t-Pb.

Taking into account the previously discussed models and the scenarios we can now estimate energy costs as a function of the ore grade. When assessing the data shown in Figure 4-9, it has been chosen a constant energy price of 0.111 $/kWh. As ore grades decline, the margin left to other costs and profit significantly reduces. For an ore grade of 0.17 wt-% as could be found in tailings, the energy costs would amount to 1,576 $/t. If we assume that the rest of the costs and benefits remain constant and equal to 1,760 $/ton, and the tailings price increases to 3,336 $/ton, it would be closely linked to the maximum historical Pb price. This means that if commodity prices increased, tailings could eventually become a cost-effective source of Pb.

However, it is important to recognize that these values should be viewed as a rough approximation. This is because, in all likelihood, other costs will also undergo changes when ore grades decline, and both commodity and electricity prices will experience fluctuations.

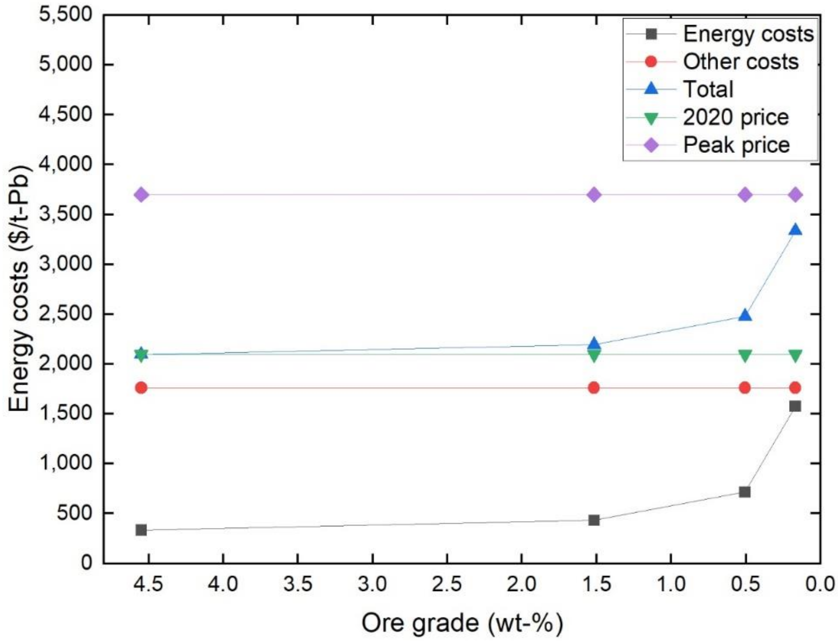


Figure 4-9. Assessment of energy costs, peak prices, and 2020 prices for Pb according to the ore grade [$/t-Pb].

This same analysis has been created for Zn (Figure 4-10). If energy costs remain constant, the maximum price for Zn obtained from tailings would increase to 4,153 $ per ton. This value is close to the historical peak, but it is lower, meaning that when tailings ore grade is reached, the new virtual price for a ton of Zn would remain below the historical peak, making it a viable source.

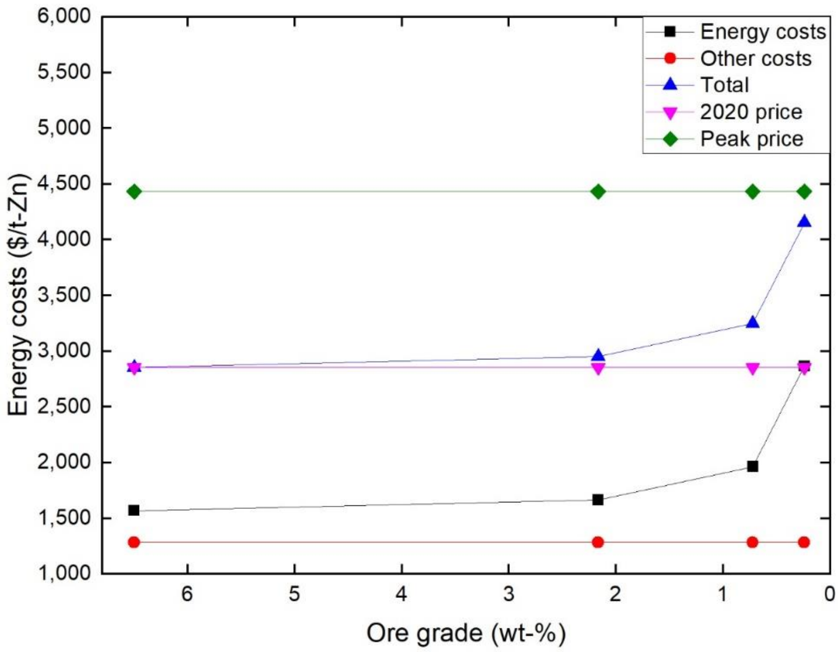


Figure 4-10. Assessment of energy costs, peak prices, and 2020 prices for Zn according to the ore grade [$/t-Zn].

Table 4-6 has been formulated to identify and present the figures mentioned for Pb and Zn for the current scenario as well as the tailings ore grade. It is important to emphasize that, regarding Pb, the energy costs experience a fivefold increase when transitioning from the current ore grade to the tailings ore grade. In the case of Zn, this increase is nearly twofold. Additionally, when comparing the current ore grade, the cost of Zn is 36% higher than that of Pb. However, in the alternative scenario examined, this difference reduces to 24%, indicating a significant rise in costs for Pb as the ore grade diminishes.

Table 4-6. Total costs of production calculated for two different ore grades for Pb and Zn.

	Pb		Zn	
($/t)	4.55[1] wt-%	0.17[2] wt-%	6.5[1] wt-%	0.24[2] wt-%
Energy costs	334.46	1,576	1,569	2,855
Other costs	1,760	1,760	1,285	1,285
Total	2,095	3,336	2,855	4,153

[1] Current ore grade.

[2] Tailings ore grade.

4.7. Conclusions

In this chapter the behavior of specific extraction and beneficiation energy for Pb-Zn deposits has been analyzed in relation to declining ore grades. Such deposits serve as a proxy of what is likely to happen to the entire mining sector when mines become depleted through a potential need for accelerated extraction in order to meet the growing demand for raw materials. It has been observed that the energy requirement would increase significantly when tailings' ore grade is reached, reaching approximately twice the current energy consumption for both metals. An even more challenging scenario arises when extraction is performed at the so-called limit ore grade, with values being 300 times higher in the case of Pb and more than 70 times higher in the case of Zn. The main conclusions for the study in this section are collected below:

- The results show that as the ore grade decreases, the specific energy required for concentration increases. This increase is attributed to the greater quantity of rock processed during the comminution process and the additional units required for ore concentration during the flotation stages.
- Three different scenarios with different ore grade at the beginning of the process have been analyzed. With the first scenario, referred to the current ore grade in mines, the energy calculated is 0.26 toe to extract a ton of Pb and 1.22 toe to extract a ton of Zn. The second scenario is referred to the tailings ore grade, obtaining 0.55 toe to extract a ton of Pb and 2.22 to extract a ton of Zn. The findings indicate that there are no significant limitations in terms of energy for both the current ore grade and tailings ore grade.
- In the last scenario considered, which involves the limit ore grade set at 5x10-5 wt-%, extracting one ton of Pb would require 76.91 toe, while extracting one ton of Zn would require 85.5 toe. This would necessitate processing millions of tons of ore, making it economically unviable. If the limit ore grade is reached, the energy requirements would also increase significantly, following an exponential growth pattern, as illustrated in the study. Specifically, when reducing the ore grade by one and two orders of magnitude, the energy required for both Pb and Zn extraction would increase by more than 9 times and almost 85 times, respectively.
- The cost assessment carried out indicates that for both commodities, even if processing costs increase, there is still margin for profit in tailings extraction.

The reason behind this increase in energy requirement is that even when considering constant O&M (Operation and Maintenance) costs, investment costs, royalties, and profit, the overall costs would remain below the maximum historical peak price of the respective commodities. In summary, obtaining minerals from tailings would be arguably cost effective.

This process, which has been carried out for Pb and Zn, can also be evaluated for other metals such as Ni, Co, and PGMs, as will be discussed in the following chapter.

Chapter 5. Limit of recovery: how future evolution of ore grades could influence energy consumption and prices for nickel, cobalt, and PGMs

5.1. Introduction to the chapter

In line with the methodology used in the previous chapter, this chapter focuses on calculating the specific energy for concentration when the ore grade decreases for three different metals: nickel (Ni), cobalt (Co), and platinum group metals (PGMs). A general overview of these three metals is conducted through a literature review, highlighting the top producing countries and examining the evolution of demand in recent years. Next, we will describe the applied flowsheet for the simulation, which will be conducted using various concentrations. Furthermore, a proposed limit of recovery (LOR) is introduced to understand the potential implications in terms of energy if this limit is reached by any of the metals studied in this chapter. A sensitivity analysis is then conducted to analyze possible cost allocation options. The variation in the obtained results and the significance of cost allocation when extracting metals as by-products are also discussed. The final section concentrates on the economic assessment, analyzing the impact of energy costs on metal extraction prices. The information presented in this chapter can be found in **PAPER II**.

5.2. General overview

Nickel (Ni), cobalt (Co), and the platinum group metals (PGMs) have recently become strategically crucial for the economy, driven by their increased demand due to extensive technological applications [243]. Ni and Co are used as battery materials, catalysts, medicines, and permanent magnets [244]–[247]. By contrast, PGMs are extensively used in catalyst converters to reduce emissions, which have grown phenomenally over the last decade [248]. Two of the three group of metals analyzed in this chapter, Co and PGMs (PGMs are considered as a single metal) are included in the European list of critical raw materials - CRM [117]. The case of Ni is somewhat unique. Although Ni does not meet the thresholds for Critical Raw Materials (CRM), it is considered strategic due to potential issues arising from production capacity and contractual arrangements [117].

The evolution of the past and future demand can be seen in Figure 5-1. In the case of Ni, the demand is projected to increase from 1,800 kton in 2010 to 5,800 kton by 2050 [249], [250]. For Co, there is an expected increase from 60 kton to 390 kton during the same period [39], [250]. However, PGMs could witness a substantial two-order-of-magnitude increase, rising from 0.045 kton to 1.7 kton during the same years [251]. These values indicate that Ni is expected to increase by more than 3 times, Co by more than 6 times, while PGMs are anticipated to surge by almost 38 times.

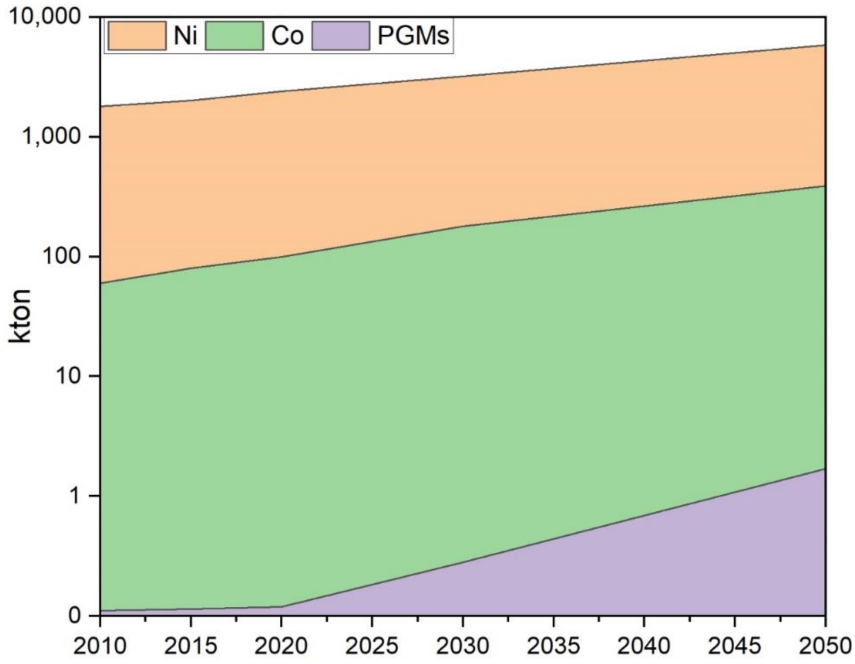


Figure 5-1. Historical demand for Ni, Co and PGMs for the last decade and projected demand until 2050. Note that there a logarithmic scale is employed to enhance the comprehension of the data [kton] (adapted from [149], [241], [242]*], and* [239]*).*

5.2.1. Nickel

Ni was discovered in the 18th century, and it was primarily used as an alloy to create the German silver, which was used years after as a substitute for silver [185]. In 1950, Ni production experienced rapid growth, as evident in Figure 5-2 [185]. This growth trend persisted well into the 21st century, with a significant portion being utilized for stainless steel production, which constitutes nearly 60% of the total production.

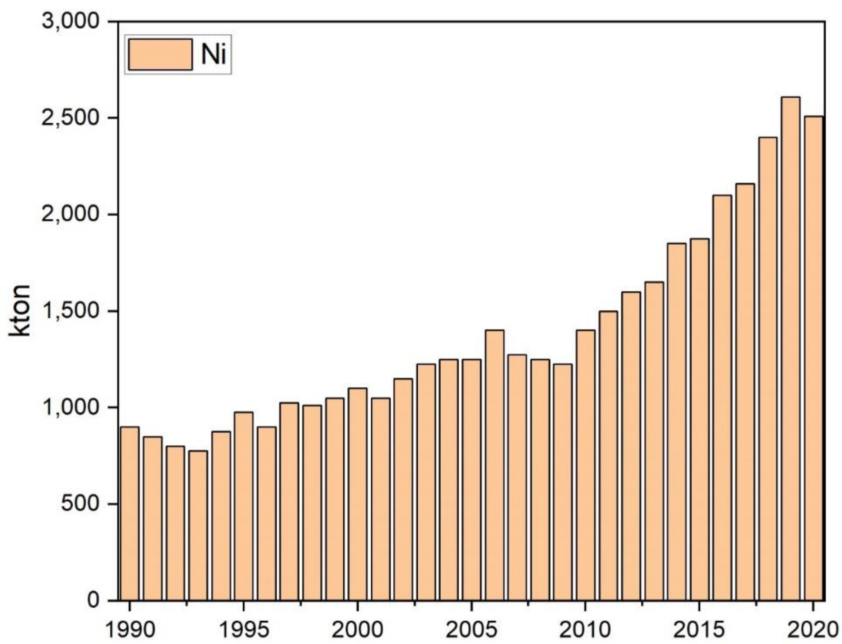


Figure 5-2. Ni global production in the last 30 years [252].

There are many countries in the world with Ni reserves, with Australia and Indonesia leading the sector with more than 19,000 kton. and 21,000 kton, respectively [253], [254]. On the other hand, the most producers of Ni are Indonesia with 560 kton, followed by Philippines with 340 kton [31].

The production peak for Ni is projected to occur between 2025 and 2033, as indicated by simulations conducted by various authors [182], [255]. With this insight, it can be assumed that the sustainability of this metal will depend on achieving a robust recycling rate and the capacity to meet anticipated demand primarily through recycled Ni.

5.2.2. Cobalt

Since the Bronze Age, Co has been used to provide color for ceramics [256]. However, it was not isolated as a pure metal until 1735 [256]. It possesses important properties (i.e. chemical stability and high temperature resistance) that make it essential for high technology industries, such as rechargeable batteries and superalloys [182], [256], [257].

Co is usually mined with Ni since it is found in Ni minerals [185]. However, there are two kinds of resources used to extract Ni: laterite and sulfide ores. Around 70% of Ni resources are found in laterite ores, which account for only 40% of global production and are primarily extracted to obtain ferronickel [185]. However, the Co content in laterites is too low to be economically viable to obtain Co as by-product [185]. Therefore, Co is usually obtained from Ni sulfide ores, where the Co percentage is higher and the energy cost of extraction is lower.

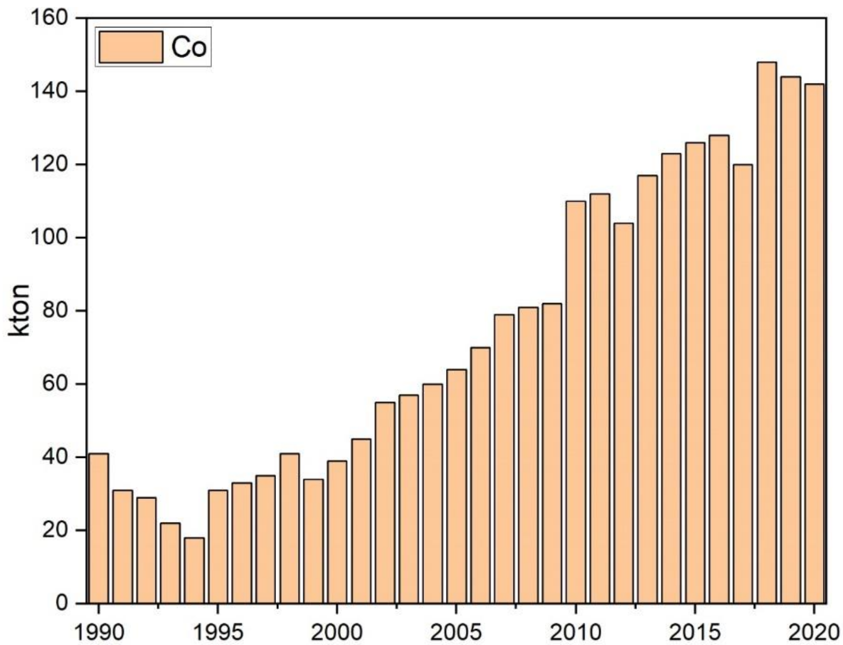


Figure 5-3. Co global production in the last 30 years [252].

Co is identified as a high-risk (in terms of availability) metal due to its expected production, demand, and scarcity on Earth [252]. Figure 5-3 shows how Co production has increased over the last two decades by more than 100%, and according to different authors [39], [252], it will increase by more than 500% by 2030.

On the other hand, it is important to mention that Co is primarily produced in the Democratic Republic of Congo (DRC), holding more than 60% of the world's production [258]. Furthermore, DRC contains the highest reserves of Co, followed by Australia who possesses one-third of the DRC reserves [259]. However, mining production for Co in DRC is unregulated with a history of political instability and armed conflicts. As a result, it is regarded as a high-risk business environment [252]. This could have implications for the future of production in this country, as processors and industrial consumers are increasingly emphasizing ethical considerations. There is now a focus on responsibly sourcing raw materials and reducing dependence on unregulated artisanal Co mining [252].

5.2.3. Platinum Group Metals (PGMs)

PGMs can also be found in Ni ores dissolved or present as distinct mineral grains [185], [260]. PGMs are composed of six metals: ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt).

PGMs are complex minerals due to their scarcity in the crust, their dependence on technology development, and their low recycling rate [261], [262]. Although they are widespread, it is not economically viable to recover them from every deposit due to their low concentration. Thus, the regions where is feasible to extract these metals are placed in particular countries, such as Canada, Russia, South Africa, and the United States [262].

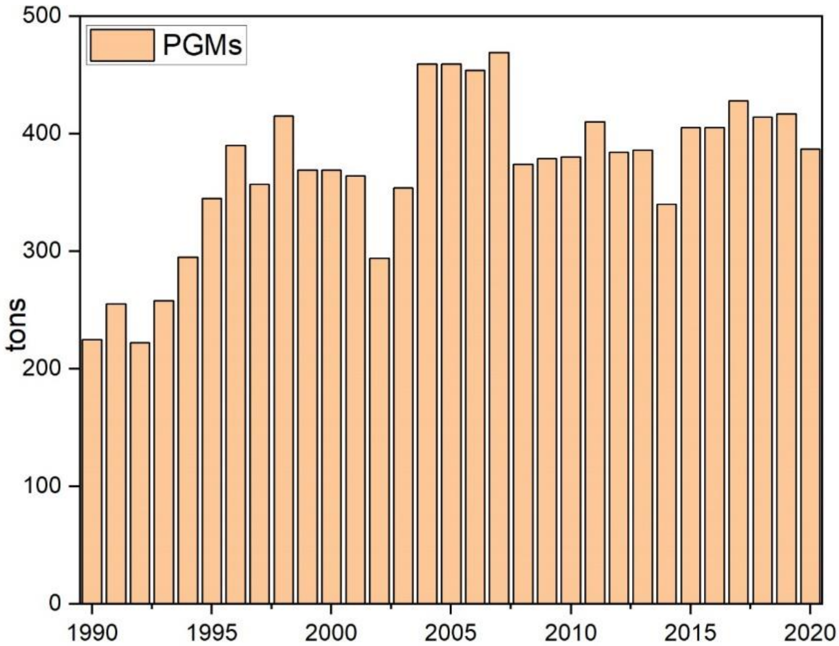


Figure 5-4. PGMs global production in the last 30 years [185], [263].

Additionally, PGMs are characterized by their high melting points, making them inert to a wide number of substances even at high temperatures, and therefore, corrosion resistant [264]. Due to these factors, they are widely used in catalyzers and in the automobile industry as catalytic converters [265]. Therefore, the use of PGMs in these sectors informs of the production data in Figure 5-4. The global production has doubled in the last three decades, but appears to have stabilized and remained consistent for the past five years [266]. The automobile industry has been their leading consumer, accounting for approximately 82% of global rhodium consumption, 76% of palladium consumption, and 44% of platinum consumption [267].

South Africa stands as the largest producer of PGMs globally, accounting for over 95% of the total PGMs production [268], [269]. With this estimated reserves, it is projected that PGMs can be extracted for another 200 years at the current production rate [255]. However, due to the continuously rising demand for PGMs, some authors predict that the peak for PGMs production could occur as early as 2020 [182]. Therefore, recycling has become a crucial component for the continued supply of future demand.

5.3. Explanation of the model

As previously explained, Ni, Co, and PGMs are usually extracted in unison due to they occur together in Nature [260]. Although laterite reserves are higher than sulfide reserves, this study will focus on sulfides. The reason for this is the extraction of by-products, such as Co and PGMs from Ni minerals, which is more viable than laterites when these metals are concentrated [270]. Apart from the metal concentration in the ore, it is essential to mention that the specific energy to extract Ni from laterites is higher than the specific energy to extract Ni from sulfide ores [271]–[273].

For the purposes of this study, pentlandite has been chosen as the mineral from which these elements are extracted [39], [274]. This mineral possesses the highest Ni concentration, making it more energy-efficient to extract compared to other ores. In the simulation process, a standard mine has been utilized, with a predefined concentration of pentlandite and other gangue minerals like quartz. Consequently, additional mineral composition and concentrations are needed in order to create the simulation. Once the specific concentration of each mineral has been determined, various scenarios will be generated to simulate the future dynamics of a mine.

Given that the desired mineral is pentlandite, the extraction process will primarily target this ore, thereby decreasing its concentration in the mine until it reaches the depletion point expected in the future. This approach facilitates the examination of multiple scenarios, each involving a reduction in pentlandite concentration, consequently leading to an increase in the specific energy required for each stage.

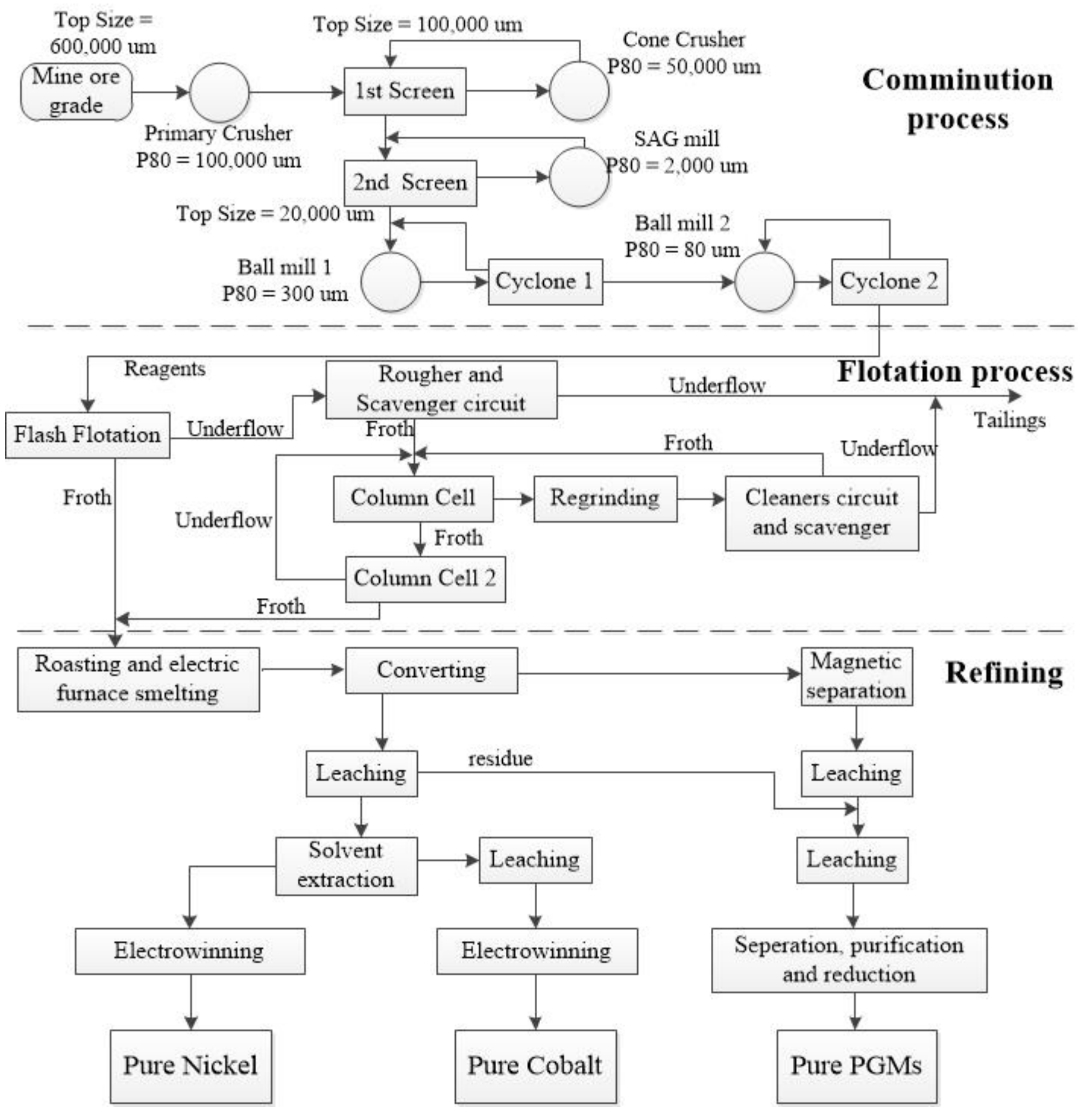


Figure 5-5. Flowsheet for the extraction of Ni, Co and PGMs

Figure 5-5 has been constructed using data sourced from the literature review [185], [188]–[191], and its purpose is to identify the key stages in the process and the most critical data for introduction into the simulation. It is evident from this figure that both the comminution and flotation processes are common to all metals. Additionally, it is clear that once the flotation process is complete, PGMs are separated from pentlandite through gravitational means [185]. Furthermore, in the metallurgical process, PGMs undergo a refining stage to obtain the six individual metals that comprise PGMs [275], [276]. Similarly, pentlandite undergoes a refining process to separate Ni and Co, resulting in the production of pure metals for each element.

The beneficiation process is divided in three main stages: comminution, flotation and refining. In this way, a concentration process is required before and after each stage in order to introduce all the data to the software. In this study, various authors have been referred to, so an average concentration in each step can be established [185], [190], [277]. Multiple data from different mines were analyzed in this study to simulate the most accurate conditions, including the minerals and their concentrations.

Table 5-1. Concentration in different steps along the process of recovering Ni, Co, and PGMs [%] [185], [190], [270].

	In mined ore	After flotation	After smelting & converting
Ni	1.5-2.5	10-20	40-70
Co	0.05-0.1	0.3-0.8	0.5-2
PGMs	0.0004	0.01-0.02	0.2-0.4

Table 5-1 has been formulated to identify the concentration of the metals at various stages in the beneficiation process. Therefore, it is worth stating that the values "in mined ore" are related to the typical values found in the literature review. Then, different scenarios can be created reducing the concentration in mined ore as suggested in Table 5-2. This can be used as a template for simulating the decrease in ore grade of any given mine.

Table 5-2. Concentration for the different scenarios created in the simulation of extraction for Ni, Co, and PGMs [wt-%].

	Ni	Co	PGMs		Ni	Co	PGMs
Sce. 1	3	0.16	$4x10^{-4}$	Sce. 7	$4.1x10^{-3}$	$2.19x10^{-4}$	$5.49x10^{-7}$
Sce. 2	1	0.0533	$1.33x10^{-4}$	Sce. 8	$1.37x10^{-3}$	$7.32x10^{-5}$	$1.83x10^{-7}$
Sce. 3	0.33	0.0178	$4.44x10^{-5}$	Sce. 9	$4.57x10^{-4}$	$2.44x10^{-5}$	$6.1x10^{-8}$
Sce. 4	0.11	$5.93x10^{-3}$	$1.48x10^{-5}$	Sce. 10	$1.52x10^{-4}$	$8.13x10^{-6}$	$2.03x10^{-8}$
Sce. 5	0.037	$1.98x10^{-3}$	$4.94x10^{-6}$	Sce. 11	$5.08x10^{-5}$	$2.71x10^{-6}$	$6.77x10^{-9}$
Sce. 6	0.012	$6.58x10^{-4}$	$1.65x10^{-6}$	Sce. 12	$1.69x10^{-5}$	$9.03x10^{-7}$	$2.26x10^{-9}$

This approach ensures that the ore grade values in the later scenarios remain sufficiently low, while the obtained results reflect a concentration level below the limit found in the literature review. It is also notable that the ore grade at the beginning of the process for PGMs is considerably lower than that of Ni. Furthermore, the values reached in the final scenario for PGMs are significantly lower (five orders of magnitude) compared to Ni. This difference can be attributed to the availability of these metals in the Earth's crust, with PGMs being less abundant than Ni.

5.4. Results

When undertaking the simulation, three main energy flows must be considered, which relate to the three stages described in the flowsheet. The first is the comminution energy stage. At this stage, the size of the rock extracted in the mines is reduced to the particle size required for further steps. While the ore grade decreases with each scenario, the embodied energy increases as more rock must be processed to obtain the same amount of ore [162]. Furthermore, as more embodied energy is needed, the specific energy increases accordingly [178], [278], [279].

The concentration at the beginning of the flotation process will determine the design of the flowsheet. Since the concentration in the scenarios decreases consecutively, more cleaners, column cells, roughers, and scavengers will be needed to reach the desired concentration levels at the end of the process. This also entails an increase in the specific energy of the flotation process. In contrast, it is important to note that the specific energy in the refining stage will remain constant throughout the different scenarios. The reason behind this is that the concentration at the beginning of this stage must be the same in all scenarios and has to remain constant.

Once the simulation is completed, the software provides data for the different units used in the comminution process. In this case, the primary crusher, the cone crusher, the SAG mill, different Ball mills and re-grinding. Table 5-3 illustrates the specific energy of each unit during the comminution process. These values will not be altered during the study since particle size has to be reduced in all the cases. The values obtained with this simulation have been compared with those found in the literature [231] and are within the same order of magnitude. As can be seen, the highest consumption comes from the Ball Mill 1, followed by the Ball Mill 2. The reduction ratio could explain this since these units aim to reduce particle size by two orders of magnitude. It is therefore possible to see that re-grinding requires less energy than SAG mills, even if it has a higher specific energy. The reason is the particle size required for the final product. Re-grinding is introduced in the comminution process to decrease particle size considerably. In this case, efficiency drops as the process must be repeated more than once to obtain the desired size.

Table 5-3. Power demand and energy required during the comminution process for Ni, Co, and PGMs extraction.

Equipment	Power demand [MW]	Specific energy [kWh/t rock]
Primary crusher	0.365	0.38
Cone crusher	0.477	0.88
SAG mill	3.975	7.27
Ball mill 1	22.92	12.05
Ball mill 2	11.96	9.68
Re-grinding	3.73	10.46

As a result, the energy for the entire stage has been calculated. Since different scenarios have been created to simulate the behavior of a mine in the future, more flotation units will be needed with each subsequent scenario to reach the desired concentration. The process described in this study is the one used in current mines, but each following scenario will have more roughers, cleaners, and scavengers, which will result in an increase in specific energy during the whole process, as shown. Selected scenarios are presented in Table 5-4, including, for comparative purposes, the specific energy required for concentration during both the comminution and the flotation stage of the beneficiation process.

Table 5-4. Specific energy for concentration in the comminution and flotation stages for Ni, Co, and PGMs [data in GJ/t-ore].

GJ/t-rock	Comminution	Flotation	Both
Scenario 1 (conc. in mine)	5,526.37	2.29	5,528.66
Scenario 4	149,212	3,800.6	153,012.6
Scenario 8	1.21 $\times 10^{7}$	54,559.3	1.21 $\times 10^{7}$
Scenario 12	9.79 $\times 10^{8}$	3,098,853	9.82 $\times 10^{8}$

Once the concentration reaches the desired level, the refining process begins in order to obtain pure metals. Since all the metals are present in the same feed, specifically in pentlandite, it is necessary to transport it to the metallurgical plant for further processing. Here, metals are purified by different chemical processes. Although metallurgy processes can be ultimately simulated with the software, it has been decided to obtain the value for the different metals from literature to simplify the calculations. To that end, the values used are 100 GJ/t and 129 GJ/t, for Ni and Co, respectively [112]. As for PGMs, the value chosen is 315 GJ/t [185].

5.5. Analysis and discussion

5.5.1. Energy share in the different stages of the beneficiation process

As stated previously, the ore concentration in mines for some specific minerals is decreasing which could lead to a lack of capacity to meet market demand [46], [47]. Nevertheless, it is possible to estimate how the specific energy for concentration will behave for each metal that is extracted. It is important to note that for the sake of simplifying the analysis, all six PGMs have been treated as a single metal, and the beneficiation process is assumed to be identical for all of these metals. The final separation of each metal occurs during the refining stage. Conducting the analysis for each PGMs individually would not have yielded any discernible differences in the study's outcomes.

When the concentration of a metal is very low, ore handling becomes an essential process. The lower the ore grade, the greater amount rock must be extracted, processed, and transported, which in turn relates to the amount of diesel used to transport the rock from the mine to the plant to process it. For the three metals analyzed in this study, Ecoinvent database was consulted for the ore handling data [177]. Ore handling can represent an important share of the energy consumption in the beneficiation process and can be very different depending on the metal extracted. For instance, in this case, PGMs have an ore handling value of 1,030 GJ/t-PGMs, while for Ni it is only 11.2 GJ/t-Ni. As for Co, it is almost 40% of the total energy obtained from the rest of the stages. These differences can be attributed to variations in the ore grade at the initial stage of the process.

5.5.2. Cost allocation

As some metals are extracted as by-products, it becomes necessary to allocate costs to the extraction energy. This allocation is crucial because a difference in cost allocation can determine whether a metal extraction is viable or potentially more profitable.

The first allocation applied is based on market price, as explained in section 3.4 and using Equation (3-7). The prices chosen come from the year 2020. These prices are 14,109 \$/ton for Ni, 35,200 \$/ton for Co, and 35,000,000 \$/ton for PGMs. With this approach, it has been chosen the cost allocation obtained is 61%, 6%, and 33%, for Ni, Co, and PGMs, respectively, as it can be seen in Figure 5-6A.

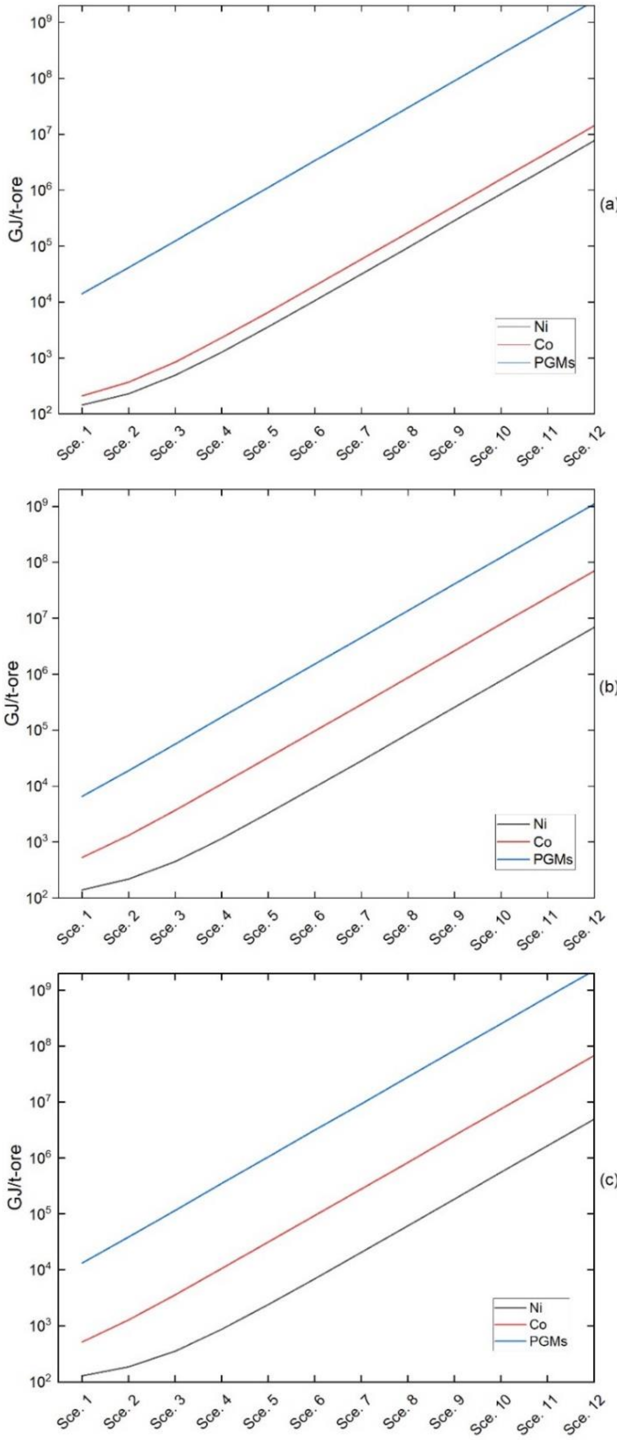


Figure 5-6. Cost allocation for Ni, Co and PGMs using different approaches. A) metal market prices, B) Ecoinvent database, C) Thermodynamic rarity. Specific energy for concentration is in GJ/t-ore

The second allocation studied comes from Ecoinvent database aforementioned in section 3.4 [177]. Results are shown in the Figure 5-6B, which illustrates an allocation for two different mines, one located in South Africa and another located in Russia. Cost allocation is different in both mines as they are calculated according to the main metal sold and the by-products extracted. For instance, in the South African mine, cost allocation for Ni represents 7% (being the main metal Pt with 66%), while in the Russian mine, it represents 47% (being Pt 11%). The average of both mines has been calculated based on their respective allocation by mass and revenue, obtaining 50% for Ni, 30% for Co, and 20% for PGMs.

The last cost allocation proposed has been undertaken considering the thermodynamic rarity values of these metals represented in Table 3-1 in section 3.2.3 [112]. Results are shown in Figure 5-6C. With this approach, the cost distribution has been calculated as follows: 40% for Ni, 29% for Co, and 31% for PGMs.

Table 5-5 summarizes the values obtained with each methodology used for cost allocation calculation. In the first case, when assessing the economic viability of a mine using market prices, the distribution provides a larger share to metals with higher market prices, even if the quantity extracted is lower for some metals. However, this allocation is not based on physical properties or sustainability conditions and can be highly volatile, depending on political and demand factors. In the second case, using data obtained from Ecoinvent, the allocation in tons could vary depending on the mine and the main metal extracted. However, these two approaches do not fully capture the situation of these metals and their scarcity. The third approach, based on thermodynamic rarity, allocates costs not based on economic terms but rather on the scarcity of these elements in the Earth's crust. More comprehensive and complementary studies have been conducted to analyze different cost allocation strategies that take into account market prices, tonnage, and energy considerations [280].

Table 5-5. Summary of the different types of cost allocation methods analyzed in the case of Ni, Co, and PGMs.

	Ni	Co	PGMs
Market price (2010-2020)	61%	6%	33%
Ecoinvent	50%	30%	20%
Thermodynamic rarity	40%	29%	31%

Nevertheless, as depicted in Figure 5-6, cost allocation using data from Ecoinvent and thermodynamic rarity might yield similar results. However, for the specific purposes of this analysis and the analysis conducted, it has been determined to utilize thermodynamic rarity as it places greater emphasis on metal scarcity, which is an indicator rooted in the physical state of a metal.

5.5.3. Limit of recovery

As mentioned in section 3.5, there are different studies and considerations to calculate the limit of recovery. This thesis adopts the approach presented by Rötzer et al. [53], considering the uncertainty surrounding future technological advancements. As a result, the best available technology has been applied to develop this model [281]. Regarding ore grade, Sverdrup et al. [182] considers that the limit of extraction for a mineral in any mine is 0.5 g/t. However, there is no technology currently capable of reducing concentrations to lower levels, and such a process would not be economically feasible [182].

In this case, the limit of recovery (LOR) is applied to calculate the limit of extraction. As it was already explained in section 3.5, the concentration chosen is 2.4 x10^{-6} wt-%, which represents the metal content in tailings of PGMs [185]. According to Figure 5-6C, the energy associated to such a limit would be set at 992,124 GJ for Ni and Co. Table 5-6 presents the LOR values for PGMs, Ni, and Co. In the case of Ni, the value obtained was even lower than the value for crustal concentration. This can be attributed to the relatively high concentration of Ni in mines, which is several orders of magnitude above the proposed limit. Hence, when the energy used for the LOR is applied in Ni, the minimum concentration for this metal produces an incompatibility, being lower than the crustal concentration. Since it is not possible to have lower ore grades than the crustal concentration, this value has been selected as the minimum ore grade to be able to extract Ni.

Table 5-6. Limit of recovery (LOR) obtained in this study and crustal concentration for Ni, Co, and PGMs [wt-%].

Metal	LOR	Crustal concentration
Nickel	4.00 x10^{-4}	4.00x10^{-4}
Cobalt	6.89 x10^{-5}	5.15 x10^{-7}
PGMs	2.40 x10^{-6}	3.95 x10^{-8}

Figure 5-6 illustrates the trend expected for the beneficiation process obtained for Ni, Co and PGMs found after carrying out the simulation (note that every black dot represents a scenario, in some cases, for scale reasons, not all the 12 scenarios are present in all the figures). In this case, cost allocation has been carried out using thermodynamic rarity.

Besides the dots corresponding to the ore grade corresponding to each scenario, three other key points must be considered. Firstly, current ore grade. As explained, these values have been obtained from the literature [185]. Various studies have proven that recovering metals from tailings can be profitable [282], [283]. They could be essential to cover future demand for certain metals, and even in some cases, the concentration in those tailings could be similar to the current ore grades in mines [284]. Concentration from tailings for PGMs is 2.4x10^{-6} wt-%, 0.3% and 0.014% for Ni and Co, respectively [185]. The last key point is the LOR, which corresponds to the first column in Table 5-6 and that, in the case of Ni, it is equivalent to the crustal concentration.

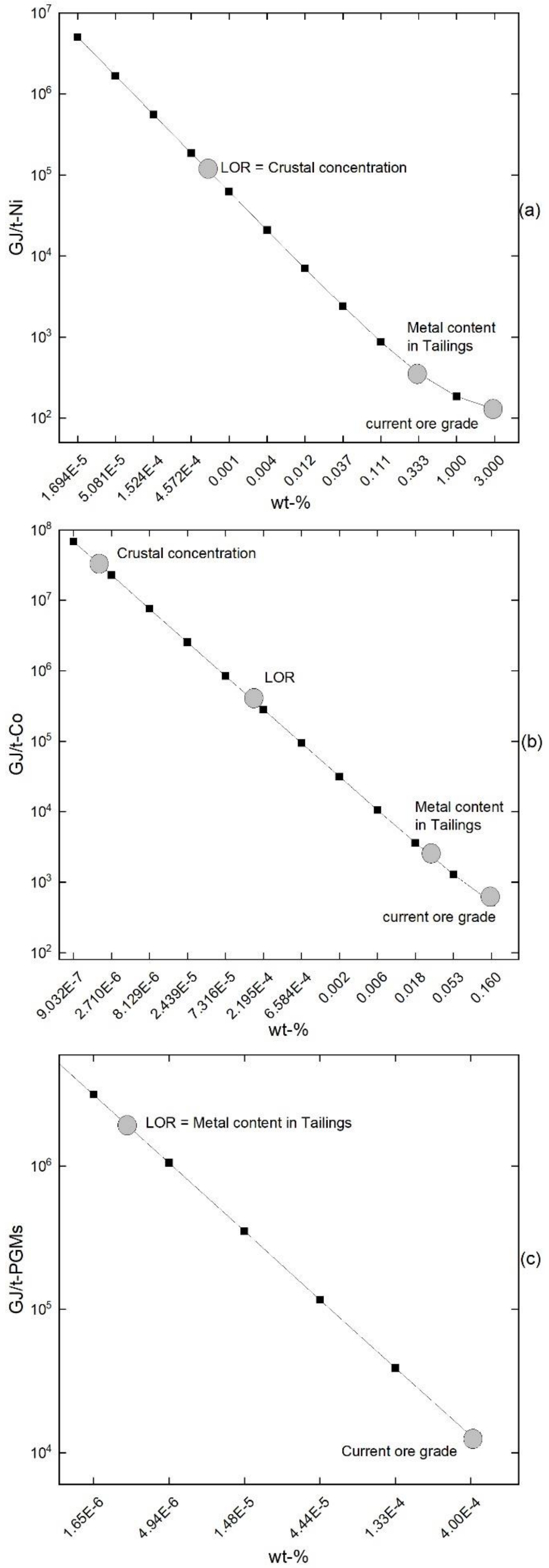


Figure 5-7. Estimation of the specific energy for concentration for Ni (A), Co (B), and PGMs (C) [GJ/t-ore] with cost allocation carried out using thermodynamic rarity

In the case of Ni (Figure 5-7A), in the first scenario, the primary energy share corresponds to the refining process. However, when the ore grade decreases, comminution becomes more relevant. This can be observed in the curve, shifting towards an exponential trend. The tailings ore grade (0.3 wt-%) is reached around Scenario 3. This could become more relevant in the near future, as current tailings still contain a relevant amount of Ni that could soon become economically profitable to recover if the average ore grade in the mines decreases to that extent. A similar situation can be seen for Co (Figure 5-7B), where tailings ore grade is reached before Scenario 3. Still, the tailing ore grade for Co is one order of magnitude lower than the tailings ore grade for Ni. In both cases, the LOR is still several orders of magnitude lower and, as stated before, in the case of Ni, the LOR value is equivalent to the crustal concentration. As for PGMs (Figure 5-7C), current ore grade in the mines is considerably lower. As previously discussed, the limit for LOR was established using the energy needed to extract a ton of PGMs from tailings, and in this case, LOR is equivalent to the ore grade in tailings. Comparing these values, it is evident that LOR is only two orders of magnitude lower than the current ore grade. This situation could create potential supply problems in the future if all mines start to become depleted.

5.6. Analysis and implications of energy consumption

An estimation was conducted to observe how the specific energy for concentration (measured in GJ/t of metal) as the ore grade decreases until it reaches minimal values. As such, three values have been used for comparative purposes: current ore grade in mines, tailings ore grade, and LOR (minimum concentration). Additionally, to put these results into perspective, they have been converted into tons of oil equivalent (toe) per ton of metal, simply multiplying the value in GJ by the conversion factor 0.024. Table 5-7 summarizes the values obtained for each scenario and metal.

Table 5-7. Comparison of the specific energy for Ni, Co, and PGMsl for three scenarios: A) current ore grade, B) tailings ore grade, C) LOR

	Ni			Co			PGMs		
Sce.	wt-%	GJ/t-Ni	toe/t-Ni	wt-%	GJ/t-Co	toe/t-Co	wt-%	GJ/t-PGMss	toe/t-PGMs s
A	3	128.39	3.06	0.16	514.86	12.29	$4x10^{-4}$	13,210.65	315.53
B	0.3	355.49	8.49	0.01	3,601.84	86.02	$2.4x10^{-6}$	992,124	23,696
C	$4x10^{-4}$	992,124	23,696	$6.9x10^{-5}$	992,124	23,696	$2.4x10^{-6}$	992,124	23,696

In 2020, the production of Ni was 2,510,000 tons, 142,000 tons for Co, and 383 tons for PGMs [242]. If these values were multiplied by the corresponding values of toe/t for each metal, the total amount would be over 9.56 Mtoe. Australia endows one of the largest reserves in the world of Ni [185]. In this way, this energy would represent more than 31% of the total Australian mining energy consumption in 2019 [285]. It is also noteworthy to highlight that in the case of tailings (scenario B), the energy, when compared to scenario A (current ore grade), increases almost three-fold in the case of Ni, while for Co, this same value increases seven-fold. A more drastic increase can be seen when comparing scenarios B and C.

To provide context for the situation regarding PGMs, the best-case scenario (Scenario A) depicts a situation where energy consumption has been multiplied by the estimated remaining reserves, which stand at 70 kton according to the United States Geological Survey (USGS). Consequently, to extract these reserves, over 22 Mtoe (Million Tons of Oil Equivalent) of energy would be required. This represents approximately 16% of the total energy consumption in Australia in 2019 [285].

5.6.1. Economic assessment

With the simulation carried out and the specific energy data obtained, it is possible to proceed with an economic assessment to evaluate the energy costs for each metal and compare them with their respective current market prices. Comminution and flotation are mainly powered by electricity. Diesel is used during the ore handling phase, while natural gas and coal are used during the different metallurgy processes. Consequently, since all the values previously obtained are in energy terms, converting them into monetary terms using energy prices is a simple process.

As Australia is a country with a prominent mining industry, electricity, and energy prices for this country are going to be used. Although there are countries with a higher current production of the metals considered in this study, Australia also has one of the world's highest mineral reserves. Additionally, the Australian Government periodically publishes electricity and energy prices. As such, according to the Australian Energy Regulator, the average prices in 2020 were 0.29 USD/kWh, 0.073 USD/kWh, and 62 USD/ton, for electricity, natural gas, and coal, respectively, while for diesel, the price was 1.22 USD/l [286]. Combining this data with the specific energy previously calculated, it is possible to determine the energy costs for the simulations for each metal as a function of the evolution of the ore grade (Figure 5-8).

Additionally, a comparison can be made between the energy costs of each metal in each scenario and simulation, and the current price of each metal. According to USGS statistics, in 2020, the average Ni price was 14,109 USD/ton. For Co it was 35,200 USD/ton, and more than 30,000,000 USD/ton for PGMs [287]. As a result, the price for PGMs has been calculated as an average of the six metals included in the PGMs group. As the metal market prices can be very volatile and change considerably over time, three prices are included in the analysis carried out in Figure 5-8: 1) 2020 price, 2) maximum historical price, and 3) current price multiplied by ten.

Considering the energy costs calculated for scenario 1, it is possible to obtain the share of the metal price that corresponds to the energy costs. In the case of Ni, current energy costs represent 63% of the metal price. A similar situation can be seen for Co, with a 67% share, while for PGMs, this number is only around 3%.

Furthermore, electricity and diesel prices fluctuate based on economic and political issues. An example of this situation is the increase that occurred at the beginning of

2022 in Australia when the electricity price increased 100% [286]. For this reason, different scenarios have been created considering: 1) the aforementioned energy prices, 2) a two-fold increase in energy prices, and 3) a five-fold increase in energy prices.

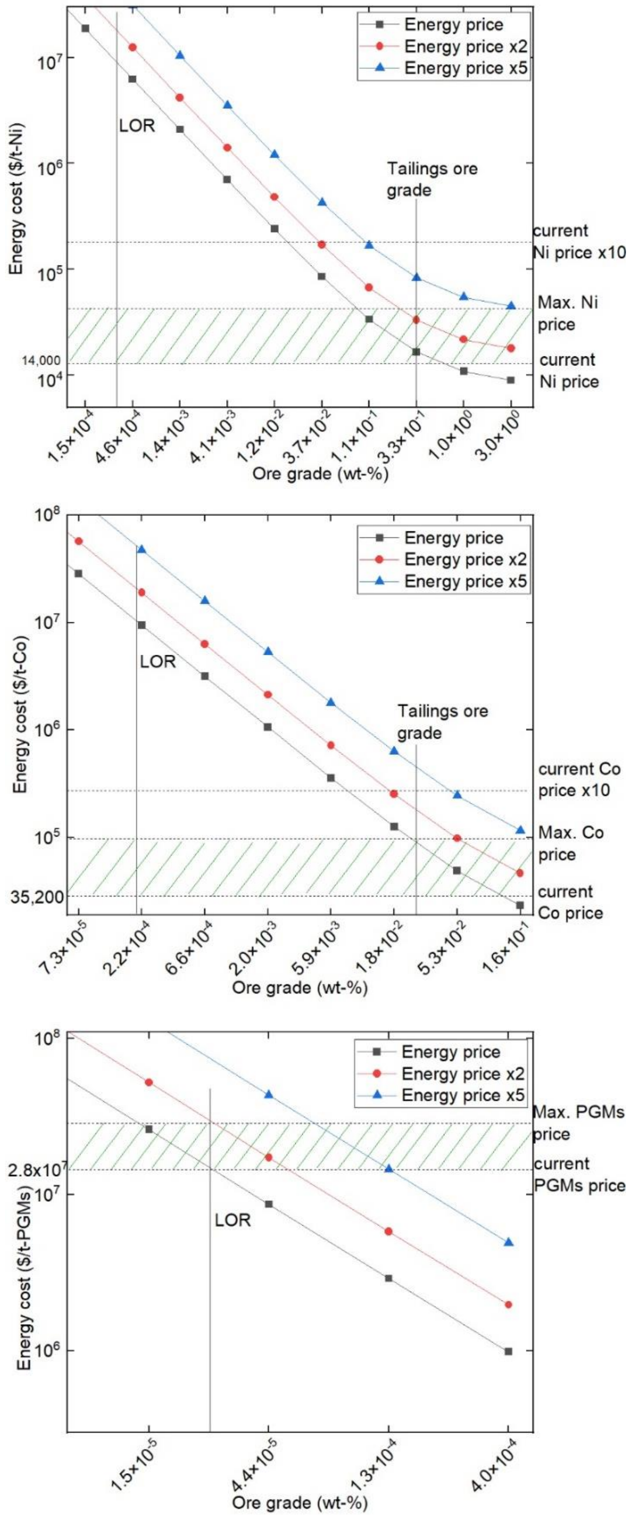


Figure 5-8. Energy cost as a function of the ore grade for Ni, Co and PGMs. The striped area represents the area between the current and maximum historical price of each metal.

Analyzing the relationship between energy and metal market prices, the case of Ni is especially representative because the striped area covers the situations where extraction from tailings could be profitable given the current energy price and if this price were to double. A different situation can be seen if the energy price increases fivefold. In this case, it would not be economically beneficial to extract Ni from tailings, even with a severe increase in the metal market price.

Regarding Co, the striped area would cover the first two energy price scenarios (current price and price multiplied by a factor of two) when considering the current ore grade in mines. Still, in the case of tailings, the situation is different and could only be profitable under certain conditions and maintaining current energy prices. Even a slight increase in energy price could make this process unprofitable if the metal market price remains within the striped area. However, if Co price increases, it would be viable to recover the metal from tailings and even from materials with an even lower concentration. Nonetheless, the energy costs associated would be considerably higher as it would be necessary to increase the amount of rock processed.

Lastly, PGMs present a unique situation due to the scarcity of these elements in the crust and their current market prices. As previously mentioned, the current energy cost only represents 3% of the current PGMs price. This is why the striped area is so high with respect to the current ore grade compared to the situation observed in the two previous elements. This can be explained by the very high price PGMs usually have, which can only be compared to that of gold. In this case, PGMs tailings with the lowest ore grade have been selected as the limit of recovery (LOR) to determine the minimum energy required for extracting any metal. If the ore grade decreases to that level and the energy costs are maintained, it would still be profitable to recover PGMs. The energy costs would have to increase more than two-fold to make the recovery unprofitable. However, it is worth noting that these prices may already incorporate certain energy costs associated with other metals, thereby reducing the initial share of energy costs, and increasing the overall profit. It is also important to consider that apart from energy costs, there are other expenses such as operation, maintenance, and management that need to be factored in when determining the overall profitability of these metals.

In this regard, it is essential to mention that mines are designed to be economically profitable. It is commonly observed that the metal that generates the maximum profit receives higher cost allocation since the market price of the metal is higher [288]. On the other hand, companion metals, with a lower market price, receive less allocation to obtain more benefits when metals are sold. Although there are no universally standardized criteria when applying cost allocation, economic assessment is commonly employed in the mining industry as mining companies main goal is to derive profits from mineral extraction. For that reason, an analysis has been carried out to identify what would happen if allocation changed. Since Ni is the most extracted metal out of the three used in this study, a more significant share of the total cost allocation will be considered, starting from 40% to 70%. These results will then be compared with the current price. Table 5-8 summarizes the results of this analysis.

Based on the results of this analysis, the main conclusion is that by increasing the cost allocation for Ni, the extracting costs for Co and PGMs reduce considerably (almost 50% in the case of PGMs), while Ni extracting costs increased only slightly. This can be easily seen if the energy costs are compared with current metal prices. As mentioned, the energy cost for Ni, Co, and PGMs represents 63%, 67%, and 3%, respectively, of the current price. However, if this comparison were made with the highest allocation for Ni (70%), the energy cost associated with this metal would be 69% of the current Ni price, while for Co, it would change to 47% and 1.5% for PGMs.

Table 5-8. Extracting costs obtained according to different allocations for Ni, Co, and PGMs [€].

	Current price			Current price x2			Current price x5		
	Ni	Co	PGMs	Ni	Co	PGMs	Ni	Co	PGMs
Ni 40% Co 29% PGMs 31%	8,985	23,292	983,960	17,970	46,583	1,967,920	44,925	116,459	4,919,799
Ni 50% Co 24% PGMs 26%	9,223	21,063	829,338	18,446	42,125	1,658,676	46,115	105,313	4,146,690
Ni 60% Co 19% PGMs 21%	9,461	18,833	674,716	18,922	37,667	1,349,432	47,305	94,167	3,373,580
Ni 70% Co 14% PGMs 16%	9,699	16,604	520,094	19,398	33,208	1,040,188	48,495	83,021	2,600,470

5.7. Conclusions

This study examined Ni, Co, and PGMs from various perspectives. The specific energy for concentration has been calculated for the different processes carried out during the beneficiation process. The amount of energy needed to extract a ton of different metals has been calculated using current concentration in mines, in tailings, or when an ore grade limit is reached. In this case, several key factors have been considered, including the energy cost of extraction, the limit of recovery (LOR) for each metal, and the potential impact of price fluctuations on the mining sector. These approaches allow for the examination of outcomes in different scenarios. The main conclusions are summarized as follows:

- As mines become depleted, the recovery of metals from tailings emerges as a potentially viable solution. However, the energy requirements would increase significantly, reaching 2.5 times higher than the current ore grade for Ni, 7 times higher for Co, and more than 75 times higher for PGMs.

- A cut-off grade, referred to as the limit of recovery (LOR), has been calculated and proposed. The LOR was determined based on the maximum energy of extraction, which was obtained from the PGMs content in tailings, which is 2.4×10^{-6}. The energy calculated for PGMs is then extrapolated to the energy curve for Ni and Co, obtaining the LOR for these metals, which is 4×10^{-4} for Ni, and 6.9×10^{-5}.
- Values of specific energy obtained for low ore grade mines are very high. In the case of Ni, the energy extracting from the LOR respecting the current ore grade is almost 8,000 higher, 2,000 times higher in the case of Co, while for PGMs is 75 times higher.
- It has been stated that the cost allocation provided by the thermodynamic rarity is the most accurate for this study. This is because the methodology is not based on market prices or political situations, but the scarcity of each metal in the Earth's crust.
- It has been observed that extracting Ni from tailings could be profitable with both the current energy price and even if this price were to double. In the case of Co, recovering it from tailings would be profitable with the current energy price, assuming the Co market price remains at its peak. As for PGMs, the market price is already very high, making it profitable to extract PGMs from tailings at the current energy price.
- The economic assessment has also shown the importance of cost allocation. The current energy cost would represent 63%, 67%, and 3% of the energy price of Ni, Co, and PGMs, respectively, with the thermodynamic rarity allocation. As a result, in order to evaluate the profitability of the extraction of a metal, the market price must be taken into account.

Continuing this same line of research, the subsequent chapter will delve into the assessment of niobium and tantalum extraction from mines, as well as the feasibility of extracting these elements from tailings.

Chapter 6. Assessment of the energy cost of extracting niobium and tantalum from the tin slags of the old Penouta mine.

6.1. Introduction to the chapter

Similar to previous chapters, the same analysis will be carried out here, in particular for coltan, which is a metallic ore composed of niobium (Nb) and tantalum (Ta). The energy cost of extraction will be calculated when the ore grade declines. Selected concentrations will be compared to assess the feasibility of extracting the metals from these ore grades. One concentration is the metal content in tailings. The decision to analyze this point stems from the recognition that with limited global reserves of these metals, mine tailings could emerge as significant sources in the future. The selected mine is a real mine located in Penouta, Galicia, in the north of Spain. While the mine was not originally designed for the extraction of niobium or tantalum, the tailings exhibited a substantial concentration of these two metals, making it interesting to analyze their potential from an economic perspective. Subsequently, a simulation has been conducted in HSC Chemistry, not only for calculating the energy cost of extraction but also to assess the impact and feasibility of the extracting process for tailings. The information of this chapter can be found in **PAPER III** and **PAPER IV**.

6.2. General overview

Kumar et al. [99] have referred to the 21st Century as the Technological Age. However, due to the significant importance of niobium and tantalum, Monsalve et al. [289] have argued that we live in the Coltan Age, rather than the Technology age.

Ta and Nb are becoming key metals in the green energy transition, occurring in large amounts of electric vehicles. This is why both elements are listed as critical raw materials in various studies (e.g., Calvo et al. [112] and Moss et al. [290]) and by institutions like the European Commission's Critical Raw Materials list [117] and the United States Government's report on Critical Defense Materials [291].

Although coltan is vital for a functioning society, various issues related to its extraction and production must be considered [292], [293]. For example, coltan extraction is mainly concentrated in the Democratic Republic of Congo (DRC) and Rwanda, two countries that arguably do not respect human rights and whose extraction processes have been questioned many times by international organizations [292]. The United Nations has published several reports asking for governments, markets, and companies to monitor the supply chain of these metals [294], [295]. A similar movement is also led by the Group of 8 (G8). With the promotion of a voluntarily certified trade chain (CTC) in mineral production, the aim is to prevent poverty and encourage political stabilization. The use of materials from conflict countries, could be reduced and a reward provided for suppliers who focus on using “blood free” materials [296]. Besides, other sources could be explored to meet the demand.

In this respect, the long mining tradition has left many abandoned facilities and discarded materials such as tailings, which are also a source of concern [297]. This can be attributed to various factors, including technological limitations during the extraction process and the relatively low prices of the commodities. Accordingly, waste rock that in the past was considered non-profitable might even have higher metal content than current operative mines [297]. Such is the case of a mine in Kasese, Uganda, where Co-rich tailings generated during the primary extraction of copper are now being reprocessed years after the mine ceased operations [282]. On the other hand, if the remediation process is insufficient, it can cause a series of environmental impacts. For example, tailings can contain certain elements whose mobility and dispersion may pose an environmental hazard for soils, water, ecosystems, and people [128], [129].

Wastes from abandoned mines could become a relevant source of raw materials in the future, thereby increasing the domestic supply of metals that are currently almost all imported. However, the metallurgical processes to recover valuable metals from tailings usually involve the use of toxic substances. Therefore, the processes that can be applied have to be studied in depth, analyzing how the use of reagents could be minimized to avoid further impacts.

The main goal of this analysis is to evaluate the evolution of the specific energy needed to concentrate Nb and Ta as a function of ore grade decline. This way, it will be possible to estimate the point at which tailings become a viable alternative to current mines from an energy perspective. Various studies in the literature follow a similar approach, recovering gold through a unique beneficiation process [175]. In the particular case of Nb and Ta, as they are both recovered during the beneficiation and refining stages as by-products of tin ores, the complexity of the process is higher, and the consequences of ore grade decline are worth studying in more detail.

Lastly, the analysis presented has been carried out using specialized software called HSC Chemistry, modelling the entire mining and metallurgical processes required to obtain pure Ta and Nb as a final product. Accordingly, the software was set and optimized to maximize its efficiency and identify costs of chemicals, water, electricity, and emissions.

6.3. Niobium and tantalum production and availability

Given that both metals are related to the use of new technologies, the global extraction of Nb and Ta has increased in the last decades [284]. According to the United States Geological Survey (USGS), Brazil is the largest Nb producer at a global level, and this trend has been maintained over the most recent decades (Figure 6-1). Furthermore, in 2020, Brazil accounted for 91% of the world's Nb production, making it the primary producer, followed by Canada with an avearege of 8% [287]. Nb reserves are also mainly concentrated in Brazil (95%) and Canada (3.5%), and to a lesser extent in Angola, Australia, and South Africa, among others [298].

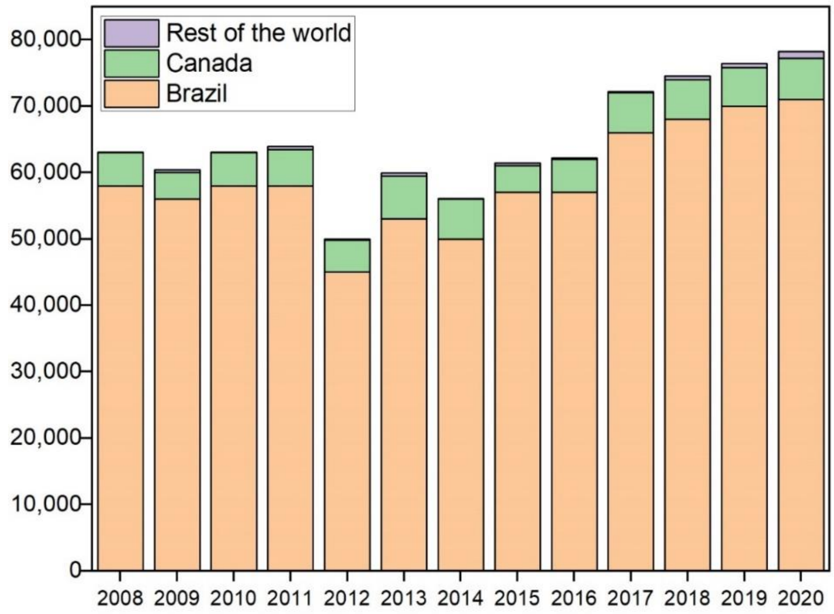


Figure 6-1. Global production of Nb in the last 15 years. Data in metric tons, adapted from [287].

As for Ta, one of the most valuable ores from where this metal is extracted is coltan. Coltan is a combination of two minerals: tantalite ($(Fe,Mn)Ta_2O_6$), where Tapredominates, and columbite ($(Fe,Mn)Nb_2O_6$), where Nb predominates. For this reason, coltan is also an important source of the latter.

Australia has been the largest producer of this metal for several years, holding more than 60% of the total share in 2005 [299]. However, in 2008, there was a noticeable reduction in Australian production (see Figure 6-2). This was mainly due to the closure of one of its main exploitations in 2010, Sons of Gwalia, which reduced Australia's production drastically [292], [299]. More recently, the Wodgina mine, also located in Australia, ceased production in 2017 as Ta concentration was too low to be cost-effective [300]. However, in 2018, a new mine was opened in Pilgangoora, extracting Ta as by-product of lithium [301]. This is why starting from 2010, African countries, especially those in the Great Lakes Region, have significantly increased their Ta production, contributing to more than 50% of the global share. Nonetheless, it is important to approach this figure with caution, as not all mining production is consistently reported in official sources, and the actual amount extracted could potentially be even higher than reported [302].

Although Central Africa has been the main producer of Ta in the last decade, the largest reserves are not located in that region. According to Nikishina et al. [303], South America holds 41% of the total Ta reserves of the world, followed by Australia with 21%. As for Nb, reserves are mainly concentrated in Brazil, with 16,000,000 tons, and Canada, with 1,600,000 tons [304].

Still, there is a limited amount of both elements in the Earth's crust. Sverdrup et al. state that the Ta maximum production peak occurred in 2005 [182], while Calvo et al. claim it will occur in 2039 [255]. As for Nb, the expected maximum production peak could be around 2030 [182]. While there may be a significant difference between these estimations, the order of magnitude remains quite similar (note that this data has been calculated taking into account the historical data production, which it could not be accurate for the reasons abovementioned). Even with an increase in reserves, it may only slightly delay the inevitable depletion in the long run [255]. When considering the expected growing demand for Nb and Ta, the supply of these metals could be at risk in the medium term.

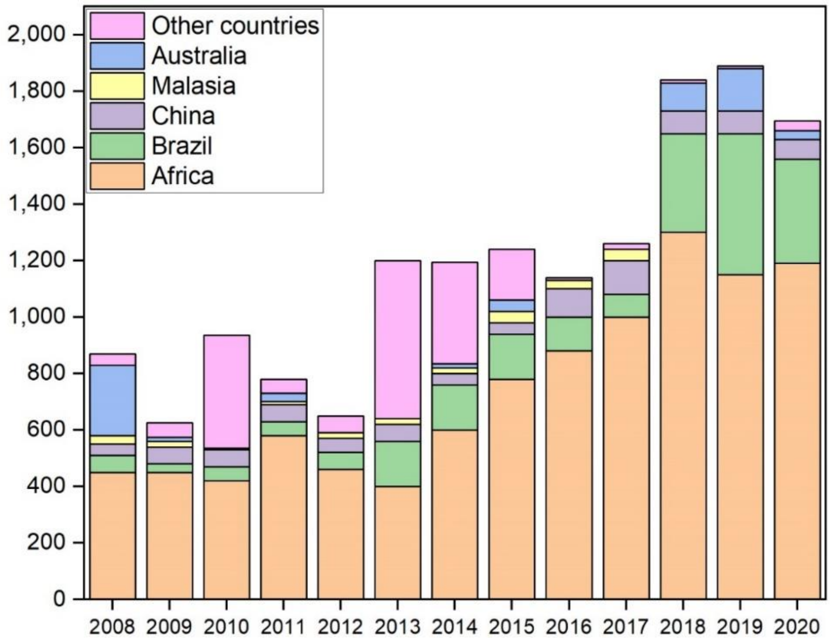


Figure 6-2. Global production of Ta in the last 15 years. Data in metric tons, adapted from [53].

6.4. Explanation of the model

As was explained in the previous section, Ta and Nb often occur together in different minerals and in combination with oxide impurities [305]. As these metals have similar chemical and physical properties, it is difficult and costly to separate them and obtain a high metal concentration [306]. Ta and Nb sources can be divided into three main groups: pyrochlore, alkaline, and granites [307]. Within these sources, many minerals contain Ta and Nb. Still, only two are currently cost-effective: titano-niobates and tantalum-niobates [308]. But if the ore grade decreased to a point where the process was no longer cost-effective, it would be necessary to look for alternative sources for these metals [284], [309].

The flowsheet drawn in Figure 6-3 illustrates a general process for the extraction of Nb and Ta as by-products of a tin mine [188]–[191], [310].

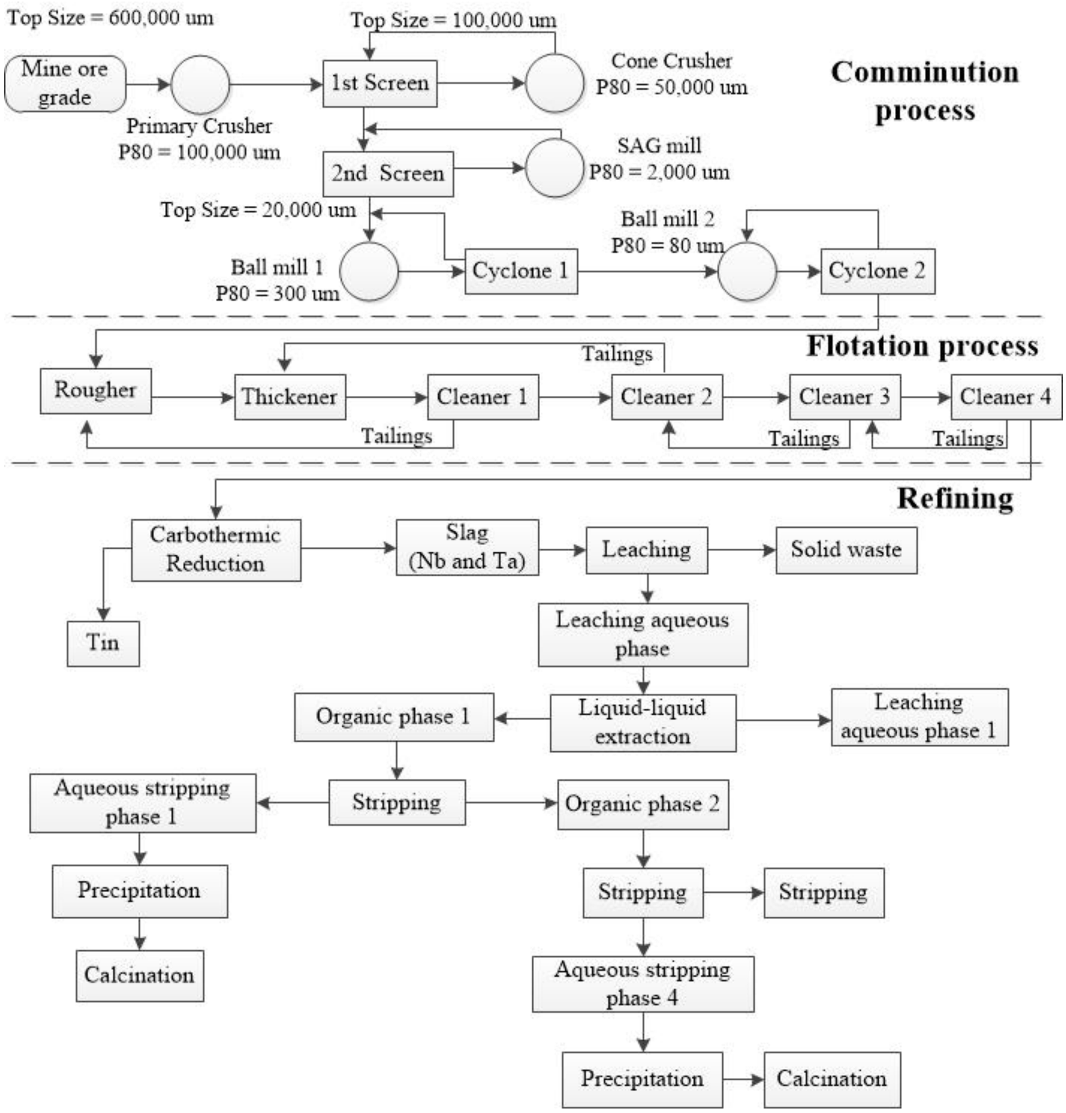


Figure 6-3. Flowsheet for the extraction of Ta and Nb

An extensive literature review has been carried out to obtain reliable data to run the simulation: ore grade in the mines, concentration needed before refining the feed, the number of cleaners and roughers needed to concentrate the mineral, and power used in the comminution process, etc.

The average coltan concentration in the crust is around 2 ppm (parts per million) [292], [308], however, in the mines, this concentration is higher. For the simulation, cassiterite-columbite mineral-bearing has been chosen as a reference, with a global average in a mine of 0.2 wt-% [307], [311]. This value is similar to the one found in the Penouta Mine (Spain) [312], [313]. However, although the global average concentration is 0.2 wt-%, this value could vary in a certain range. Accordingly, based on the literature review, it is possible to find a range of concentrations for Ta and Nb in mined ore, as reflected in Table 6-1 [312].

Table 6-1 also shows the concentration during the beneficiation process for both elements. The concentration gradually increases in the first steps. After the flotation process, the Ta concentration must be 8.45 wt-% for Ta and 5.40 wt-% for Nb, something that is achieved using additives. Then, the purification of each metal is carried out during the refining process, reaching a final concentration of 79.67 wt-% and 98.45 wt-% for Ta and Nb, respectively.

Table 6-1. Concentration along the beneficiation and refining process for Ta and Nb [wt-%]

	In mined ore [312]	After flotation [309]	After refining [306], [309]
Ta_2O_5	0.51-3.7	8.45	79.67
Nb_2O_5	0.16-2.22	5.40	98.45

The first step is to determine the amount of rock per hour to be treated, selected as 1 ton per hour (tph). After the setup of all the required equipment, flows, and the identification of reactions taking place, the quantities of reagents necessary for the entire process, including each unit, were determined. Additionally, the outputs of metals and electricity usage, among other factors, were obtained. These details will be described in the following sections.

The ore grade and energy consumption evolution are then analyzed using twelve different scenarios. The initial concentration is calculated as the average between the lowest and highest concentration values, 2.1 wt-% and 1.2 wt-% for Ta and Nb, respectively. Accordingly, this concentration is decreased consecutively by one third in each scenario. This way, the future behavior of mines can be simulated, estimating the specific energy for concentration for each metal from current mines to the worst-case scenario.

The specific data used in the simulation for the different steps of the extraction of Ta and Nb are described next.

6.4.1. Comminution

In the simulation, Nb and Ta are extracted from Sn ores, specifically, cassiterite. Thus, it is necessary to establish a feed for the comminution process to proceed with the calculations. Twelve different feeds have been defined, one per scenario, as shown in Table 6-2, to analyze the evolution of energy consumption.

As stated previously in section 3.6.2, Bond Index is an important factor for the calculations in the comminution process (which holds the highest energy share for low ore grades). This study has selected a value found in the bibliography (12 kWh/t) according to certain parameters, such as the bearing mineral and the concentration of metals in the mineral [194]. Different Bond indices could influence the final results obtained in the model.

Table 6-2. Feed for every scenario created in the simulation of the recovery process for Ta and Nb.

Scenario	Feed [t/h]	Scenario	Feed [t/h]
1	400	7	800
2	450	8	1,000
3	500	9	1,400
4	550	10	1,800
5	600	11	2,400
6	700	12	3,000

If the ore grade decreases, it is necessary to process more rock to obtain the same amount of ore [314]. For this reason, the feed is increased by 50 t/h until the fifth scenario. Then, it increases from 100 t/h up to 600 t/h, reaching the feeds limit for the final scenario, 3,000 t/h. This last scenario considers a very low ore grade in the mine, close to depletion.

With this noticeable increase between scenarios, the software can reach the concentration goals established during the different stages of the simulation, avoiding any feed deficit.

Various studies have been conducted to determine the optimal particle size for the comminution process as it could affect the entire method [315], [316]. A too-large particle size could negatively affect further steps and lead to a less efficient flotation process. On the other hand, a too-small particle size could decrease the efficiency of the additives.

The comminution process begins with the crushing stage (Figure 6-4). As directed from the literature review [185], [191], the particle size is reduced from 600 mm to 50 µm in the regrinding unit, which has been incorporated at the beginning of the flotation process. With a top size of 600 mm, the feed is introduced to the Jaw Crusher to reduce the particle size to 100,000 µm. Some particles will have a smaller or larger size at the end, so a screen is applied to separate them. Larger particles are sent to the Cone Crusher unit, reducing its size to 50,000 µm to accomplish the requirements. Another screen is applied to filter the feed with a top size of 20,000 µm, sending larger particles to be reduced in a SAG Mill. When the feed of the second screen is filtered, the grinding stage starts, which is composed of a Ball Mill circuit followed by cyclones. In the first unit, the size is reduced to 300 µm, while in the second Ball Mill, the size is decreased to 80 µm. Cyclones are incorporated after every Ball Mill to avoid the presence of larger particles in further steps. The final step in the comminution process is regrinding. This step is applied at the beginning of the flotation process, reducing the particle size to 50 µm.

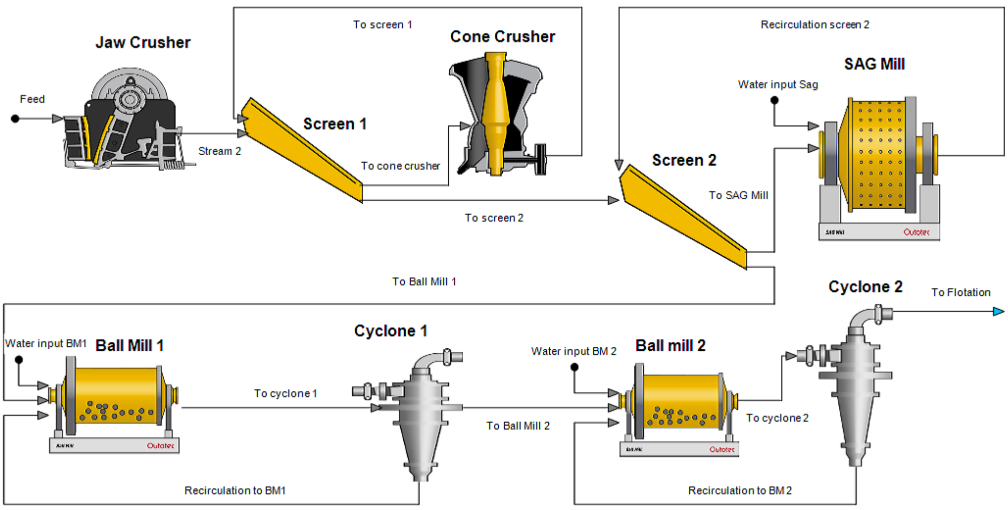


Figure 6-4. Comminution process in the simulation of recovery for Ta and Nb.

Table 6-3 summarizes the power demanded in every unit and the specific energy in kWh per ton of rock for scenario 1. The grinding process has the highest power demand. This could be explained due to the small particle size required in later steps. The smaller the particle size, the lower the efficiency, and therefore, more energy is needed to reduce the size to these values. These numbers are within the same order of magnitude as those obtained by Latchireddi et al. [231].

Table 6-3. Detail of the units of the comminution process for scenario 1 in the recovery of Ta and Nb.

Equipment	Power demand [MW]	Specific energy [kWh/t rock]
Primary crusher	0.36	0.38
Cone crusher	0.47	0.88
SAG mill	3.97	7.27
Grinding - Ball mill 1	22.92	12.05
Grinding - Ball mill 2	11.96	9.68
Re-grinding	3.73	10.46

6.4.2. Flotation

After the comminution process, the feed is introduced to a rougher where it is diverted into two outputs, the concentrated feed, and the tailings. The concentrated feed is sent to the last Ball Mill and, subsequently, to a thickener to separate the pulp. Then, several cleaners are applied to increase the feed concentration before sending it to the metallurgical process. The design of each cleaner in the process takes into account factors such as residence time, volume cell, or power requirements. However, it is important to note that the kinetics of the reactions are not being specifically considered in this analysis. Instead, the design parameters are based on data from the existing literature and previous studies [316], [317].

The lower the ore grade in the initial feed, the more cleaners have to be introduced before the flotation process, and more specific energy is required to obtain the concentration required at the end of the process.

6.4.3. Refining

As Nb and Ta have similar chemical and physical properties, their separation and purification processes are considerably difficult [308]. Still, they can be recovered from the slags generated after a carbothermic reduction [309], [318]. The metallurgical process developed in the flowsheet has been divided into two steps: 1) Sn recovery, 2) Ta and Nb recovery [318].

Figure 6-5 shows the flowsheet of the processes used to recover the three metals generated with HSC Chemistry. The process starts with the tailings coming from a particular mine, in our case, Penouta. For the recovery of Sn, the feed is sent to the refinery so carbothermic reduction can be applied. After this process, Sn is obtained with a concentration higher than 96%, while the slags contain a significant concentration of Ta and Nb, 25% and 21%, respectively [309]. As the final product should be 99.99% Sn, it is necessary to apply an electrorefining process in order to increase its concentration. To that end, an electrolyte of H_2SO_4 is prepared in order to separate impurities from Sn, increasing its concentration to the desired value [309].

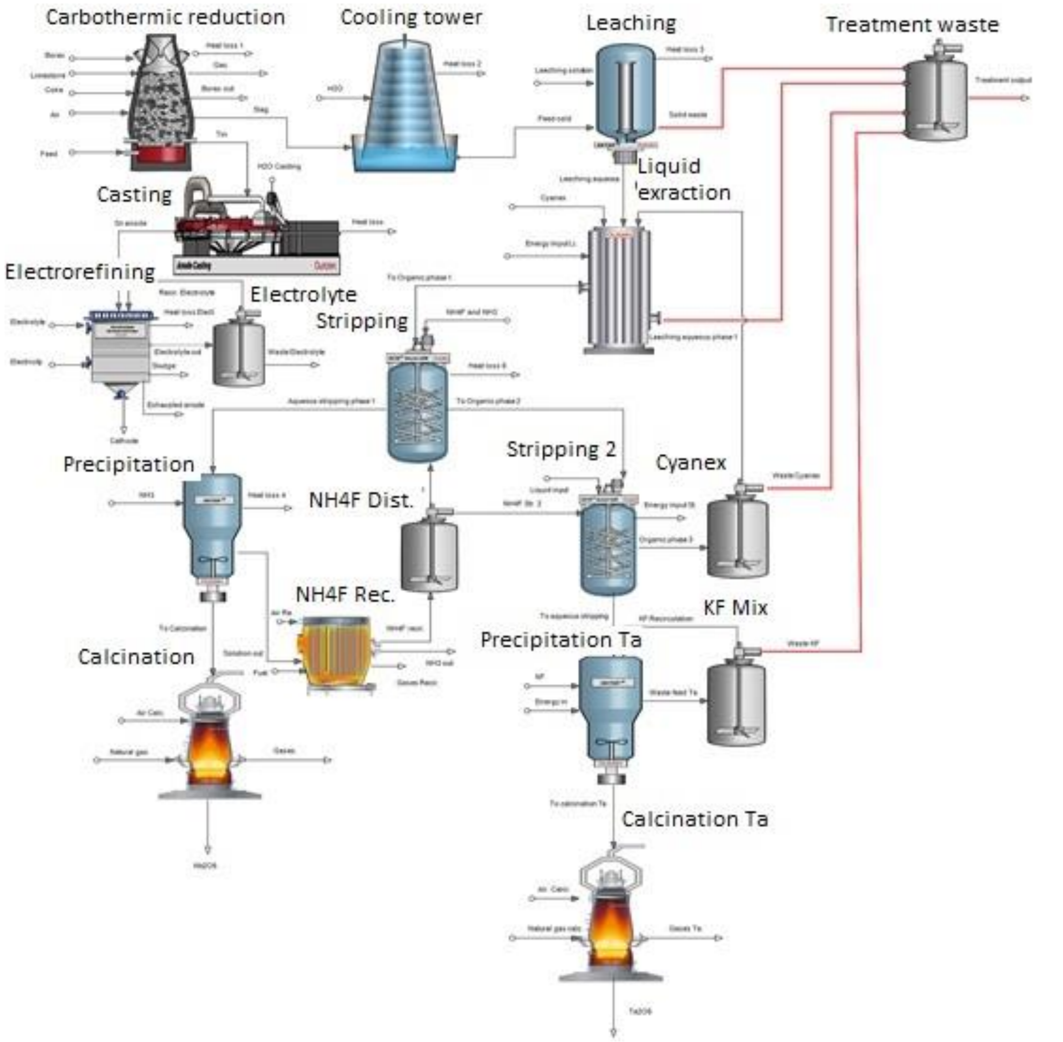


Figure 6-5. Flowsheet of the process used to recover Sn along with Nb and Ta from the slags generated in the carbothermic reduction.

On the other hand, slags are sent to different units to extract Nb and Ta. The feed is first sent to the leaching unit, obtaining solid waste and other outputs in an aqueous phase, which ends in the liquid-liquid extraction unit. It is then mixed with organic additives, discarding the leaching aqueous phase, and redirecting the organic phase output into the stripping unit. Additionally, NH_3 and NH_4F are added since this is the unit where Nb and Ta will be separated. By using these additives, a new enriched Nb aqueous phase is formed, finishing in the precipitation unit. Meanwhile, the other output, still in the organic phase, is sent to a new stripping unit to also convert it into an aqueous phase. It follows precipitation for both feeds, aiming at eliminating any impurities before continuing with the last phase of the process, calcination. Calcination is used to eliminate the undesired water and humidity, recovering at the end of the process, Nb with a concentration close to 99% and Ta with a concentration of 78%.

It is important to mention that there are also several recirculation units, and a vast number of reagents which are needed for this process. To reduce the total use of chemicals, feeds are recirculated and introduced again in the units when possible. One example is the “mixing Cyanex 923” unit, where 95% of the total Cyanex 923 is recirculated in order to maximize its use. Another one is the “mixing KF” unit. It is not possible to use 100% of this reagent due to the conditions needed in the extraction of Ta. For that reason, a recirculation of 65% is assumed, thereby re-using it as many times as possible. Results

It has been largely observed that energy requirements increase as ore grade decreases. However, more efficient machines and units could be developed and used to maintain the energy for the beneficiation process within the same order of magnitude. This is in line with additional studies, stating that, as reserves partially rely on economic factors, they could increase in the next two centuries for both metals, thus, eliminating possible risks of supply or bottlenecks [319]. That said, the question now is whether the recovery of key elements from low-grade deposits such as Nb and Ta would be cost-effective enough with the use of current technology. This process has been carried out at a lab scale [309], [318], validating the results obtained. Then, it has been up scaled with the software HSC chemistry.

6.5. Results

6.5.1. Specific energy for concentration

Ore grade values of Ta range from 2.1 wt-% in Scenario 1 to 0.000012 wt-% in Scenario 12, and from 1.2 to 0.000007 wt-% for Nb. Comminution and flotation processes are common for the three metals to be recovered: Sn, Ta and Nb. A cost allocation based on the metal output has been applied, with the following share: 80% for Sn, 12% for Ta and 8% for Nb. While cost allocation based on metal output has been applied in this study due to data availability, future research could potentially explore an additional analysis using market prices or thermodynamic rarity.

Table 6-4 illustrates the evolution of the specific energy for the concentration stage for Ta and Nb applied during the flotation process for the 12 scenarios.

Table 6-4. Ore grade decreased for the simulation and evolution of the specific energy for concentration obtained during the flotation stage for Ta and Nb. Data for ore grade wt-% and for the energy GJ/t-ore.

	Ore grade Ta	Ta	Ore grade Nb	Nb
Scenario 1 (con. in mine)	2.1	0.68	1.2	1.21
Scenario 2	0.7	1.14	0.4	2.17
Scenario 3	0.23	2.12	0.13	4.26
Scenario 4	0.077	6.11	0.044	12.23
Scenario 5	0.026	17.30	0.015	21.16
Scenario 6	0.0086	45.89	0.005	48.25
Scenario 7	0.0028	136.57	0.0016	178.23
Scenario 8	9.6×10^{-4}	328.41	5.48×10^{-4}	360.23
Scenario 9	3.2×10^{-4}	703.33	1.82×10^{-4}	768.15
Scenario 10	1.06×10^{-4}	1,729.44	6.09×10^{-5}	1,974.79
Scenario 11	3.55×10^{-5}	4,495.87	2.03×10^{-5}	5,280.51
Scenario 12	1.18×10^{-5}	13,135.13	6.77×10^{-6}	16,192.05

As shown, the specific energy required for concentration increases exponentially. In the case of Ta, the energy increases by almost 60% when the ore grade is reduced by one-third, moving from the first scenario to the second. In the case of Nb, the energy increases by nearly 55%. For ore grades lower than the 6th scenario, the energy increases by more than 30% for each scenario being calculated. This underscores the significant amount of energy that needs to be added to this process for low concentrations.

6.5.2. Specific energy for refining

Ta and Nb are extracted as by-products of Sn, as the slag generated during the beneficiation process of this metal contains a very high concentration of both elements. Therefore, a fair allocation must also be applied. At this stage, since both elements share the same processes, Ta and Nb account each for 50% of the costs.

It is also important to note that the metallurgical processes for both metals remain the same in all scenarios. This is because the concentration at the beginning of the metallurgical stage is always the same, and hence, the same processes will apply to every scenario.

With all processes simulated in HSC and the considered allocation procedure, the values calculated for Ta and Nb total refining process are 13.69 GJ/t-Ta and 13.21 GJ/t-Nb, respectively. This data is within the same order of magnitude as data found in other studies [320].

For these calculations, 31.4 MJ/kg has been chosen for the High Heating Value (HHV) for all the calculations where coal is required [240]. Additionally, natural gas is introduced in the calcination process at the end of the refining process; the value used in this case is 42.2 MJ/kg [321].

6.5.3. Total energy requirements as a function of ore grade

After carrying out the simulation, the energy requirements of depleted mines can be appropriately assessed. Two situations are compared: extraction from current mines and extraction from tailings.

Current ore grade in mines has already been established and is represented by Scenario 1, being 2.1 wt-% and 1.2 wt-% for Ta and Nb, respectively. Various authors state that there is a minimum concentration value from which beneficiation could be still profitable [170], [182]. Hence, we could even go beyond and analyze the extraction energy costs. In this case, LOR will not be used. Instead, the so-called ultimate recoverable resources (URR), which are defined as the total amount of a certain mineral that could ever be recovered and produced [322], will determine the lowest ore grade . Sverdrup and Rangnasdottir [182] proposed this limit grade at $5x10^{-5}$ wt-% for any metal. These authors' limit is based on the well-known Hubbert's peak model [323].

Figure 6-6 shows the evolution, in logarithmic scale, of the total specific energy for Ta and Nb, including the comminution, the flotation and the refining stage. Tailings 1 and 2, and URR depicted in Figure 6-6 are three relevant points with a particular concentration. The average values considered for "Tailings 1" are $4.4x10^{-3}$ wt-% for Ta and $3.6x10^{-3}$ wt-% for Nb, corresponding to those of the Penouta mine in Spain [283]. Tailings 2 is an even lower value that has been arbitrarily reduced one order of magnitude with respect to Tailings 1, i.e. $3.2x10^{-4}$ wt-% for Ta and $1.83x10^{-4}$ wt-% for Nb.

As observed, the specific energy experiences significant growth in both cases as the ore grade declines. It is important to note that the results are on a logarithmic scale, which means that the curve becomes exponential when the ore grade is drastically reduced or, in other words, when the mine approaches depletion. This aligns with the values calculated in this thesis for other commodities, as well as with findings from other studies, where the evolution of the energy consumption as a function of the ore grade in different mines was analyzed [47].

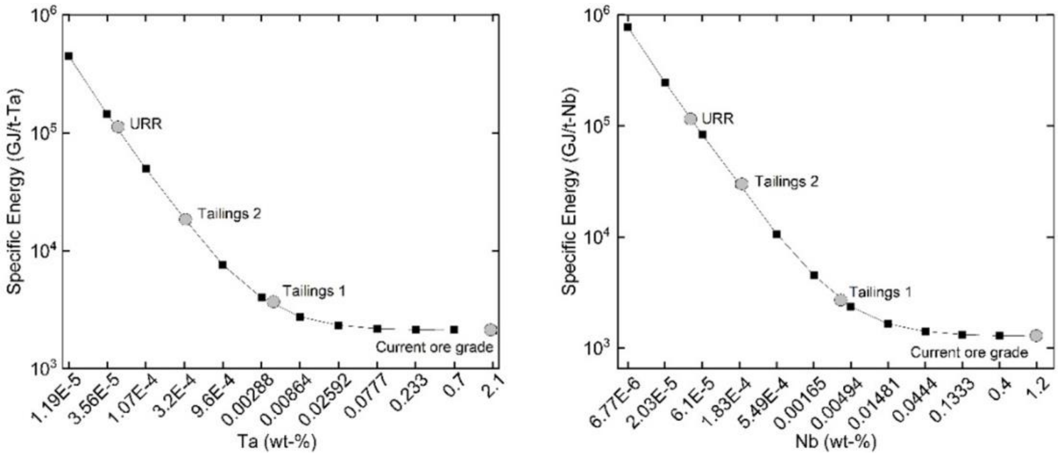


Figure 6-6. Specific energy for concentration for Ta (left) and Nb (right). In both cases, the Y axis is in log scale. For the sake of clarity, the points representing the scenarios have been joined to form a continuous line.

In the current case study, several reasons account for this growth. Firstly, the amount of rock that has to be processed in each scenario grows considerably [178], [278], [279]. As the ore grade decreases at the beginning of the beneficiation process, the feed that reaches the flotation circuit is less concentrated, implying that more units are needed to concentrate the feed. Alternatively, more time is required to obtain the desired grade for further processing, which results in more specific energy for the flotation stage. Unlike what is observed in the comminution and flotation processes, the specific energy for concentration for the refining stage is always the same, as stated in the previous section.

Table 6-5 illustrates the energy requirements obtained. As can be seen, with current ore grades, the energy required to recover Ta and Nb is around 900 GJ/ton for Ta and 80 GJ/ton for Nb. Reducing the concentration at the Tailings 1 grade would increase energy costs to about 2,140 GJ/ton of Ta and 1,550 GJ/ton of Nb. Going beyond this and considering Tailings 2 concentration would increase that energy to 17,540 GJ/ton of Ta and 28,700 GJ/ton of Nb. All such figures can be compared with energy requirements for the beneficiation of gold, one of the commodities for which ore grades are very low. As seen in Table 6-5 extracting Ta and Nb from tailings 1 or 2 would entail energy costs that are well below current energy costs for the recovery of a ton of gold, which according to Calvo et al. [47] is 145,000 GJ/t-gold. Accordingly, extracting Ta from Tailings 1 would require an energy cost equivalent to 1.48% of the energy cost for gold extraction. On the other hand, if the ore grade was equivalent to that in Tailings 2, the energy cost for Ta extraction would be 12.09% of the energy cost for gold extraction. For Nb, the figures would be 1.07 and 19.79%, for Tailings 1 and Tailings 2 grades, respectively. Such high energy costs for gold are only justified by its elevated market price, which in 2021 reached an average price of 58,000 $/kg [242]. Comparatively, the price of Ta was 160 $/kg and for Nb 20$/kg that same year, i.e. 0.28 and 0.03% of gold market price, respectively [242].

Table 6-5. Comparison of the specific energy and % of the energy compared with the gold beneficiation process, for the case of Ta and Nb.

Ore grade	Ta Wt-%	GJ/t-Ta	toe/t-Ta	%Com. gold[1]	Nb Wt-%	GJ/t-Nb	toe/t-Nb	%Com. gold[1]
Current	2.10	916.70	21.89	0.63%	1.20	78.47	1.87	0.05%
Tailings 1	$4.4x10^{-3}$	2,144.8	51.22	1.48%	$3.6x10^{-3}$	1,552.6	37.08	1.07%
Tailings 2	$3.2x10^{-4}$	17,541.8	418.97	12.09%	$1.83x10^{-4}$	28,709.7	685.70	19.79%
URR	$5x10^{-5}$	142,413	3,401	98.21%	$5x10^{-5}$	81,912	1,956	56.49%

[1] *% compared with the average energy requirements for gold beneficiation* [47].

Considering the URR concentration of $5x10^{-5}$ wt-%, the energy costs would increase to 3,401 toe/t for Ta and 1,956 toe/t for Nb, reaching similar energy costs as for current gold extraction (Table 6-5).

To put these values into context, considering the worst-case scenario from a production perspective, some authors estimate a future production of 6.5 kton of Ta in 2050 [251]. Regarding Nb, the expected demand for 2050 could increase up to 250 kton [319]. If this amount had to be extracted from mines that have reached their limit grade, the energy needed would represent almost 20% of the renewable energy generated that same year [324].

6.5.4. Economic assessment

Knowing the anticipated energy increases resulting from declining mine grades, we can economically assess the feasibility of extracting these elements from tailings. High energy costs in conjunction with low commodity prices are pivotal factors in determining the viability of recovering materials from tailings. Hence, it is imperative to take both these aspects into consideration.

The primary energy source applied during the comminution process is electricity. For the refining process, natural gas and coal also come into play. Energy values can be transformed into monetary values through energy prices. For the study, it has been decided to choose the prices in Spain since the mine is located in this country. In this way, the average price for electricity in 2021 in Spain has been chosen as 0.25 $/kWh according to Eurostat [325], and for natural gas and coal, 0.086 $/kWh and 123$/ton, respectively. It should be noted that ore handling energy costs (most of them in the form of diesel) are not considered here, as they are entirely allocated to the paying metal Sn.

Accordingly, the estimated energy costs for Ta and Nb in scenario 1 (i.e. considering current ore grades) are 1,861 $/t and 1,984 $/t, respectively, which constitute 1.16 and 9.92% of the average price for Ta and Nb in 2022 [242] (Ta: 160,000 $/t, Nb: 20,000 $/t). This leaves room for maneuver, even if further costs need to be added, including investment costs, wages, water and chemical costs, emission abatement costs, etc. Figure 6-7 has been formulated, considering different scenarios with rising energy costs. For instance, electricity prices increased from 0.14 $/kWh to 0.31 $/kWh from January 2021 to January 2022 in Spain [326]. Triggered by the soaring demand and supply chain disruptions, commodity prices also increase. For instance, Ni and Li recorded an increase of around 30% and 110% in the last year, respectively [242].

As shown in Figure 6-7, for the Tailings 1 scenario, with constant energy prices, energy costs rise by a factor of 10. For Ta, energy costs still represent only a small fraction of current commodity prices (10%). If energy prices were to double, energy costs would represent 50% of current commodity prices, putting the viability of its extraction at risk. Tailings 2 scenario would be unfeasible even at current energy prices.

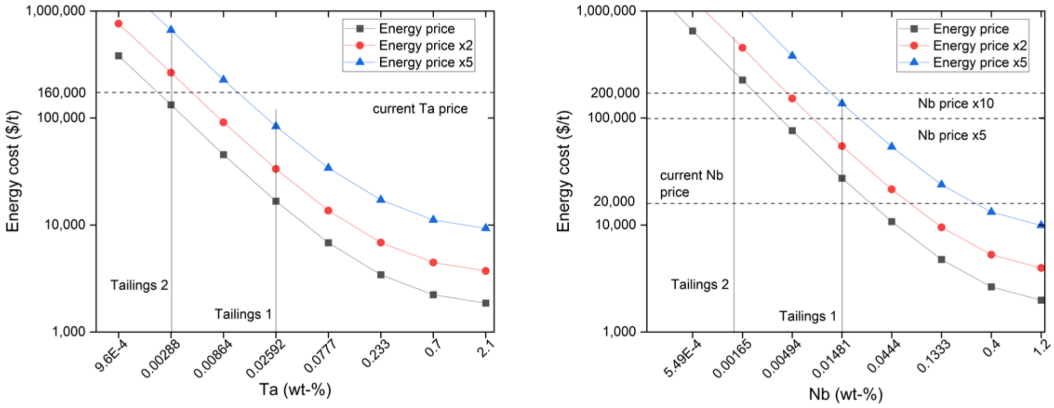


Figure 6-7. Evolution of energy costs as a function of ore grade decline for different scenarios for Ta and Nb.

The case of Nb is slightly different since its current price is eight times lower than the Ta price, yet, energy costs are similar due to their production routes. This means that Nb recovery from Tailings 1 is not cost-effective, even considering low energy prices. If Nb prices were to increase fivefold, its recovery would likely be profitable if energy prices doubled. However, this would not be the case if at the same time energy prices increased fivefold. In that case, Nb extraction would only be likely viable if its market price increased tenfold. Extraction from Tailings 2 would be unfeasible in any analyzed scenario.

However, these results need to be interpreted with caution, as they are particularly sensitive to the metallogenesis of the ore and the allocation procedure. Nb extraction is disfavored due to its low market price and a higher cost allocation towards Ta would improve its viability. Similarly, as stated before, ore handling energy costs were entirely assigned to the paying metal tin. Allocating part of such costs to Ta or Nb would radically change the outcome, questioning their profitability even at current ore grades.

6.6. Case study. The old Penouta mine

6.6.1. History and potential of the Penouta Mine

We conducted a case study analyzing the slags generated during the Sn beneficiation process in the Penouta mine. The history of this mine, located in the North-West of Spain, goes back to the beginning of the 20th century when the area was first exploited, and small amounts of cassiterite were extracted. Mining activity was then resumed in the 1960s until 1971, allowing Penouta to become Europe’s leading Sn mine. During its last years of activity, around 1,600,000 tons of rock were extracted, containing around 640 tons of cassiterite and 170 tons of tantalite concentrate [327]. This deposit is characterized by a greisenized, altered and kaolinized granite mass surrounded by metamorphic rocks. It also contains disseminated cassiterite and columbo-tantalite minerals [60]. In the 21st century, new studies were carried out. Between both zones analyzed, estimated resources add up to 11,910,402 tons of ore, with a Sn and Ta content of 428 and 35 ppm, respectively.

Valero et al. [90] carried out an analysis to calculate the cumulative expected material demand from 2016 to 2050 in green technologies, including wind energy, solar photovoltaic, solar thermal power and light-duty vehicles. It was estimated that the amount of Ta and Nb required could be around 54.60 ktons for Ta and 2,287.95 ktons for Nb. This means that if the entire Ta present in Penouta mine tailings could be recovered, it would account for more than 43% of the total needs from 2016 to 2050. As for Nb, this value would reach 1%. This demonstrates the potential of this mine if the amount of metals that is still there was feasible to extract.

6.6.2. Process details

The process of recovering Sn, Ta, and Nb has been widely studied by Allain et al. [328] and Subramanian et al. [329]. The hydrometallurgy processes used to recover these elements are based on strong acids, which are economically and environmentally challenging. One of these studies considers a greener approach for the selective dissolution of the amorphous slag matrix, obtaining a concentration similar to the commercial grade [328]. The study of Allain et al. [327]also reflects the high mass losses produced by sequential acid and alkaline leaching, while the sequential acid-basic-acid leaching is the most favorable, with concentrations of 63% [328]. One of the main disadvantages of this process is the high amount of chemicals needed to purify the metals. Another study analyzes the availability to purify Nb and Ta from tin slags with a very low ore grade [329].

Although the recovery ratio of the metals is very high and the results are promising, as stated, a vast number of processes, time, and a large amount of chemicals are required [329]. As a result, the environmental impact is significantly high, and with the reagents applied, it makes this process less cost-efficient compared with the proposed process.

In the present study, alternative chemicals to those proposed in the literature are used during the leaching process, thereby reducing material losses as well as increasing the metal yields. In the same approach used in our case study, the aim is to reuse reagents as much as possible to decrease the environmental impact of the whole process.

The starting point of this study is based on the waste generated when the Penouta mine was abandoned, also known as tailings. Therefore, the initial concentration will be the same as what was found in these tailings. As can be observed in the flowsheet in Figure 6-5, it was determined that various recirculation units should be incorporated. Particularly, we introduced five units that recirculate reagents and water. These units are crucial as the requirements of chemicals could increase up to 50% if there were no recirculation. Additionally, a final unit named "treatment waste" was included in the simulation. The undesired outputs are recirculated to this unit to proceed with further treatment and decrease the overall environmental impact of the plant. Table 6-6 shows the most abundant reagents that reach this unit. This can be used to better understand the importance of waste treatment as more than 10,000 kg/h of water is discarded and mixed with other substances.

Table 6-6. Certain reagents that end in the treatment waste unit recovering Ta and Nb (in kg/h).

Variable	Amount
H_2O	11,510
HF	370
H_2SO_4	2030
CaF_2	80

Once the initial model of the treatment plant is ready, a preliminary analysis of the different inputs needed to purify the three dominant metals present in this mine (Sn, Nb, Ta), as well as a thermodynamic analysis for a future set up of the metallurgy plant, is undertaken.

Table 6-7 shows information about the flowrates of the different reagents introduced in the system. A significant number and amount of chemicals are used in the aforementioned process to recover Sn, Nb, and Ta. Nonetheless, sulfuric acid is the most used reagent, with 2.03 t/h. This is consistent with the beneficiation process of 1 ton of rock.

Table 6-7. Summary of the inputs introduced in the metallurgy process for a ton of rock [data in t/h].

Reagents	Electr.[1]	Casting	C. Tower[2]	Leaching	Liquid. Extra	Stripping	Pre. Nb[3]	Calc. Nb[4]	Stripping 2	Pre. Ta[5]	Calc. Ta[6]
H_2O	5.17	0.08	0.13	1.97	-	3.28	-	-	0.8	0.45	-
HF	-	-	-	0.49	-	-	-	-	-	-	-
H_2SO_4	0.65	-	-	1.38	-	-	-	-	-	-	-
Cyanex	-	-	-	-	4.2	-	-	-	-	-	-
NH_4F	-	-	-	-	-	0.04	-	-	0.17	-	-
NH_3	-	-	-	-	-	0.01	0.60	-	0.03	-	-
KF	-	-	-	-	-	-	-	-	-	0.76	-
Natural gas	-	-	-	-	-	-	-	0.0038	0.022	-	0.0063

[1]Electrolysis; [2]Cooling tower; [3]Precipitation Nb; [4]Calcination Nb; [5]Precipitation Ta; [6]Calcination Ta

6.6.3. Electricity Consumption and Gas Emissions

The electricity required for the hydrometallurgy processes, as well as the gases produced are also considered in the study.

Electricity is needed during the process to move the blades that combine the reagents with the feed [170]. During the simulation with HSC, it is not possible to directly obtain figures on electricity consumption as this parameter is related to the feed introduced and the size of the units. However, some authors state that an average value could be between 0.05 and 0.1 kW/m^3 [330].

Since the volume of every hydrometallurgy unit is known, it is then possible to calculate the electricity needed for our process, choosing the highest electricity consumption value (see Table 6-8).

Table 6-8. Electricity needed on each unit in the recoevering process of Ta and Nb.

Unit	Electricity (kW)
Electrolyte mix	1.06
Leaching	0.42
Liquid-Liquid extraction	0.84
Stripping	0.96
Precipitation	0.52
Mixing reagents	0.43
Stripping 2	0.86
Mixing Cyanex 923	0.42
Precipitation Ta	1.31
Mixing KF	1.30

The highest energy values correspond to the units that precipitate and recirculate Ta. This is in line with the results obtained during the simulation since the volumetric relation between H_2O and the reagent used to precipitate Ta is significantly high. Consequently, recirculation units must be similar to previous units since the amount of feed introduced is within the same order of magnitude, and therefore, it will have a high energy consumption.

According to some studies, the electricity needed to send tin to electrorefining could be between 150–200 kW/t/tin [208]. Therefore, with the amount of pure Sn obtained in our simulation, the electricity needed would be in the range of 75–100 kW.

As for gaseous emissions, mainly CO and CO_2 are generated in three main units: carbothermic reduction, Nb calcination, and Ta calcination (Table 6-9). In the carbothermic reduction, as it is necessary to increase the temperature to 1200 °C so that the process can occur, 0.23 t/h (around 24% of the feed) of coke is introduced, producing 0.84 t/h of CO_2 emissions to the atmosphere. Additionally, both Nb calcination and Ta calcination also require a temperature of 1200 °C to eliminate the humidity from the feeds. In these cases, 0.02 t/h and 0.01 t/h of natural gas are introduced in the Nb calcination unit and Ta calcination unit, respectively. Compared to the emissions of the carbothermic reduction, they have almost negligible gas emissions to the atmosphere.

Table 6-9. Gases emissions per unit obtained from the simulation of recovering Ta and Nb (in t/h).

Output Gases	Carbothermic	Calc. Nb	Calc. Ta
CO	0.06	0.003	0.005
CO2	0.84	0.05	0.013

6.6.4. Analysis of the inputs and outputs during the recovery process

After processing one ton of ore coming from the tailings of the Penouta mine, it has been calculated that around 0.6 tons of metals can be recovered, the majority of which corresponds to Sn.

In order to analyze the process, it is essential to assess a mass balance of the system. To that purpose, Table 6-10 has been formulated to summarize the mass balance of the three metals (Sn, Ta and Nb) at the beginning and at the end of the beneficiation process. As it is shown, more than 92% of Sn, 95% of Ta, and 67% of Nb are recovered, reaching high recovery yields. This shows how much metal is recovered with a feed of 1 t/h of ore. The main difference between these metals is that Sn is recovered after two metallurgy processes using a very small number of reagents. A total of 0.50 tons of Sn are recovered per hour and considerably lower amounts of Nb and Ta. Besides, the latter elements are recovered as by-products. Their initial concentration is very small, and a higher number of processes and chemicals are needed to purify them.

Table 6-10. Summary of the mass balance for Sn, Ta, and Nb using a ton of rock as input in the metallurgy process. Note that the recovery yield is based on the metal output and not the metal content.

	Beginning of the process		End of the process		Recovery yield
	t/h	wt-%	t/h	wt-%	%
Sn	0.54	54.35	0.50	99.99	92
Ta	0.06	6.51	0.06	79.67	95
Nb	0.04	4.68	0.03	98.45	67

However, more than 40% of the inputs end up as waste rock along the process. Additionally, this material is usually contaminated with chemicals and additives applied during the flotation and the refining process, generating further consequences during waste management. This means that if the entire metal content in the Penouta mines is extracted in this process, it would generate more than 5,000 kton of waste rock.

Additionally, as mentioned, several metallurgical processes are needed to purify Nb and Ta from that ore. Various reagents must be mixed with the feed to produce changes in the phases and separate them so that they finally end up precipitating in the form of almost pure metal. At the end of the simulation, to obtain 30 kg of Nb and 50 kg of Ta, more than 3,000 kg of chemicals have to be used to reach full separation. Moreover, the amount of water needed in the process is not negligible.

The type of reagents used in each metallurgical unit have also been analyzed (Figure 6-8). This way, it is possible to compare the reagents used in each specific part of the process and their proportion relative to the total usage in each unit.

In this case, it is also possible to see how the carbothermic reduction is the unit where a greater number of different reagents are introduced (borax, limestone, and coke). Moreover, the liquid-liquid extraction process also stands out as a crucial unit since the phase changes from aqueous to organic. Specifically, it is the only unit that uses Solvesso (solvent) and Cyanex 923 (extraction agent). Additionally, HF is only used in the leaching unit and KF in the precipitation of Ta, while NH_3 is used in three different units, stripping 1 and 2, and precipitation.

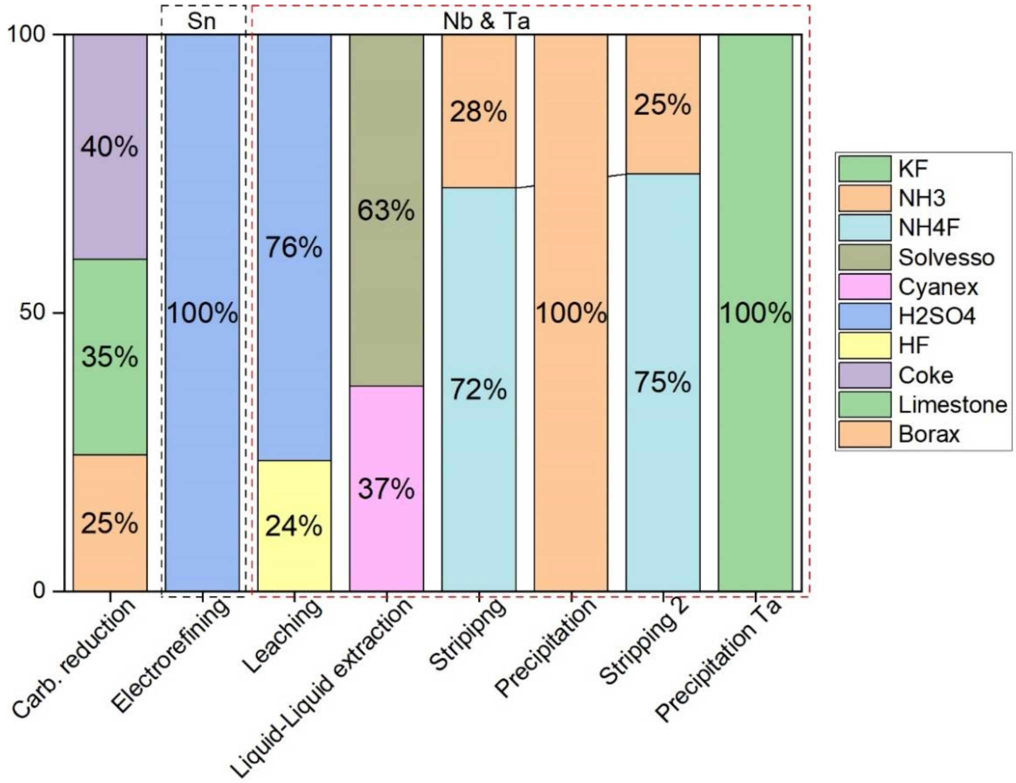


Figure 6-8. Share of reagents needed in each unit of the treatment and beneficiation process of Sn, Nb, and Ta.

Among the materials used during the beneficiation process, water is the largest input in the system with almost 12 t/h, which is a common rate used in metallurgical processes [331]. Of these 12 t/h of water needed, and almost half (5.12 t/h) are used in the electrorefining unit (Figure 6-9). The rest is used in the remaining processes to concentrate the Nb and Ta (see Table 6-7). The second unit, where more water is required, is in the stripping phase because of the high volumetric relation between the organic and the aqueous phase.

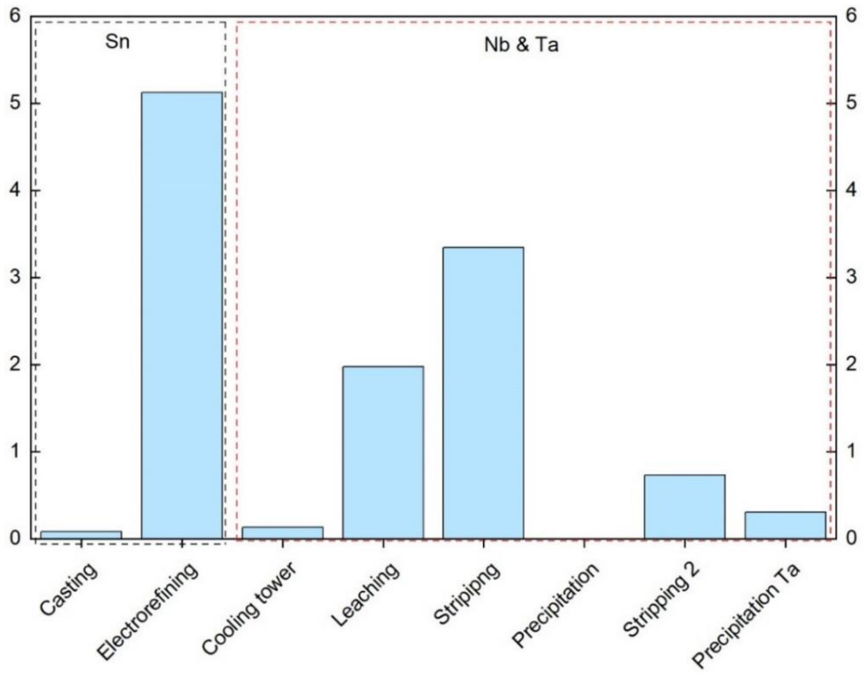


Figure 6-9. Water requirements in the beneficiation process of Sn, Nb, and Ta (in t/h).

According to the results obtained during the simulation, the percentage of recovery at the end of the process from the rock is 45%, 3%, and 5% for Sn, Nb, and Ta, respectively. However, if only Sn slags are considered, values for Nb and Ta increase to almost three times, with 7.8% and 15.6%, respectively. In terms of metal content, the recovery yield for Nb is higher than 50%, while for Ta is around 56%. This data can be found in Table 6-11. These values are considerably higher than those that can be found in the literature [332].

Table 6-11. Summary of the metallurgy process for the recovery of the Ta and Nb [t/h]. Note that all the data is based on the metal content, unless other specifications are mentioned.

	Slags Carb. Reduc.	End of the process (Nb/Ta)	Recovery yield %	Recovery yield in terms of rock %
Sn	0.016	-	-	-
Ta	0.065	0.0364	56%	15.6%
Nb	0.042	0.0218	52%	7.8%
Wastes	-	0.3114	-	76.6%

6.7. Conclusions

An assessment of extracting Nb and Ta from Sn mines has been carried out. The specific energy for concentration for both has been calculated through HSC Chemistry. Since the energy of extraction for low ore grades is becoming very high, other sources of extraction have been analyzed, such as tailings. Hence, the main conclusions achieved in this chapter are listed below.

- Various scenarios have been developed to project the mine's evolution in response to declining ore grades. Among these scenarios, we examine the concentration levels for tailings, denoted as Tailings 1, and Tailings 2, which is roughly one order of magnitude lower than that of Tailings 1. Additionally, the concept of URR is applied, which signifies the maximum extractable concentration from a mine, constrained by technological and financial factors. As expected, it was observed that the amount of energy required to extract a ton of Ta and Nb would considerably increase when ore grade declines, even if the best available technology were applied. In the case of Ta, the value would be more than twice the current energy cost if it had to be recovered from tailings 1, while in the case of Nb, this value would be almost 20 times higher than the current energy cost. However, for the first three scenarios, energy costs would still be significantly lower than current gold energy requirements.
- A preliminary economic assessment shows that at the current commodity and energy prices and considering that ore handling costs are allocated to tin in its entirety, the recovery of Ta in the tailings 1 scenario would be cost-effective, even if energy prices would double. On the contrary, the recovery of Nb would not be favored because of its current low market price. If Nb prices increased or if most energy costs were allocated to Ta, the situation would change.
- The case study of the abandoned Penouta mine has been analyzed. The mine was reopened upon the discovery of a feasible potential for extracting Nb and Ta concentrations from the tailings. A more comprehensive analysis

into extracting metals from tailings has been undertaken. The results obtained from the simulation are very promising since the recovery of Nb and Ta after Sn beneficiation has been demonstrated to be possible. Furthermore, even if the Penouta mine was mainly aimed at obtaining Sn, all metals could also be extracted from the slags as by-products with current available technology. Considering that the current demand of pure Nb in 2017 was 6,400 tons while the demand of Ta was 2,079 tons, according to our simulation, the metal output from the mine could represent more than 1% and 7.4% of the annual market share for Nb and Ta, respectively. These values represent a moderate scenario since the input introduced could be higher than 1 t/h of rock, depending on the capacity of the mine and ore quality.

- After carrying out the simulation of the refining of tailings, it has been obtained a potential recovery yield of 92%, 95%, and 67% for Sn, Ta, and Nb respectively. These percentages correspond to pure Sn (99.99%) and high concentrated Ta (79.67%) and Nb (98.45%).
- The main disadvantage found in the simulated process is the number of chemicals that are required, as well as the use of water in the process. This issue could affect the cost-effectiveness of a future processing plant. Additionally, the environmental impacts related to all the reagents discarded should also be closely monitored and find ways to reduce or mitigate them. An example is the Ta precipitation unit. Despite water humidity and KF being recirculated at a 65% rate, high amounts of water are still needed, and a large part of this humidity is discarded and hence lost.
- Until now, in Penouta, Nb and Ta ended up in tailings, but we have proved that there are ways to recover a very significant amount of these elements annually from there. This opens an opportunity to recover metals more efficiently, that could be a way to overcome future shortages of elements and mineral depletion.

Apart from the analysis of extracting metals from tailings, another solution will be explained in the next chapter, which proposes a methodology to collect WEEE in order to recover critical metals from this sector

Chapter 7. Eco-credit system to incentivize the recycling of waste electric and electronic equipment based on a thermodynamic approach

7.1. Introduction to the chapter

There are crucial aspects that have to be considered to avoid extracting metals from mines and make this industry more sustainable. Therefore, in addition to tailings as it was seen in the previous chapter, another alternative could be the recovery of metals from WEEE due to the significant number of devices manufactured. Due to the use of the electric and electronic equipment (EEE), increasing significantly in the last decades, this chapter will focus on the end-of-life metals that are manufactured in these devices. However, the main challenge associated with this option is the lack of collection for these devices. Many devices are stored at home or not sent for correct recycling, resulting in the loss of the embodied metals. To address these situations, a thermodynamic assessment has been conducted to identify electric and electronic equipment within critical metals. Therefore, an expression has been developed to evaluate the devices based on various parameters, including their lifetime, device condition, and the thermodynamic rarity of the metals they contain. Applying this expression provides the so-called Eco-credits, which can be exchanged for incentives based on the results. The information pertaining to this chapter can be found in **PAPER V**.

7.2. General overview

Due to various reasons, such as device malfunction or the availability of newer and updated versions, a significant portion of electric and electronic devices are either sent to landfills or, in the best-case scenario, taken to recycling centers where only major materials like plastics, iron, aluminum, and copper are recovered. Furthermore, it has been observed that a large number of devices sent to developing countries eventually end up in landfills [333], [334]. This practice has several associated disadvantages due to the release of gases into the atmosphere and the transfer of toxic substances into the soil and water [335], [336]. Additionally, this process can pose significant health risks as there are over one thousand toxic substances associated with e-waste. Commonly polluting metals include barium, beryllium, cadmium, cobalt, chromium, copper, iron, lead, lithium, lanthanum, mercury, manganese, molybdenum, nickel, and hexavalent chromium [335]. Mercury is a prime example and one of the most toxic substances, as high concentrations can cause ailments such as insomnia, memory loss, tremors, and other adverse effects that can ultimately lead to fatal consequences in the long term [337].

Thus, reusing and recycling electronic devices could offer a viable alternative to mining raw materials, given the various metals present in these devices and their global production volumes. An example of this is shown in Table 7-1, where the composition of a smartphone is displayed. Around 1.35 billion units for smartphones were sold in 2021 [108], [338]. Thus, if we multiply the quantity of metals in a smartphone by the total number of smartphones sold in that period, more than 75.6 tons of gold and more than 35,500 tons of cobalt are stocked in these devices. These figures emphasize the substantial quantity of metals utilized in this sector and the imperative need to recover them as an alternative solution to mitigate the depletion of mines.

Table 7-1. Composition for a smartphone. IPhone 6 [339]

Element	g	Element	g
Aluminum	31.14	Lithium	0.87
Arsenic	0.01	Magnesium	0.65
Sulfur	0.44	Manganese	0.29
Bismuth	0.02	Molybdenum	0.02
Calcium	0.44	Nickel	2.72
Carbon	19.85	Gold	0.014
Chlorine	0.01	Oxygen	18.71
Cobalt	6.59	Lead	0.04
Cupper	7.84	Potassium	0.33
Chrome	4.94	Silicon	8.14
Tin	0.66	Tantalum	0.02
Phosphorus	0.03	Titanium	0.3
Gallium	0.01	Tungsten	0.02
Hydrogen	5.52	Vanadium	0.04
Iron	18.63	Zinc	0.69

However, managing e-waste poses a significant challenge for both society and companies. This process entails the collection, recycling, and subsequent production of secondary raw materials that need to be reintroduced into the industry. The primary issue lies in the collection of WEEE, which is inadequately developed. Furthermore, the lack of proper infrastructure for e-waste processing exacerbates the problem. Compounding the situation is the occurrence of unofficial and illegal collection practices [340].

According to Directive 2012/19/EU of the European Union, from 2016 onwards, the minimum collection rate shall be 45%, calculated from the total weight of WEEE collected in a given year in the Member State concerned, expressed as a percentage of the average weight of EEE placed on the market in the three preceding years in that Member State. From 2019 onwards, the minimum collection rate shall be 65% of the average weight of EEE placed to the market in the preceding years in the Member State concerned [341].

One of the main goals of the collection system is to avoid the storage of EEE that are no longer used, rewarding its deposition in collection points as soon as possible as its value decreases with its age. On the other hand, circular economy principles are in line with the extension of the lifetime of products, so less energy and resources are needed. Thus, the aim with the methodology presented in this chapter is to incentivize the extension of the lifetime of a product and the fastest deposition once the product is no longer used, avoiding its storage in houses. Still, it is impossible to determine if a five-year-old tablet has been used during its whole lifetime or it has been used for three years and then stored the last two years.

It is a crucial parameter to be analyzed when reuse and recycling is considered, as a large number of devices get discarded despite still being functional, simply because a new model of device is available on the market. This means that there are many devices ready to be reused but are not because there are no systems that facilitate an appropriate collection. Moreover, the lifetime parameter is important to avoid incentivizing the “throw away culture”, as the main goal is to promote the use of the given product during its whole lifetime.

According to Lu et al. [342], the decision to reuse or recycle is influenced not only by the physical condition of the device but also by the presence of outdated or obsolete systems.

This study proposes an eco-credit system to incentivize users when they send old devices to appropriate collection points. The methodology is based on a thermodynamic approach, which considers the physical value of the materials contained in the devices.

Other studies have been carried out trying to evaluate the environmental burden of WEEE proposing a resource efficiency index (Kitajima et al. [104]). In their expression, the concept of “Total Material Requirement” (TMR) is used, defined as the total amount of crude metals, ores, soils, removed surface soils, etc. needed to obtain a unit amount of refined metals. A large TMR value means that a huge amount of ore has to be extracted from Earth’s environment to get the material.

Similarly, Szargut and Stanek [343] proposed to replace the value added tax (VAT) with a new one based on the composition of the device and the cumulative consumption of non-renewable exergy. The VAT suggested is based on an equation developed through the extraction of the minerals and fuel, being the VAT depending on the impact to the environment of manufacturing each device.

In contrast to previous studies like Kitajima et al. [104] and Szargut and Stanek [343], which evaluated the environmental impact of WEEE, our study introduces a more comprehensive approach to calculating eco-credits. Our method assigns equal importance to both the lifetime and the device's condition, in addition to its composition. This approach, provides a more robust assessment of multiple device parameters. Besides metal extraction, we also consider two other crucial factors: the device's state and its lifespan, contributing to the resource efficiency index.

The goal is to encourage device reuse, which takes precedence in the hierarchical sequence of the 3R principles: Reduce, Reuse, and Recycle. Nevertheless, our study, in conjunction with these other approaches, aims to contribute to a more environmentally friendly economy by discouraging the depletion of non-renewable resources, minimizing stockpiling, and advocating for responsible recycling. We will use two case studies, namely tablets and LEDs, to illustrate these concepts.

7.3. Eco-credits index

As stated before, society needs to understand the importance of recycling and handling WEEE properly. Knowing the physical value in terms of materials that a given device contains can be the first step to contribute to that purpose. To that end, the idea proposed is to develop an expression to evaluate WEEE, obtaining as a result the so-called eco-credits, which are granted through a mobile application once a certain device is sent to a specific recycling point.

According to the requirements established in the WEEE directive, the recycling rate should increase yearly to achieve the goals set [344]. One of the activities that could improve recycling ratios could be the use of monetary incentives directly given to device users when they actively participate in the recycling process (currently this is already being tested in pilot experiences).

However, it's important for the methodology to also incorporate the perspectives of stakeholders engaged in the recycling process. Consequently, the equation to calculate eco-credits, which may eventually translate into economic benefits or similar incentives, has been crafted with input from recycling and repair companies, along with other relevant stakeholders. To strike a balance among these diverse factors, the eco-credit formula encompasses three terms, as illustrated in equation (7-1):

$$Eco - Credits = A \cdot \sum_{i=1}^{n} a_i\, rarity_i + B \cdot EoL \text{ state} + \mathrm{C} \cdot lifetime\ factor \qquad (7\text{-}1)$$

When analyzing a device, the evaluation extends beyond its physical attributes and materials; it also encompasses additional parameters that identify the device's potential for reuse. Thus, in addition to the physical characteristics, the equation (7-1) takes into account the device's condition (whether it is operational or not) and its total lifespan (measured in months since the device was purchased). In summary, Equation (7-1) considers the following parameters:

- Rarity: This first term of the equation provides the physical value related to materials contained in the devices, as it is explained in section 3.2.3. This is combined with the recyclability of the materials. Unfortunately, not all materials used in the devices can be recycled with current End of Life (EoL) technologies. In order to take this into account, for each raw material included in a device, its rarity needs to be multiplied by a factor that considers its recyclability, a_i, which will be equal to its recyclability ratio whenever it can be recycled (a value that will vary from 0 to 1, no matter the state of the device). The value will be between 0 if it is not hypothetically recyclable at all and 1 if it can be recycled completely. These values correspond to recycling processes provided by the recycling company, and they can be updated in the future if those processes are improved. This way, the eco-credit formula can be also applied using new values, just by changing the given factor.
- EoL state: The state of a product is going to determine its reusability. This is included in the second term of equation (7-1) . The EoL state value will only account for three different values: 1 if the device works perfectly, 0.5 if it is not working but can be repaired and 0 if it is not possible to fix the product.
- Lifetime: The third term of equation (7-1) is related to the average lifetime expected for each specific device and the real usage.

Accordingly, when a user takes the device to a WEEE collection point, the device is checked. Several parameters must be introduced by the user and then verified by a technician: type of WEEE, whether it can be directly reused, repaired, recycled, etc. Then, the expression is used to obtain the final number of the so-called eco-credits, which will then appear on the mobile phone of the user through an app. Afterwards, these eco-credits can be exchanged in the form of different incentive schemes.

As evident from equation (7-1) the three different terms are preceded by a weighting factor (A, B, C) that give the adequate importance to each term and that can be allocated based on the preferences of the managing entity. The values for these parameters will allow promoting one term over the others.

The first factor, A, presents values that have from three to four orders of magnitude higher than the second and third term. The second parameter (B) ranges from 1 to 10 due to the values that can present EoL (0 to 1). Setting the exact values for A and B is an arbitrary process and they can be fixed by the entities who will provide the incentives associated to eco-credits (depending on their interest in weighting the three terms of the equation) or be set under another criteria. These parameters, A and B, are multiplying terms that do not depend on time so their values will only define the cross with the ordinates axis in a figure where eco-credits against time are represented (see Table 7-2).

Table 7-2. A, B, C factors for tablets and LEDs for eco-credits calculation.

	Tablet	LED
A	10^{-4}	$10^{-4}/7=1.43\text{x}10^{-5}$
B	10	10/7=1.43
C	15	15/7=2.14

7.4. Methodology

7.4.1. Composition of the devices and rarity

It is important to stress that thermodynamic rarity does not consider the distribution of materials in specific components. Materials can be homogenously spread throughout a whole system or found in almost a pure form in several components. This fact would certainly affect the recyclability of a device, which is not the object of this study, but the rarity would remain the same. This way, to calculate the thermodynamic rarity (see section 3.2.3) of a device or specific component, equation (7-2) should be applied, once the composition in terms of elements contained (m_i) in device (A) are known:

$$R(A) = \sum_{i=1}^{n} m_i \, R_i \qquad (7\text{-}2)$$

For the purpose of this study, the composition of the following devices has been analyzed: LEDs, Tablets, laptops and smartphones. These devices have been selected because of the expected increase in sales and the criticality of the materials contained in them. Additionally, an increase in the number of certain key materials included in such technologies is expected due to technological improvements. This is because certain elements can confer specific features to the devices, improving their functionality, increasing and improving battery life, device efficiency orscreens, among others.

According to the methodology explained previously, thermodynamic rarity will be used to identify which devices of those studied have a higher impact in terms of raw material depletion. To proceed with the evaluation, an extended literature review has been undertaken to determine the metal composition of each product. This information has been gathered from several reports and studies [148], [345], [354]–[358], [346]–[353], which can be found in the annexes. In that table, it is possible to see the metals and other materials, such as plastic, that are used in the manufacturing of smartphones, tablets, laptops, and LED bulbs.

To better understand why this methodology based on thermodynamics has been applied, Figure 7-1 shows the contribution, in percentage, for some elements present in an average laptop both in grams (mass terms) and in kJ (rarity). As outlined, the contribution of copper in weight is higher than the 7% while in rarity decreases until 3%. However, the most significant case is carried out with Co. This metal accounts for only 1.5% of the total weight of the laptop, but in terms of rarity, it constitutes 25% of the total value. Therefore, its rarity is higher when compared to other abundant elements, such as Fe for instance. This can be explained due to the scarcity of Co in the crust and consequently, its exergy replacement cost is higher.

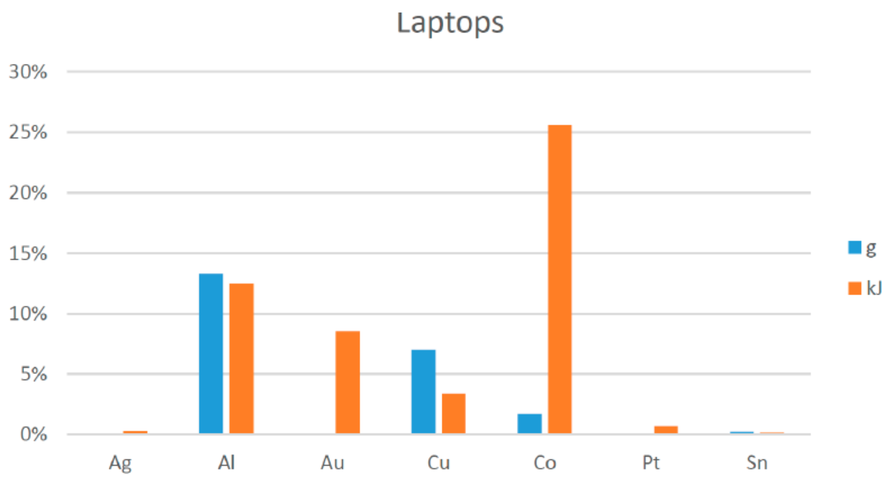


Figure 7-1. Contribution in weight (g) and exergy (kJ) for different elements present in a laptop.

The case of Au is also important to highlight, since it is the second with the lowest concentration in the Earth’s crust, being the PGMs only lower than gold. As it is seen, the contribution in mass is very low, being close to 0%, but in rarity, this figure increases three orders of magnitude.

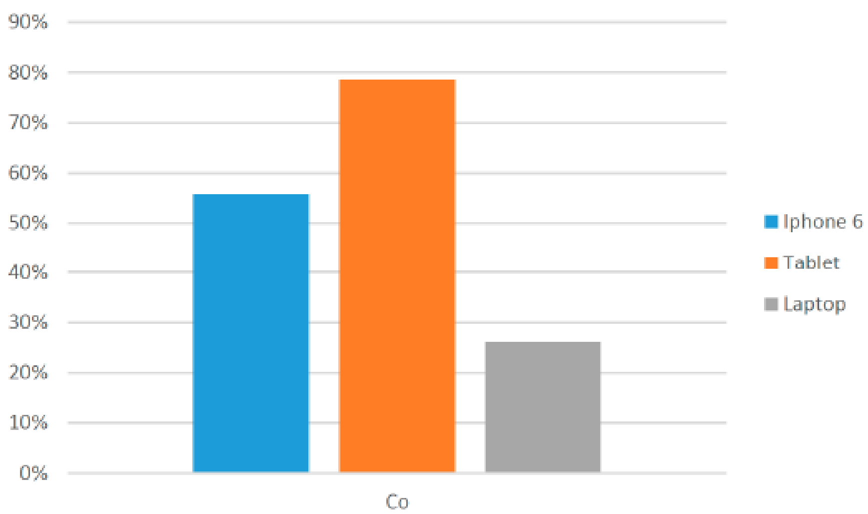


Figure 7-2. Rarity share of cobalt in Iphone 6, tablet, and a laptop.

We can also compare the amount of Co of different devices, as it is an element widely used in batteries and considered strategically or critically important in various regions like Europe and the United States(Figure 7-2). In the case of the devices analyzed, the iPhone 6, tablet and the laptop, cobalt rarity represents 56%, 79% and 29%, respectively, of the total thermodynamic rarity, as it is a key metal in the batteries. The demand for these products will increase the following years but also in electric vehicles, where cobalt demand is expected to grow exponentially, as vehicle batteries are composed by more than 65% of this metal and therefore can be considered a strategic element for the vehicle sector [92], [359].

As illustrated in Table 7-3, a laptop presents the highest thermodynamic rarity value among all the devices analyzed. This is a consequence of the number of materials included in it, as its size is much larger than the rest of the devices and therefore it needs more elements. This way, the more electronic components a device has, the higher its thermodynamic rarity, as every component contains small quantities of minor but very valuable metals.

It should be stated that all the numbers included are calculated for a single device. A different situation could be observed if these calculations were carried out considering all the sales of each device (mobile phone, tablet, laptop) sold each year.

Table 7-3. Thermodynamic rarity of the metals in different EEE [kJ].

Element	iPhone 6	Tablet	Laptop	LED bulb
Ag		194.84	8,222.58	31.73
Al	21,228.47	317.81	349,035.83	11,925.15
As	4.28	9.63		
Au	9,286.29	9,816.94	238,790.37	2,825.69
Bi	10.91			
Cd		1.29		
Ce			0.05	0.04
Co	72,556.72	139,553.32	715,658.07	
Cr	202.02	3.10		
Cu	2,731.90	1,937.07	94,083.46	808.27
Eu			0.00	
Fe	593.91	73.95		40.88
Ga	7,548.28			6,967.06
Gd			0.04	
Ge				
Hg		2.87		
In		6,623.29	14,556.69	
K	219.97			
Kr				
La			0.04	
Li	851.15	4,340.11		
Lr				
Mg	378.97	163.89		
Mn	21.24	1,048.58		

Mo	21.12			
Nd			710.32	
Ni	2,384.17	10,871.50	867.77	648.48
P	0.16			
Pb	1.63	22.26	248.86	0.00
Pd		956.67	478,335.52	
Pr			235.81	
Pt			19,133.42	
Sb		34.40		
Si	630.44			
Sn	298.95	414.68	42,12.45	909.47
Ta	9,718.38		82,6062.22	
Te			113.00	
Ti	79.93	50.25		3.22
V	62.89			
W	160.47			
Y			2.44	
Zn	1,161.16	1,032.60	168.28	
TOTAL	130,153.41	177,469.06	2,750,437.22	24,159.99

7.4.2. Lifespan: Average lifetime and lifetime usage

Lifespan is an essential parameter when estimating WEEE generation. It serves as a fixed parameter that represents an average value, offering an expectation of the duration during which equipment is likely to function properly before becoming obsolete.

To determine this parameter, a literature review has been carried out (see Table 7-4) highlighting the lifetime for the devices assessed.

Table 7-4. Average lifetime for some of the analyzed devices.

	Tablets	Laptops	Smartphones	LEDs[1]
Lifetime	36 months [346]	102 months [360]	21.75 months [345], [361]	54.8 months [362]

An alternative system to make the lifetime parameter more accurate is through the application of the Weibull distribution. Weibull distribution function can represent a probability distribution that considers the different lifespans between individual owners and the dynamic nature of product obsolescence. Furthermore, it has been demonstrated to be the most suitable fit for the lifespan of the majority of products [107], [363]–[365]. In fact, this is the formula included in the Commission Implementing Regulation (EU) 2017/699 of 18 April 2017 that establishes a common methodology for the calculation of the weight of electrical and electronic equipment (EEE) placed on the market of each Member State and a common methodology for the calculation of the quantity of waste electrical and electronic equipment (WEEE) generated by weight in each Member State.

[1] It is considered that the LED is turning on once and leave it on for the rest of the lifetime.

The Weibull distribution is defined by a time varying shape parameter α (t) and a scale parameter β (t) as is shown in equation (7-3):

$$EL^{(p)}(t,n) = \frac{\alpha(t)}{\beta(t)^{\alpha(t)}}(n-t)^{\alpha(t)-1}e^{-[(n-t)/\beta(t)^{\alpha(t)}]} \tag{7-3}$$

Due to social and technical factors [366], lifespan can differ between products and countries, so it is a time dependent term in the eco-credit equation. Some countries have this information available through consumer surveys, stock levels and during certain periods, as well as from sorting and sampling of the waste stream. However, it is difficult to find governments that collect and openly publish this information and when they do so, it is normally out of date.

Lifespan data from France, Italy, Netherlands and Belgium have been obtained using consumer surveys [363]–[365]. However, gathering this kind of information can be a challenge. Then, in the absence of more detailed data, they have been included in the calculations performed for Tablets and LEDs (Figure 7-3 and Figure 7-4). Note that if data were updated later, it could be easily incorporated in the methodology.

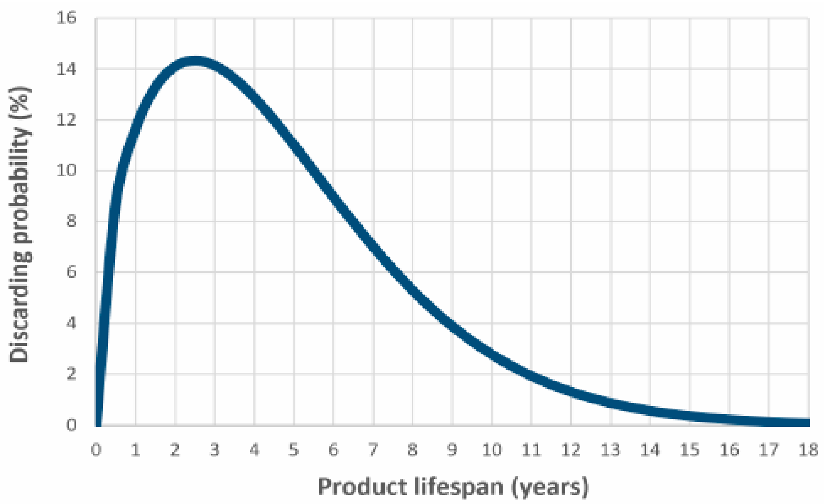


Figure 7-3. Discarding probability for tablets with Weibull distribution.

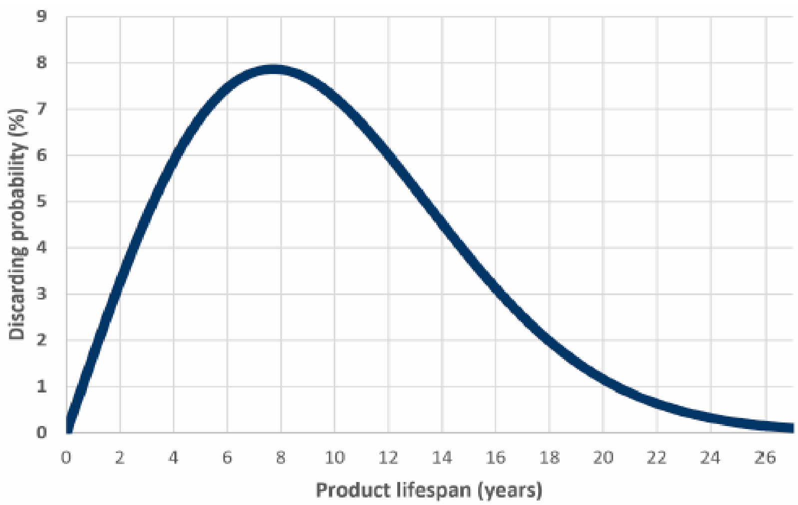


Figure 7-4. Discarding probability for LEDs with Weibull distribution.

As it can be seen in Figure 7-3 and Figure 7-4, the maximum peak use for tablets is around 3.5 years, then, the function decreases until it reaches 17 years. In the case of LEDs, the peak is found at 8,5 years and decreases until it reaches 27 years.

In both cases we can observe that the peaks are extended for a long period. The reason behind is that the lifespan reported covers the interval between the purchase and shipment of the new product and the final discard of the device, including both the period of use and hibernation [363]. Data including only the period of use have not been found in bibliography.

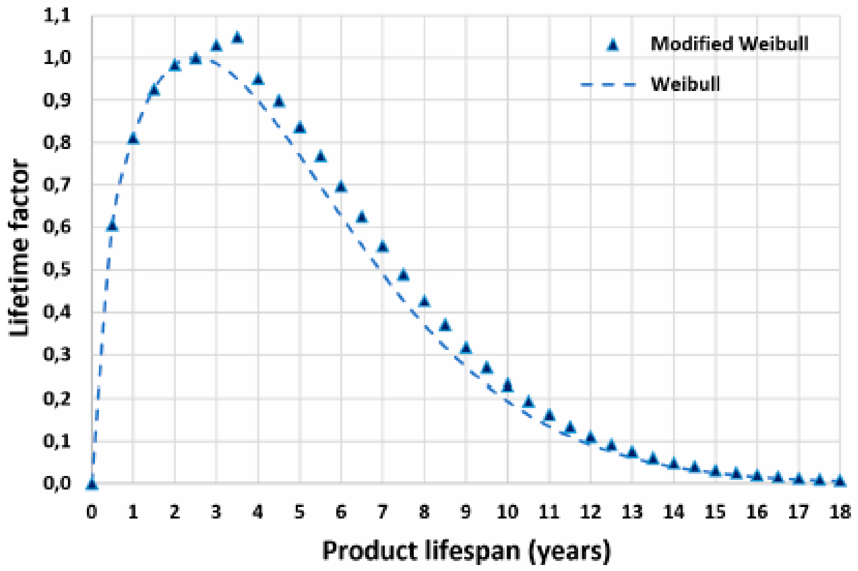


Figure 7-5. Lifetime factor calculation for the case of a tablet for the Eco-credit calculation.

In summary, the lifetime factor of the equation (7-1) is going to be calculated by means of the Weibull distribution according to the following procedure. Firstly, the Weibull distribution is obtained for the given WEEE. Then, this distribution is normalized between 0 to 1. Last, the normalized value is assimilated to the lifetime factor in the equation (7-3). This is shown in Figure 7-5. Note that if the aim is that consumers lengthen as much as possible the use of EEE, the maximum of the Weibull curve could be extended for several years. Thus, a user that extends the lifetime of a tablet or a mobile phone beyond its lifetime during a certain period, is not penalized. On the other hand, users who return devices before the expected lifespan may face penalties, although the severity of the penalty decreases as the return is closer to the expected lifespan. However, this extension cannot be kept indefinitely, as this would be encouraging the stockpiling of non-used equipment, a practice that should be avoided.

7.5. Case study: eco-credit calculation

7.5.1. Tablet

Approximately 11 million tablets are sold annually, considering the variety of manufacturers and various formats and sizes available. For the purposes of this study, we have utilized an average composition representative of a 10.1-inch tablet, as detailed in the tables provided in Annex 2.

To obtain the eco-credits, equation (7-1) is applied. For the first term of the equation, and according to the composition of tablets, the thermodynamic rarity corresponding to the metals of our average tablet accounts for 177,469.05 kJ. Additionally, plastic components and glass from screen account for a representative mass share (22.5 g of PMMA, 165 g of plastics, considered as ABS, and 62.02 g of silicon) that need to be additionally included in the rarity calculation. The rarity value for silicon is 1.4 kJ/g [170]. For PMMA and ABS thermodynamic rarity can be considered equal to their corresponding High Heating Value (HHV), 26.75 kJ/g and 39.84 kJ/g, respectively [367]. Considering those data, the final thermodynamic rarity value for an average tablet is equal to 184,807.91 kJ.

From the perspective of recycling, if the user provides a device that is neither working nor reparable, the only possibility remaining is to recycle its components. According to a WEEE recycling company in Spain, only PMMA (100% recyclability), plastics (95% recyclability) and some metals (aluminium 85%, iron, 100% and copper 100%) can be recycled. Note that even though some recycling figures may indicate 100% recycling, achieving total recycling of a material is impossible. For these materials, a recyclability value of 1, 0.95, 0.85, 1 and 1 are respectively assigned for a_i. Additionally, palladium, platinum, gold and silver could be extracted together (even if mixed) so a value of 0.5 is assigned for a_i. The rest of the raw materials are considered as non-recyclable so their a_i value is 0.

Table 7-5. Normalizing process for lifetime factor for tablets for the calculation of eco-credits.

Time (years)	0	1	2	3	4	5	6	7	8	9
Factor	0,1	0,2	0,3	0,5	0,75	0,99	0,95	0,85	0,7	0,6
Time (years)	10	11	12	13	14	15	16	17	18	
Factor	0,5	0,4	0,35	0,3	0,25	0,2	0,18	0,15	0,1	

According to these estimations, the first term of the equation (7-1) will be equal to 184,807.91 kJ when the tablet is working or reparable and 37,262.7 kJ whenever the tablet is not reusable. For the second term, as explained before, the EoL state will be equal to 1 if the tablet is reusable, 0.5 if it is reparable and 0 if it cannot be fixed. Finally, for the third term, depending on the lifetime of the tablet, the values shown in Table 7-5 will be assigned.

Finally, Figure 7-6 shows a case study outlining the eco-credits granted to a user that sends his/her old tablet to a proper recycling point, depending on the average lifetime and EoL state. In the case study, the following values have been assumed: A= 10^{-4}, B= 10 and C= 15. As it was aforementioned, these factors are needed to provide the similar weight to all terms of the equation.

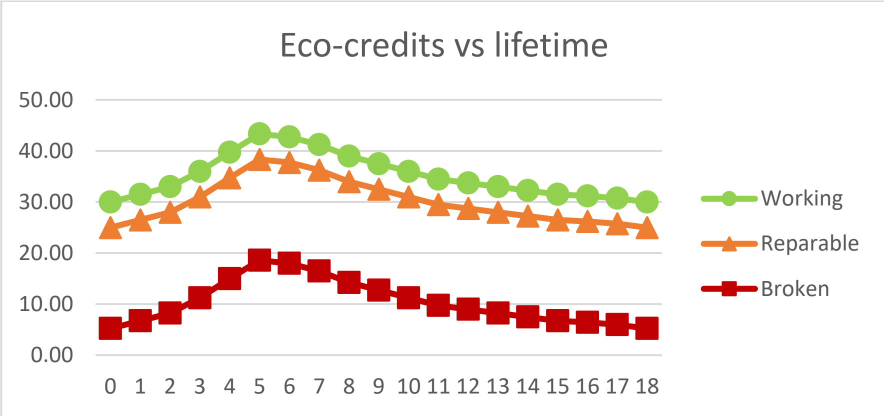


Figure 7-6. Eco-credit evaluation for tablets.

As can be seen, a working or reparable device provides a comparatively higher number of eco-credits than a broken one, therefore, the EoL state has a very high importance in this case study.

Accordingly, in this example the maximum number of eco-credits that can be obtained is 43 for a working tablet after 5 years of use. This value is reduced when the tablet is sent to the collection point before the average lifespan (penalizing the throw-away culture) or after the average lifespan (penalizing stock piling). On the other hand, the minimum eco-credits that is possible to earn is 5, which corresponds to a broken tablet in the first year of its life or to a tablet after 18 years of its purchase.

7.5.2. LEDs

The second case study corresponds to a LED bulb, specifically, a 10.5W LED bulb of 71g has been chosen [368]. The metals included in the bulb account for 23g while the rest is composed by polycarbonate, polyester and polyamide. However, when these values are converted into exergy it is possible to see how aluminium represents the highest share, corresponding to almost 50% of the entire bulb.

The first term of the equation (rarity) is 25,144.79 kJ for a working or reparable LED bulb and 13,202.1 kJ for a broken LED bulb. The same recycling values as before have been used to calculate the material available to recover from each device. Although the lifetime for LED bulbs estimated by the manufacturers is around 25 years (with a use of 3h per day), not all bulbs are used this long, therefore, it has been decided to create a lifetime average of 15 years.

These numbers must then be multiplied by different factors in order to provide the correct weighting of each parameter in the equation. For that reason, and in a similar way to tablets, three factors (A, B and C) have been used to obtain a weighted value where every term has the same order of magnitude, as it is possible to see in Table 7-2. To this aim A= 1.43×10^{-5}, B= 1.43 and C= 2.14.

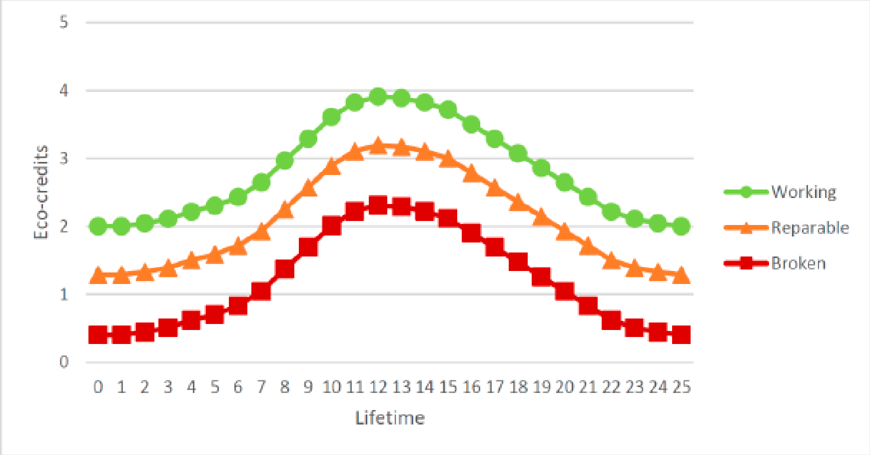


Figure 7-7. Eco-credit evaluation for LEDs.

Figure 7-7 summarizes the results obtained. As outlined, the maximum eco-credits that are possible to obtain is 3.9, 12 years after buying the bulb and if it is still working. On the other hand, the minimum eco-credits that are possible to obtain is 0.4 for a broken bulb that is disposed of the same year that it was bought or for a broken bulb that is recycled after 25 years of use (the lifetime stated by the manufacturer).

The main difference between tablets and LED bulbs is mainly related to their end of life. A tablet is more likely to be stockpiled due to obsolescence after a new device with more and updated features is bought. Whereas for LED bulbs, they are usually replaced when they stop working or if they break.

It must be stated that the extension of the lifetime of the tablet or LED bulb (or any other device for that matter) is encouraged to avoid buying a new one when the old one is still working. This approach penalizes very early and very late returns, therefore encouraging people to use their devices longer than the expected lifespan and avoiding stockpiling. For that reason, the maximum number of eco-credits can be obtained not during the average lifespan of each device, but a few years later.

7.6. Conclusions

This study has shown how the exergy analysis through the thermodynamic rarity indicator can help offering relevant information to users regarding the materials contained in the electronic devices that are being thrown away when they get to their EoL. With thermodynamic rarity we can better assess the relevance of each element that is included in the composition of the devices rather than using mass or price as an indicator. This chapter has developed a method to calculate the so-called eco-credits, as an incentive tool to reward users that send their old devices to appropriate collection points. Two case studies have been carried out, considering tablets and LED bulbs. The main conclusions of the study are collected below.

- Some authors suggest the creation of a comprehensive parameter that considers all materials involved in the device manufacturing process, tracing from mineral extraction in mines to the final market. Conversely, as previously explained, other authors have proposed the adjustment of value-added tax (VAT) for certain products to account for the materials included in the purchased product and the extraction methods used. In this study, we address this issue by introducing an index to calculate eco-credits based on thermodynamic rarity. This approach factors in the scarcity of a mineral in the Earth's crust and assigns added value to having the mineral concentrate.

- In addition to thermodynamic rarity, which considers the composition of each device, the eco-credit index incorporates two other parameters: the state of the device and its lifetime. These parameters are given equal weight in the equation compared to composition and strive for the highest possible accuracy in assessing the actual condition of the device. The intention is to ensure that devices in working order or those that can be repaired receive a different number of eco-credits than non-functional ones, regardless of common materials used in both cases. Our study aims to contribute to a more sustainable economy by discouraging the use of non-renewable resources, reducing stockpiling, and promoting responsible recycling.
- This index could be integrated into a platform or mobile app, allowing end-users to earn eco-credits by responsibly recycling their devices, which could then be exchanged for incentives.
- Two case studies have been conducted to illustrate the practical application of this approach. The first case study focuses on tablets. After determining the metal composition and converting it into rarity, the following results are obtained: The maximum eco-credits achievable is 43, which can be earned after 5 years of using a functional tablet. The minimum eco-credits achievable is 5, either for a non-functional tablet within the first year of its purchase or after 18 years of ownership. These outcomes highlight the range of eco-credits that can be earned based on the condition and lifespan of the tablet.
- The second case study involves LED bulbs. In this scenario, the maximum eco-credits achievable is 3.9, which can be earned for a functional LED bulb after 12 years of use. Conversely, the minimum eco-credits achievable is 0.4, either for a non-functional LED bulb within the first year of its purchase or after 25 years. These findings demonstrate the range of eco-credits attainable based on the condition and lifespan of the LED bulb.

Chapter 8. Conclusions / Conclusiones

8.1. Discussion

The mining industry has played a vital role in human civilization for centuries, driven by the constant demand for metals and their unique properties. However, it was during the Industrial Revolution that metal production saw a significant surge, emphasizing their crucial role in our daily lives.

Mineral resources are invaluable natural assets widely employed in various industries, including electronics, transportation, and construction. The importance of mining has grown with technological advancements, leading to the utilization of an ever-increasing quantity and variety of metals in the production of new technological devices. In this thesis, we examined metals like zinc and lead, which rank as the fourth and fifth most utilized metals globally. In contrast, PGMs find primary use in the automotive industry, while coltan is a ubiquitous presence in electronic devices. However, society often underestimates the significant number of metals used daily and the escalating demand for these resources, necessitating increased extraction and production.

This relentless extraction of metals across the periodic table has resulted in a substantial decline in ore grades in mines, exemplified by the dramatic drop in gold ore grades since 1960. This trend underscores the ongoing reduction in ore quality across various metal deposits.

Furthermore, this trend of diminishing ore grades seems to be continuing, which could lead to higher commodity prices. If this trend persists, metal extraction may become cost-prohibitive for all but a few companies, significantly impacting society, the availability of end products, and environmental considerations associated with production.

To address this situation, various governments and institutions have initiated efforts to raise awareness and invest in metal recovery to reduce dependence on mineral-rich third-party countries. The European Commission, for example, conducts reports identifying critical metals based on supply risk and economic importance, listing 34 materials of concern.

This trend is especially evident in the electronics industry, where millions of devices are produced and discarded annually. Each device contains small amounts of several metals, including critical ones. Cumulatively, these discarded devices contribute to thousands of tons of metals in landfills, with waste increasing by over 5% each year. This trajectory may eventually lead to landfills containing higher metal concentrations than mines.

Therefore, to avoid resource depletion, several solutions can be explored, such as recycling and reevaluating abandoned mines. Lead, for instance, boasts a recycling rate exceeding 60%, significantly higher than metals like platinum and germanium, which have recycling rates below 10%. Moreover, abandoned mines worldwide are being reconsidered for their potential similarity to active mines in terms of metal concentration and profitability. This analysis extends to tailings, which may contain viable ore grades if certain metals are extracted.

While efforts are underway to make the mining industry more sustainable, it's crucial to acknowledge that the primary issue lies in consumption. Raising awareness about the importance of metals and promoting their more efficient usage is imperative.

Failing to address these concerns could lead to supply bottlenecks, environmental consequences, and the challenges certain countries may face.

8.2. Conclusions

With the methodology applied in this thesis, along with the inclusion of the HSC Chemistry software, it is possible to assess the energy consumption behavior in the beneficiation process when the ore grade is reduced. Specifically, the exact energy has been calculated for the stages of comminution, flotation, and refining for Pb, Zn, Ni, Co, PGMs, Nb, and Ta. In this regard, various key factors have been taken into consideration to gain insight into the potential developments in the mining industry in the coming years. These factors include energy consumption for mineral extraction from tailings, recovery limitations, and price fluctuations in the sector. By employing these approaches, it is feasible to analyze the results considering various scenarios with different ore grades.

Specifically, three situations have been analyzed for each metal. The first scenario represents the specific energy required for concentration at the current ore grade. The second scenario is based on the energy needed if these metals were extracted from tailings with a lower ore grade. The last scenario corresponds to the minimum ore grade that could be potentially extracted in the future.

While the first scenario is based on the current ore grade and the second scenario represents the ore current grade found in tailings, the last scenario has been calculated with the ore grades based on the either the ultimate recovery resources (URR) or the limit of recovery (LOR). On one side, URR values were obtained from literature and remain the same for every metal, which is established in $5x10^{-5}$ wt-%. On the other hand, LOR was determined based on the maximum energy of extraction, which was obtained from the PGMs content in tailings, which is $2.4x10^{-6}$. The energy calculated for PGMs is then extrapolated to the energy curve for Ni and Co, obtaining the LOR for these metals, which is $4x10^{-4}$ for Ni, and $6.9x10^{-5}$ for Co.

Accordingly, the calculated energy of extraction for the minimum ore grade for Zn and Pb is 76.91 toe and 85.5 toe, respectively. For Ni, Co, and PGMs, the energy increases to 23,696 toe per ton of metal (note that the energy in this case is the same for the three metals due to the method of calculation of LOR). In the case of Ta, this value is 3,401 toe per ton, and for Nb, it is 1,956 toe per ton. The Second Law of Thermodynamics reflects that the lower the ore grade, the greater the energy required. Therefore, it is not surprising that the highest values occur with URR and LOR, particularly for metals such as PGMs.

As mines become depleted, the recovery of metals from tailings emerges as a potentially viable solution. However, the energy requirements would increase significantly. This is seen in the metals analyzed in this thesis, since the value for the energy cost would increase 2.5 times respect to the current ore grade for Ni, 7 times in the case for Co, and more than 75 times for PGMs.

Economic assessments have highlighted the significance of certain parameters for specific metals. For instance, following significant global events like the Ukraine war, the price of Ni doubled within just ten days. This increase could render the extraction of this metal from mines with lower ore grades profitable, resulting in higher total energy consumption. Another crucial parameter is cost allocation. The current energy cost calculations represent 63%, 67%, and 3% of the energy price for Ni, Co, and PGMs (Platinum Group Metals), respectively. Therefore, when assessing a mine, it is vital to consider market prices to analyze the feasibility of extracting any metal.

With this, it has been observed that extracting Ni from tailings could be profitable with both the current energy price and even if this price were to double. In the case of Co, recovering it from tailings would be profitable with the current energy price, assuming the Co market price remains at its peak. As for PGMs, the market price is already very high, making it profitable to extract PGMs from tailings at the current energy price.

The extraction of Ta and Nb from Sn tailings provides a notable example of the importance of cost allocation. The economic assessment in this study demonstrates that even if the price of Ta doubled, it would still be profitable to extract this metal from tailings, given that the combined energy costs and ore handling costs are entirely allocated to tin. However, the situation is different for Nb due to the current low market prices. If prices were to increase or if more energy were allocated to other metals, the situation would change, making the extraction of Nb profitable.

Because of the reduction of ore grade in mines, companies are looking for new ways to extract minerals from secondary resources, like abandoned mines. There are many abandoned mines worldwide that may contain significant concentrations of certain metals that could be recovered in the future, or even at present. This would be feasible because the concentrations in these tailings are similar to those in active mines, making extraction cost-effective. However, this would require multiplying the energy input, as it has been seen with Pb, requiring five times the energy at current ore grade, and Zn almost twice as much for this case.

On the other hand, it is crucial to mention the significant amount of chemicals and water required to obtain pure metals. This not only impacts the cost of the metallurgy plant but also increases the environmental impact due to chemical usage and water contamination. From an economic standpoint, it has been proven that recovering Sn, Nb, and Ta from tailings is profitable given the current metal prices. However, other factors and environmental impacts must also be considered to determine if this is the optimal solution.

A specific situation has been analyzed by studying the tailings from the Penouta mine in the North of Spain. The simulation results obtained are highly promising as they demonstrate the possibility of recovering both Nb and Ta after tin beneficiation. This recovery has the potential to represent 1% and 7.4% of the annual market share for Nb and Ta, respectively. Furthermore, the efficiency of the process is very promising. The results show that after carrying out the simulation of the refining of tailings, it has been obtained a potential recovery yield of 92%, 95%, and 67% for Sn, Ta, and Nb respectively. These percentages correspond to pure Sn (99.99%) and high concentrated Ta (79.67%) and Nb (98.45%).

Another possible solution to avoid the depletion of mines relies on recycling, such as recovering critical metals that are present in electric or electronic devices that are currently discarded or stored. It is crucial to recognize these devices at the end of their lives as an opportunity because, despite the need for further research, it could be a viable source of extraction and potentially more cost-effective than certain current mining operations. One of the main challenges associated with recycling is that the metals present in these decives are used in a dispersive manner, across various technologies with varying concentrations. This is of utmost importance because knowing where these metals are located is crucial. An expression has been developed to assess EEE using thermodynamic rarity. This is called Eco-credits, and it is based on three parameters: composition, condition, and lifespan of the device. By evaluating these parameters, owners can deposit their devices in a a recycling point and exchange them for various incentives, depending on the recycling center.

In this study, two case studies have been analyzed, tablet and LED bulbs. In the case of tablets, it could be possible to obtain up to 43 Eco-credits for a functioning device after 5 years from the date of purchase, whereas the minimum Eco-credits obtained could be 5 for a broken tablet after 18 years. For LED bulbs, the maximum Eco-credits could be 3.9 for a working bulb after 12 years, while the minimum is 0.4 Eco-credits for a broken bulb after 25 years. A pilot plant that takes into account the factors explained in Eco-credits, offers such exchange schemes is already operational in the North of Spain, making a significant impact on the neighboring community.

8.3. Limitations of the study and perspectives

The search for the minimum required ore grade for mineral extraction has been ongoing for years, yet a consensus remains elusive, posing challenges in estimating the potential for future extraction from low-grade ores. Specialized software is invaluable for understanding the beneficiation process, but obtaining the necessary data can be a hurdle, often requiring an extensive literature review.

The prevailing technology used in this study may evolve in the future, with the emergence of more efficient machines, potentially impacting the results obtained. Cost allocation methods also play a significant role, and different approaches can yield varying results, influenced by the interests of those conducting the calculations.

To further enhance this research, several future directions and perspectives can be explored:

1. Exploring the actual recovery limit, based on mineralogical barriers, for extremely low concentrations of rare metals like gold or PGMs. This can help establish an ore grade limit and develop an indicator considering the physical presence of minerals in the Earth's crust.
2. Analyzing the recoverability of new metals not considered in this thesis, such as copper, lithium, and aluminium, with a focus on recovering metals from secondary resources such as tailings, which do not require comminution and can be cost-effective.
3. Investigating the extraction of specific metals from Li-ion batteries, given their increasing use in electric vehicles and the need to assess large-scale recovery processes.

4. Conducting an environmental impact analysis of metal extraction using different ore grades, employing life cycle assessment software, like GaBi or OpenLCA, to calculate greenhouse gas emissions and assess resource impacts.

These avenues of research can provide valuable insights into sustainable mining practices, ore grade limits, and the environmental consequences of metal extraction processes.

8.4. Discusión

La industria minera ha sido una parte crucial de la civilización humana durante siglos, impulsada por la continua necesidad de las propiedades únicas y las aplicaciones de los metales a lo largo de la historia. Sin embargo, fue durante la Revolución Industrial que la producción de metales aumentó significativamente, resaltando su importancia en nuestra vida diaria.

Los recursos minerales son valiosos activos naturales ampliamente utilizados en diversas industrias, incluyendo equipos eléctricos y electrónicos, transporte y construcción, entre otras. La minería se ha convertido en una parte fundamental para los avances tecnológicos, ya que una mayor cantidad y diversidad de metales se utilizan para la fabricación de nuevos dispositivos tecnológicos. Esto se puede ver reflejado en los metales analizados en esta tesis, donde zinc y plomo son el cuarto y quinto metal más usado del mundo, respectivamente. Por otro lado, el grupo de los platinos son principalmente utilizados en la industria del automóvil, mientras el coltán están presente en cada dispositivo electrónico. Sin embargo, la sociedad a menudo subestima la gran cantidad de metales que se utilizan día a día, así como la creciente demanda de estos recursos, que deriva en una mayor extracción y producción.

Como resultado, la incesante extracción de metales ha llevado a una reducción de ley de mina de muchos metales de la tabla periódica. El oro puede servir como un ejemplo claro, ya que la ley de mina de este metal se ha visto reducido en dos órdenes de magnitud desde 1960. Esta disminución resalta la actual tendencia de reducción de la ley de mina de muchos yacimientos de metales.

Además, la tendencia de disminución de la ley de mina parece estar continuando, lo cual llevaría a un incremento de los precios de las materias primas. Si esta tendencia continua en los próximos años, los metales se volverán más costosos, dificultando su obtención y haciendo que solo unas pocas empresas puedan adquirirlos. Esto tendría un impacto significativo en la sociedad, la disponibilidad de los productos finales y de los impactos medioambientales cuando son producidos.

Con el objetivo de hace frente a esta situación, diferentes gobiernos e instituciones han empezado a concienciarse sobre esta situación. Por ejemplo, la Comisión Europea está invirtiendo grandes cantidades de dinero para recuperar metales y evitar la dependencia de terceros países que contienen minerales. Esto se puede ver en los informes realizados por la Comisión Europea, la cual identifica metales críticos basados en el riesgo de suministro y su importancia económico. Actualmente, esta lista se compone de 34 materiales.

Por ejemplo, esto se puede ver en los equipos eléctricos y electrónicos. Cada año, millones de equipos eléctricos y electrónicos son producidos mientras que los viejos son enviados a vertederos. Cada uno de esos dispositivos contiene pequeñas cantidades de muchos metales, incluyendo algunos que son críticos. Contando todos esos dispositivos, se puede afirmar que hay millones de toneladas de metales en vertederos. Esta situación está empeorando ya que estos desechos están incrementando a un ritmo de un 5% cada año. De este modo, si más metales son enviados a vertederos en los próximos años, llegará un punto donde la concentración en esos lugares sea mayor que en las minas.

Por lo tanto, para evitar el agotamiento de las minas se han mencionado algunas soluciones, como puede ser el reciclaje o las minas abandonadas. Por ejemplo, el reciclaje del plomo es mayor del 60%, el cual es un número considerablemente alto comparado con otros metales como el platino y germanio, que tienen un reciclaje por debajo del 10%. Por otra parte están las minas abandonadas. Algunas de esas minas están siendo analizadas hoy en día debido a la posibilidad de que la concentración puede ser similar a la de las minas activas, y, por lo tanto, obtener beneficio económico de ellas. Además de las minas, también se están analizando los relaves. Los relaves pueden tener una concentración de mineral interesante, con la cual se podría obtener beneficio extrayendo algunos metales desde este recurso.

A pesar de que se están estudiando nuevos enfoques para hacer esta industria más sostenible, es crucial reconocer que el consumo es el primer problema. La gente tiene que entender que los metales son necesarios para numerosos propósitos, aunque su uso sea normalmente ineficiente. Por lo tanto, es necesario concienciar sobre esta situación y promover la reducción de consumo de metales. De lo contrario, podría haber futuros problemas derivados de estas circunstancias, como cuellos de botella, cambio climático y diversos impactos medioambientales que ciertos países tendrían que afrontar.

8.5. Conclusiones

La metodología aplicada en esta tesis, junto con la inclusión del programa informático HSC Chemistry, es posible evaluar el comportamiento del consumo energético en los procesos de extracción cuando se reduce la ley de mina. En especial, se ha calculado la energía para los procesos de trituración y reducción de partícula, flotación y concentración, y refinado y purificación. De esta manera, se han tenido en cuenta diferentes factores para entender el potencial de desarrollo de la industria minera en los próximos años. Entre estos factores se encuentra la energía consumida para extraer un mineral desde los relaves, limitaciones de recuperación, y fluctuaciones del precio en el sector. Utilizando estos factores, se pueden observar los resultados en diferentes escenarios con diferentes concentraciones.

Específicamente, se han analizado tres situaciones para cada metal. El primer escenario representa la energía específica de concentración para la ley de mina actual. El segundo escenario está basado en la energía que se necesitaría si los metales fueran extraídos desde los relaves, con una concentración menor. El último escenario corresponde a la última concentración viable económicamente que se puede extraer.

El primer escenario está basado en la actual ley de mina, mientras que el segundo representa una concentración típica encontrada en los relaves. Por otro lado, el último escenario se ha calculado con diferentes concentraciones, como el valor del último recurso de recuperación (URR) o el límite de recuperación (LOR, por sus siglas en inglés). Los valores del URR han sido obtenidos de bbliografía, siendo el mismo valor para todos los metales, establecido en $5x10^{-5}$ wt-%. En el caso del LOR, ha sido determinado con la máxima energía de extracción, que fue calculada con la cantidad de PGMs en los relaves, siendo esta concentración $2.4x10^{-6}$ wt-%. De este modo, la energía calculada para los PGMs es extrapolada para la curva de energía del Ni y Co, obteniendo un valor de LOR de $4x10^{-4}$ wt-% y $6.9x10^{-5}$ wt-%, respectivamente.

De acuerdo con este proceso, la energía calculada para la concentración mínima de zinc y plomo es de 76.91 toe y 85.5 toe, respectivamente. En el caso del níquel, cobalto y grupo de los platinos, la energía aumenta a 23,696 para cada metal (hay que tener en cuenta que la energía es la misma para los 3 metales debido al método de cálculo del LOR). En el caso del tántalo, este valor es de 3,401 toe por tonelada, mientras que para el niobio es de 1,956 toe por tonelada. La segunda ley de la termodinámica refleja que, a una menor ley de mina, se necesita más energía para la extracción. Por lo tanto, no nos sorprende que el valor más alto corresponda a los valores del URR y el LOR, particularmente para el grupo de los platinos.

Debido a que las minas se están agotando, la recuperación de metales desde los relaves se posiciona como una solución potencialmente viable. Sin embargo, las necesidades energéticas incrementarían considerablemente. Esto se puede ver en los metales analizados en esta tesis, ya que la energía incrementaría 2.5 veces respecto a la actual ley de mina del Ni, en el caso del Co, este valor sería 7 veces más alto, mientras que para los PGMs dicho valor incrementaría en 75 veces.

Los estudios económicos han resaltado la importancia de ciertos parámetros para algunos metales. Por ejemplo, con eventos mundiales significativos como la guerra de Ucrania, donde el precio del níquel se dobló en tan solo 10 días. Este incremento podría hacer rentable la extracción de níquel en minas con una reducida concentración, resultando en un aumento de la energía total consumida. Otro parámetro importante es la distribución de costes. Los cálculos actuales de costos de energía representan el 63%, 67% y 3% del precio de la energía para el Ni, Co, y PGMs, respectivamente. Por lo tanto, cuando se evalúa la explotación de una mina, es vital considerar los precios del mercado para analizar viabilidad de extraer cualquier metal.

De este manera, se ha observedo que extrayendo Ni de los relaves podría ser rentable, tanto con el precio actual de la energía e incluso si este precio fuese el doble. En el caso del Co, sería rentable recuperarlo de los relaves con el actual precio de la energía, asumiento que el precio de mercado del Co se mantiene en su máximo pico histórico. Para el grupo de los platinos, el precio de mercado es ya alto, por lo que extraer estos metales de los relaves genera beneficio con los precios acuales de la energía.

La extracción de Ta y Nb de relaves de una mina de estaño proporciona un claro ejemplo de esta situación. La evaluación económica de este estudio demuestra que incluso si el precio del tántalo se doblara, seguiría siendo rentable extraer este metal de los relaves, teniendo en cuenta que los costos energéticos conjuntos y de manipulación del mineral son atribuidos todos al estaño. Sin embargo, la situación es diferente para el niobio debido al precio reducido de este metal en el mercado. Si el precio del niobio se incrementara o si más energía fuera distribuida a cualquier otro metal, la situación cambiaría, haciendo rentable la extracción de este metal.

Debido a la reducción de la concentración de minerales en las minas, las compañías están buscando nuevas fuentes secundarias para la extracción de minerales, como las minas abandonadas. Hay muchas minas abandonadas en todo el mundo que pueden contener concentraciones importantes de metales que podrían ser recuperados en el futuro, o incluso hoy en día. Esto sería posible debido a que las concentraciones en los relaves son similares a la concentración en minas activas, haciendo que la extracción sea rentable en términos de costos. No obstante, esto requeriría aumentar mucho la energía necesaria, como en el caso del Pb, que se multiplicaría por cinco y en el caso del Zn se multiplicaría por casi dos.

Por otra parte, es importante mencionar las cantidades de químicos y agua requeridos para obtener metales puros. Esto no solo afecta al coste de la planta metalúrgica, sino también incrementa los impactos medioambientales por el uso de químicos y contaminación del agua. Desde un punto de vista económico, se ha probado que es rentable extraer estaño, niobio y tántalo desde los relaves, teniendo en cuenta los precios actuales de los metales. Sin embargo, se tienen que tener en cuenta otros factores para determinar si esta es la solución óptima.

Una situación específica ha sido analizada, estudiando los relaves de la mina de Penouta, en el norte de España. Los resultados obtenidos en la simulación son muy prometedores, ya que demuestran la posibilidad de recuperar niobio y tántalo después de obtener estaño. Esta recuperación tiene el potencial de representar el 1% y 7.4% de la cuota de mercado anual para el Nb y el Ta, respectivamente. Además, también se ha visto que la eficiencia del proceso es muy prometedora. Los resultados muestran que después de llevar a cabo el refinado de los relaves, se ha obtenido una eficiencia de recuperación del 92%, 95%, y 67% para el Sn, Ta, y Nb, respectivamente. Estos porcentajes corresponden a Sn puro (99.99%) y una concentración alta de Ta (79.67%) y Nb (98.45%).

Otra solución para evitar el agotamiento de las minas es el reciclaje, principalmente en los dispositivos que contiene metales críticos, como EEE. Es esencial reconocer estos dispositivos al final de su vida útil como una oportunidad, ya que, a pesar de que se necesita más investigación, podría ser una fuente viable de extracción y ser más rentable que algunas operaciones mineras. Uno de los principales problemas asociados al reciclaje es que estos metales están dispersos en muchas tecnologías con diferentes concentraciones. Esta información es vital, ya que saber dónde se encuentran estos metales es el primer paso para su reciclaje. Para prevenir esta situación, se ha desarrollado una metodología llamada Eco-creditos y que está basada en la rareza termodinámica para evaluar los equipos eléctricos y electrónicos. Esta metodología se compone de tres parámetros: composición, estado y vida del dispositivo. Evaluando estos parámetros, los propietarios de los dispositivos pueden visitar un centro de reciclaje e intercambiar estos dispositivos por varios incentivos, dependiendo del centro de reciclaje.

En este estudio se han analizado dos casos en concreto. El primero de ellos son las tablets, con las que se puede conseguir 43 Eco-creditos como máximo para una Tablet que función después de 5 años, mientras que los mínimos Ecocréditos que se pueden obtener son 5 para una Tablet que no funciona y después de 18 años. También se han analizado las bombillas de LED. Para este caso, los máximos Ecocréditos que se pueden obtener son 3.9 para una bombilla que funciona después de 12 años, mientras que el mínimo estaría en 0.4 para una bombilla rota después de 25 años. Existe una planta piloto que ofrece dichos incentivos y que está operativa en el norte de España, teniendo un impacto significativo en la comunidad vecina.

8.6. Limitaciones del estudio y perspectivas

Durante muchos años, se ha estado buscando el valor mínimo de ley mina para extraer minerales. Sin embargo, este valor sigue sin ser encontrado e indefinido, planteando desafíos en la estimación del potencial de extracción futura a partir de minerales con reducidas concentraciones. El software especializado que se ha utilizado es una herramienta determinante para comprender el proceso de extracción. No obstante, obtener los datos necesarios puede ser un obstáculo, ya que a menudo requiere una extensa revisión de la literatura.

En este estudio se ha tenido en cuenta la tecnología predominante hoy en día, aunque es posible que evolucionen en el futuro con equipos más eficietnes, lo que podría influir en los resultados obtenidos. La distribución de costes también juega un papel significativo, debido a que diferentes enfoques pueden proporcionar resultados variados, que pueden estar influenciados por los intereses de quien realiza los cálculos.

Para mejorar aún más la investigación llevada a cabo, se pueden explorar varias direcciones y perspectivas futuras que se comentan a continuación:

1. Explorar el límite real de recuperación, basado en barreras mineralógicas, para concentraciones extremadamente bajas de metales raros como el oro o los PGMs. Esto puede ayudar a establecer un límite de ley de mineral y desarrollar un indicador que considere la presencia física de minerales en la corteza terrestre.
2. Analizar la recuperabilidad de nuevos metales no considerados en esta tesis, como el cobre, el litio y el aluminio, con un enfoque en la recuperación de metales a partir de recursos secundarios como los relaves, que no requieren del proceso de molienda y pueden ser rentables.
3. Investigar la extracción de metales específicos de baterías de iones de litio, dado su creciente uso en vehículos eléctricos y dispositivos electrónicos y la necesidad de evaluar procesos de recuperación a gran escala.
4. Realizar un análisis del impacto ambiental de la extracción de metales utilizando diferentes leyes de mineral, utilizando software de evaluación del ciclo de vida, como GaBi u OpenLCA, para calcular las emisiones de gases de efecto invernadero y evaluar los impactos en los recursos.

Estas líneas de investigación pueden proporcionar valiosos conocimientos sobre prácticas mineras sostenibles, límites de ley de mineral y las consecuencias ambientales de los procesos de extracción de metales.

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ANNEXES

Annex 1

The Module EpH is the module to illustrate E-pH (Pourbaix) diagrams. It shows the thermodynamic stability areas of different species in an aqueous solution. Stability areas are presented as a function of pH and electrochemical potential scales

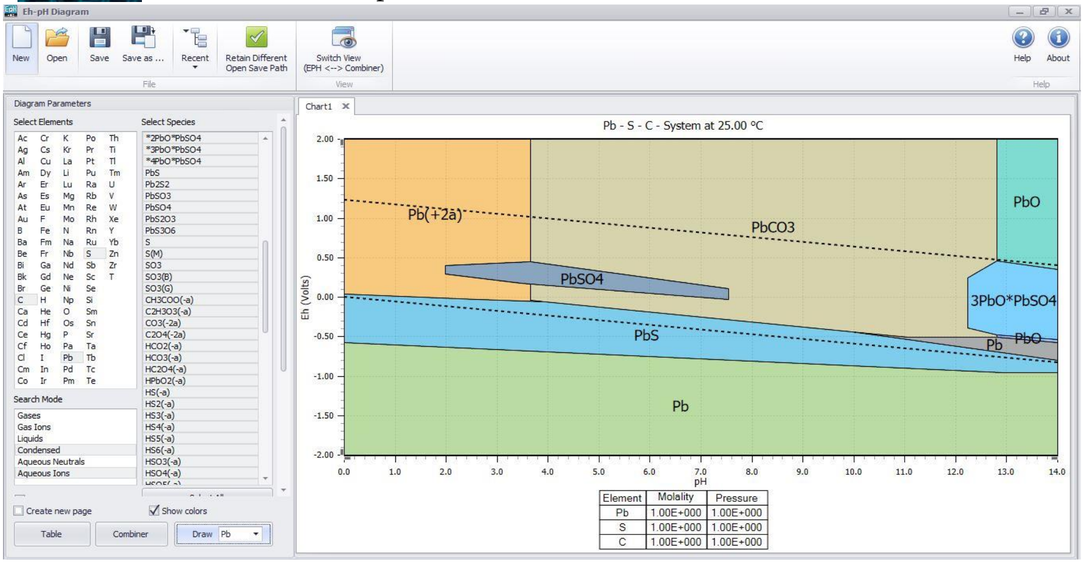

Figure A. 1. HSC Outotec, Module EpH. Screenshot of a system Pb-S-C at 25°C.

HSC database contains more than 28,000 species with data on enthalpy (H), entropy (S), and heat capacity (Cp). This module gives rough estimates of H, S, and Cp values for the chemical species that exist in the HSC database, and also for those that do not exist.

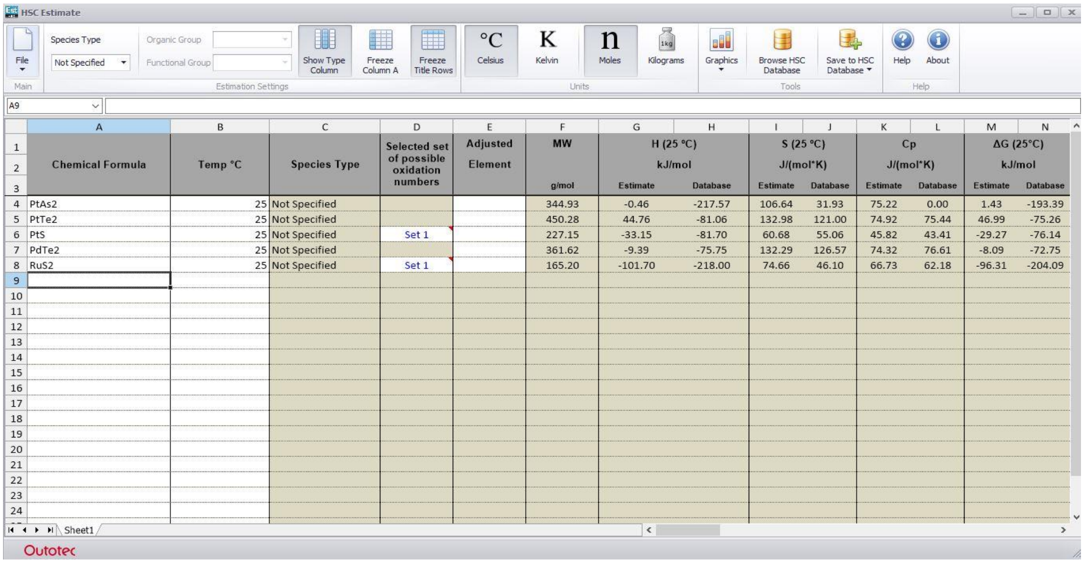

Figure A. 2. HSC Outotec. Module Est. Screenshot of the calculation of different species.

Equilibrium module enables the calculation of multi-component equilibrium compositions in heterogeneous systems. In this way, it is required to specify the chemical reaction system, with its phases and species, and provide the amounts of raw materials. Then, the software calculates the equilibrium in isothermal and isobaric conditions.

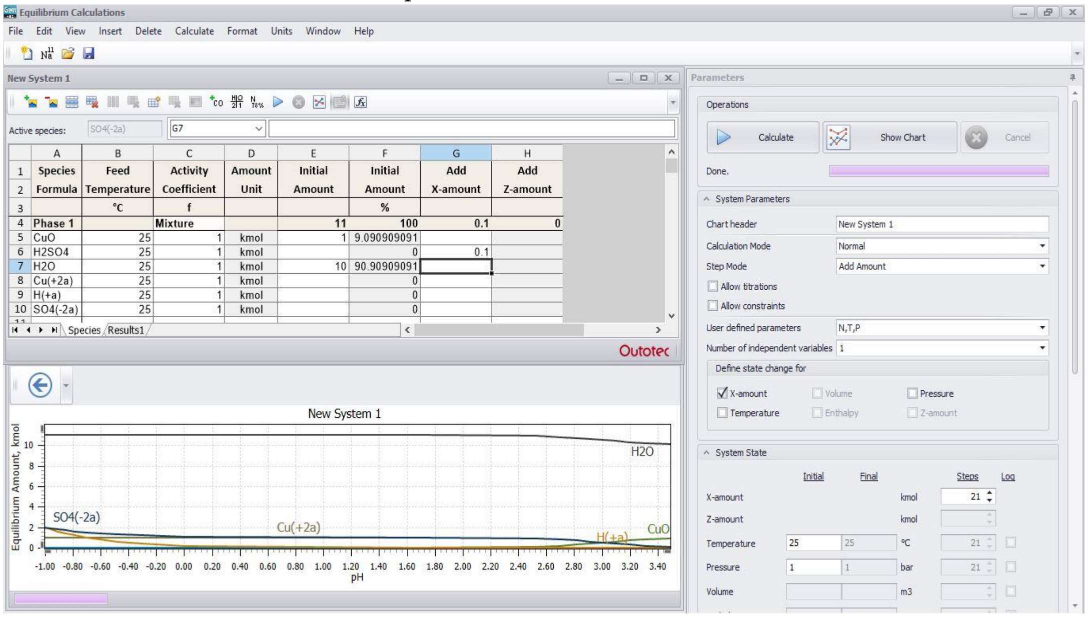

Figure A. 3. HSC Outotec. Module Gem. Screenshot of the equilibrium composition and pH.

Thera are two databases in the software. One of which was developed and created by the developers and it is called 'Main database'. The other is called 'Own database' and this can be created by the user when a specie is not in the Main database. In here, it is possible to add thermodynamic parameters to the species desired that the user adds.

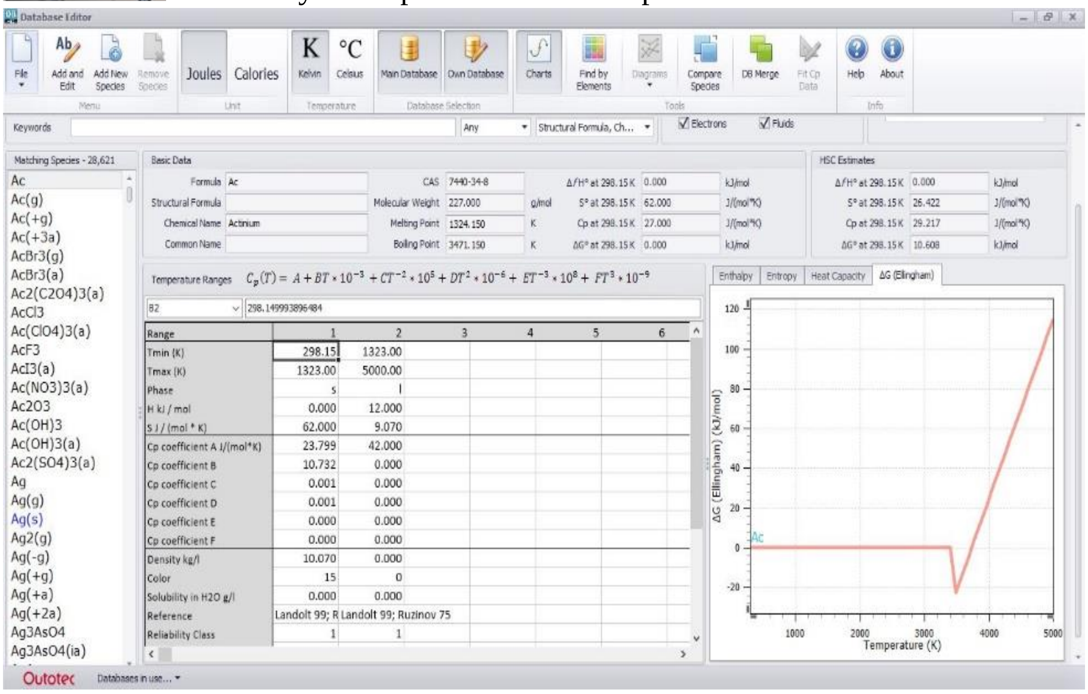

Figure A. 4. HSC Outotec. Module DB. Screenshot of the database and properties of one specie.

In this module, it is possible to represent the basic thermochemical data for specific species in a graphical chart. Different diagrams can be illustrated as a function of the temperature.

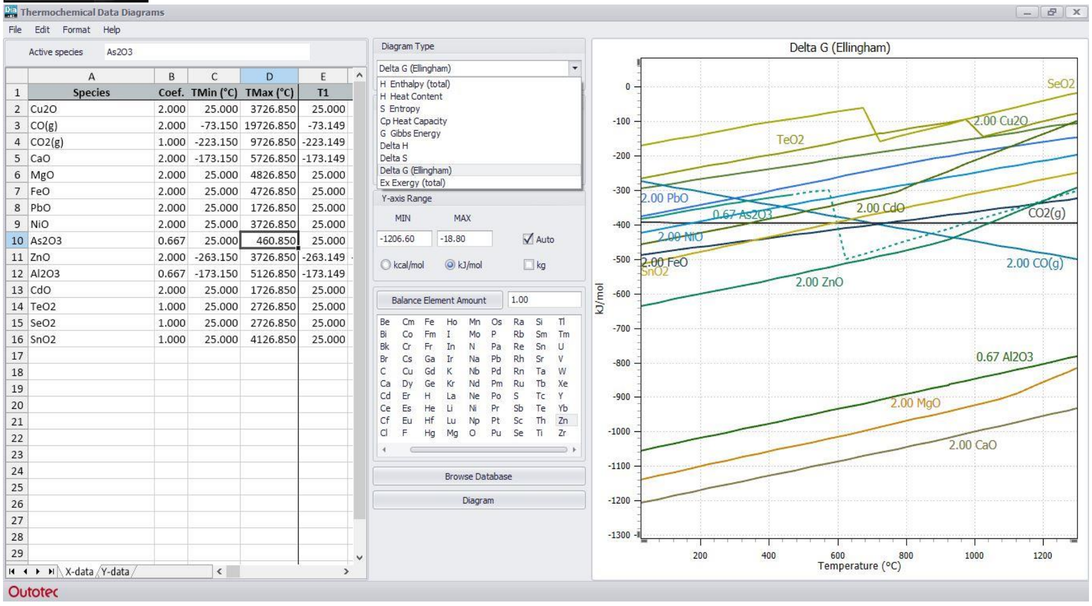

Figure A. 5. HSC Outotec. Module Dia. Screenshot of compositions for the Ellingham diagram.

The phase stability diagrams show the stability areas of condensed phases in a ternary system as a function of temperature or in isothermal conditions. This module calculates the phase stability boundaries as lines based on the reaction equations

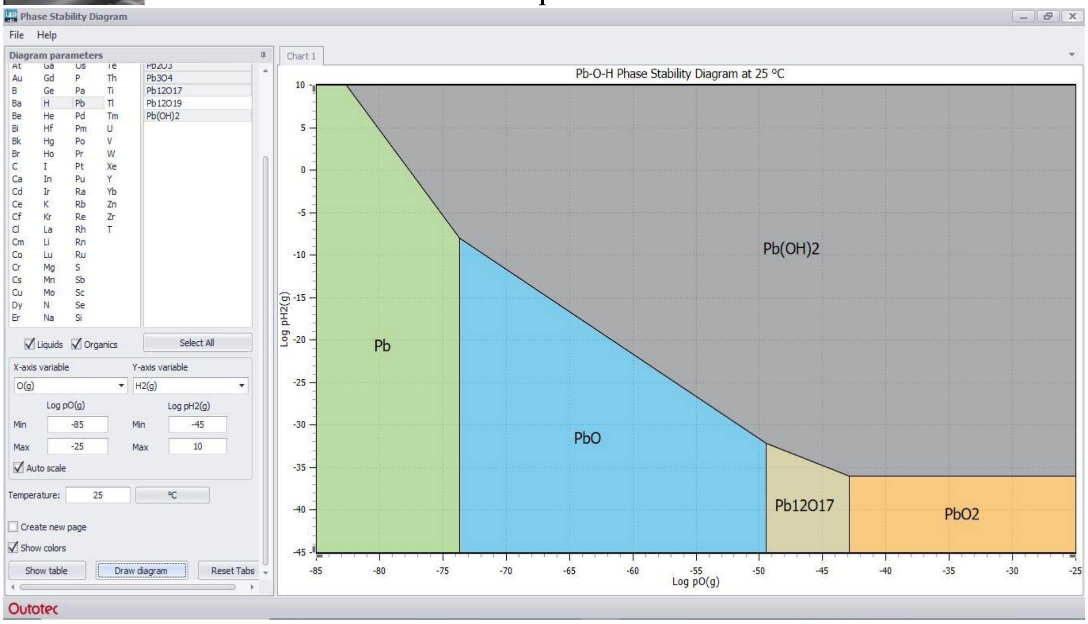

Figure A. 6. HSC Outotec. Module Lpp. Screenshot for a phase stability for Pb-O-H at 25 °C.

The main difference between of in this module and the previous one is that here the calculation of the diagrams is based on the minimum Gibbs energy. Moreover, this module also draws temperature partial pressure diagrams as well as p-p diagrams with partial pressure on both axes

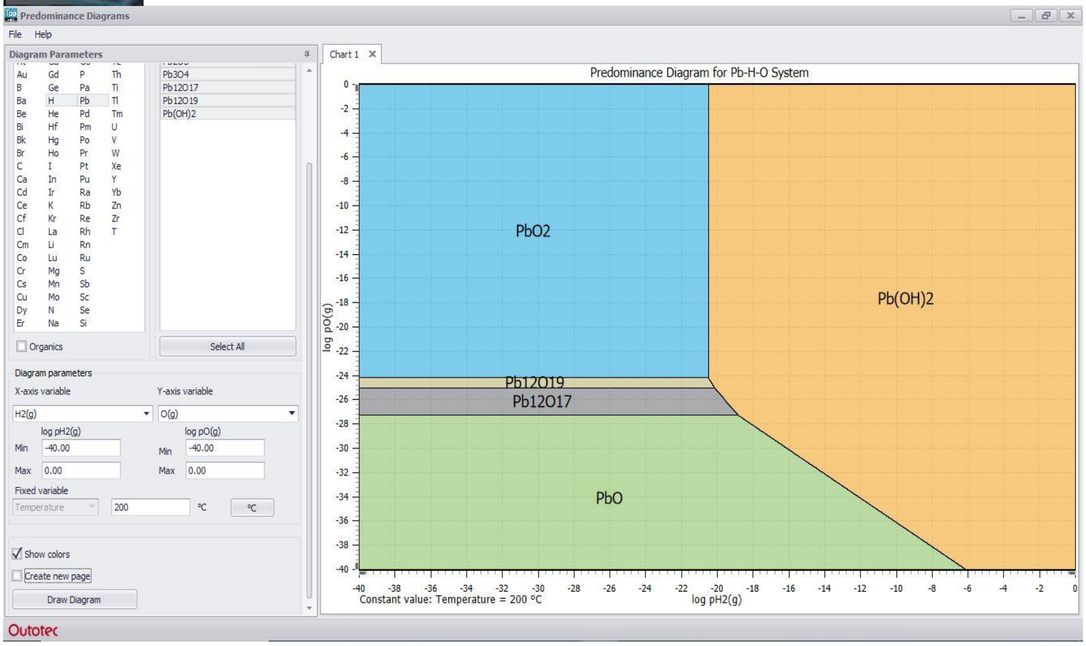

Figure A. 7. HSC Outotec. Module Tpp. Screenshot for a predominance diagram for Pb-H-O system.

This is the main module that has been used in the Thesis. In here, it is possible to simulate different processes, such as comminution, flotation and refining. Several parameters can be introduced in the units to proceed with the calculation of beneficiating minerals

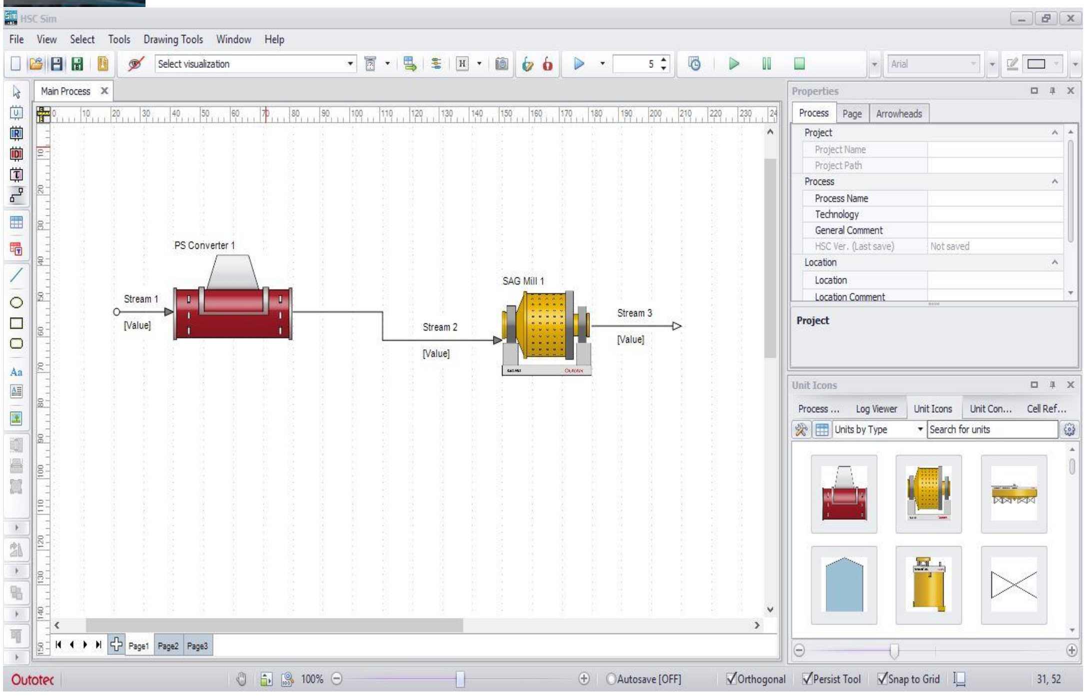

Figure A. 8. HSC Outotec. Module Sim. Screenshot of a simple process with two untis.

Annex 2

Table A. 1. Material composition for different electric and electronic devices. Values are in grams.

Element	Iphone 6	Element	Tablet	Element	Laptop	Element	Bulb LED
Al	31.14	ABS	166.925	ABS	373	Ag	0.00355
As	0.01	PMMA	22.5	PC	406	Al	17.4929
S	0.44	Silicon	61.925	Other plastic	343	Cu	2.31957
Bi	0.02	Ag	0.0218	Glass	300	Fe	1.28226
Ca	0.44	Al	0.4662	Epoxy	244	Ga	0.00923
C	19.85	As	0.0225	Cu	270	Ni	0.73982
Cl	0.01	Au	0.0148	Al	512	Pb	0.00007
Co	6.59	Cd	0.0002	Steel	871	Au	0.00426
Cu	7.84	Co	12.675	Au	0.36	Sn	2.00788
Cr	4.94	Cr	0.0759	Ag	0.92	Ti	0.01207
Sn	0.66	Cu	5.559	Pd	0.05	Ce	0.00007
P	0.03	Fe	2.3198	Ni	0.99	Y	0.00355
Ga	0.01	Hg	0.0001	Zn	0.1	Polycarbo	14.0537
H	5.52	In	0.0182	Nd	1.06	Polyester	17.6143
Fe	18.63	Li	4.43625	Sn	9.3	Polyamide	6.14931
Li	0.87	Mg	0.2811	Pb	6.1	Others	9.30668
Mg	0.65	Mn	14.3156	Co	65		
Mn	0.29	Ni	12.4028	Ta	1.7		
Mo	0.02	Pb	0.5457	Pr	0.27		
Ni	2.72	Pd	0.0001	Dy	0.06		
Au	0.014	Sb	0.0705	In	0.04		
O	18.71	Sn	0.9155	Pt	0.004		
Pb	0.04	Ti	0.1886	Y	0.0018		
K	0.33	Zn	0.6136	Gd	0.00001		
Si	8.14	Other	93	Ce	0.00008		
Ta	0.02			Eu	0.00013		
Ti	0.3			La	0.00011		
W	0.02			Te	0.00004		
V	0.04			Other	442		
Zn	0.69						
TOTAL	128.98		405		3,846.9		71

Annex 3

Table A. 2. Contribution to the papers published during the PhD.

Contribution	Paper I	Paper II	Paper III	Paper IV	Paper V
Conceptualization	X	X	X		
Methodology	X	X	X	X	
Software	X	X	X	X	
Validation	X	X	X	X	
Formal analysis	X	X	X	X	X
Investigation	X	X	X	X	X
Data Curation	X	X	X	X	X
Writing Original draft	X	X	X	X	X
Writing Review and Editing	X	X	X	X	X
Visualization	X	X	X	X	X

Paper I: *Mining energy consumption as a function of ore grade decline: the case of lead and zinc*

In this paper, I carried out the conceptualization to shape the direction and objectives of the study. I also developed the methodology applied, gathering information on lead and zinc from the bibliography to simulate the extraction process using specialized software. I was also responsible for the original draft and subsequent revisions of the paper, making changes and composing responses to the reviews. Lastly, I presented the work at international conferences.

Paper II: *Limit of recovery: How future evolution of ore grades could influence energy consumption and prices for Nickel, Cobalt, and PGMs*

I defined the objectives of this paper, where the extraction of three metals was analyzed. I gathered information from a literature review of nickel, cobalt, and platinum group metals to develop the extraction process in specialized software. I authored the initial draft as well as subsequent versions, incorporating reviewer's comments for publication. Furthermore, this work was presented at an international conference.

Paper III: *The Energy Cost of Extracting Critical Raw Materials from Tailings: The Case of Coltan*

In this case, I also undertook the conceptualization, establishing the direction and goals of the study for extracting niobium and tantalum. While some data was provided by a research center, additional information was gathered from references to enable the simulation of the extraction process within specialized software. I was responsible for all versions of the paper, including the initial draft submitted to the journal and subsequent versions updated on the platform, despite some contributions from other authors. This work was presented at an international conference..

Paper IV: *Simulation to Recover Niobium and Tantalum from the Tin Slags of the Old Penouta Mine: A Case Study*

In this paper, I developed the methodology for recovering niobium and tantalum from tailings. The process was executed by a research center, although I further developed and analyzed it using specialized software. While other authors made some minor contributions to the draft, I was responsible for the initial draft and subsequent versions. This work was also presented at an international conference.

Paper V: *Eco-credit system to incentivise the recycling of waste electric and electronic equipment based on a thermodynamic approach*

In the last paper, I conducted formal analysis and investigation. I collected extensive information from the bibliography to conduct a thorough analysis of the results. While I was responsible for the initial draft of the paper, significant contributions were made by other authors in both the first draft and the subsequent reviewed versions. I also presented this work at an international conference.

PAPER I

Volume 20 | Issue 2 Article 5

2021

Mining energy consumption as a function of ore grade decline: the case of lead and zinc

Mining energy consumption as a function of ore grade decline: The case of lead and zinc

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Abstract

Demand for raw materials is increasing exponentially. To satisfy that demand, more minerals need to be mined from the Earth's crust. As a result, minerals are being exhausted, and ore grades decline. Lower ore grade mines also mean more energy, which in turn entails fossil fuel emissions and more climate change. This paper estimates the specific energy for the beneficiation process of metals lead and zinc as case studies. The evaluation is performed with specialized software, HSC Chemistry which assesses the specific energy for every stage: comminution, flotation, and refining. Different scenarios have been established to simulate the behavior of a mine when it approaches depletion. Preliminary results show that energy consumption for lead would increase by five times when compared to the current situation if ore grades decrease until the level of tailings, while for zinc by almost two.

Keywords: energy, ore grade, lead, zinc, beneficiation, tailings

1. Introduction

Modernization and consumer culture are increasing the demand for materials to satisfy the needs of society [1]. In this respect, electric and electronic equipment (EEE) or renewable energies are developing very fast, relying on the use of a considerable amount of raw materials [2]. For instance, the EEE trend is that this industry will increase in the coming years at 3—5% [3]. More metals need to be extracted every year to satisfy this exponential demand, for which more energy needs to be brought into play [4], [5]. Mining energy still relies almost completely on fossil fuels, exacerbating the liberation of greenhouse gases to the atmosphere and accelerating climate change. It is a fact that mining is among the most polluting industries [6].

Viederman [7] defined that a sustainable society aims to ensure the health of human life, culture, and natural capital for the present and future generations. Preserving the mineral capital can only be achieved through recycling and circular economy, since minerals are limited in the Earth's crust. Accordingly, the energy required to extract the same amount of materials spirals up [8], since as we will see in this paper, extraction follows a negative logarithmic pattern with the ore grade. This is a consequence of the Second Law of Thermodynamics. Can we then expect more fossil fuel use and GHG emissions due to mining in the future? What would be the increase in energy consumption if we extracted metals from tailings? Is there an ore grade limit considering current technology?

Each year, minerals are being extracted, and the ore grade of mines is decreasing [9]. As a result, the energy to beneficiate the mineral is growing due to decreased concentration in the crust [8]. Therefore, it becomes essential to estimate future extraction costs and so anticipate potential raw material shortages. This paper will analyze the influence of ore grade decline on energy consumption for two significant metals, lead, and zinc. To that end, a specialized software called HSC Chemistry will be applied, analyzing all the processes required to mine, beneficiate the mineral, and finally refine them. The simulation allows us to obtain the energy consumption as a function of the starting ore grade,

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providing us with valuable insights to the questions raised above.

2. Lead and zinc as commodities

Lead was discovered more than 5000 years ago. Its use has been essential for civilization development, historically used to create ornaments and statues to decorate castles and cathedrals [10]. Nowadays, due to its specific properties [11], lead is the fifth most used metal, found in many different applications such as in storage batteries, sheathing electric cables, construction, tanks, and ammunition [10]. Lead is particularly essential in energy storage, as the most common batteries are lead-acid [12], vastly used in the automotive industry. According to the International Lead & Zinc Study Group, the demand for the lead rose by 2.7% in 2018 due to the increased Chinese (3.4%) and United States (3.1%) demand [13]. For the coming years, demand is expected to increase at a rate of 4.2%, with Australia experiencing the most significant growth [13]. Fig. 1 shows the lead production trend for the last decade, where China stands out over the rest producing countries. That said, Australia may play a major role as it contains the highest reserves of lead in the world, with more than 24,000 Mt [14]. The second country which follows Australia in reserves is China, with more than 18,00 Mt but already producing more than 2,00 Mt per year [14].

Regarding zinc, even if it was already known in Roman times, it was not recognized as a single metallic element until the 16th century. It was first called zinckum and eventually zinc in 1743 [10]. Zinc metal is the fourth most used metal, with extensive applications such as in galvanization, alloys (especially brass), and even zinc sulfide for electroluminescence photoconductivity [10]. Since zinc is usually found with lead in nature, it is extracted as a by-product of the latter. The beneficiation process carried out to extract lead facilitates the separation of zinc as well.

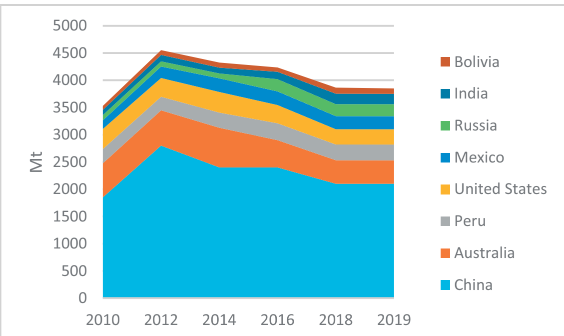

Fig. 1. World lead production [Mt] [14], [15].

Zinc mine production rose by 1.1% in 2017, and it was expected to increase this figure up to 5.1% in 2018 [13]. This increase is due to Dugald River Mine's opening in late 2017 in Australia and the Castellanos Mine opening in late 2017 in Cuba. Fig. 2 shows zinc production in the last decade, showing that after a small peak in 2012, production is increasing again. Therefore, it is expected to have a significant increase in the upcoming decades according to different authors [16], [17], which means that in that time, almost 100% of zinc should be obtained from secondary resources (being 15% nowadays [18]).

3. Case study

Based on previous studies [8, 18–20], the specific energy required for concentrating lead and its by-product, zinc, will be assessed. The reason to focus on these two metals jointly is that they are usually found together in nature [23] and hence their geological distribution is similar [24]. For the analysis, models in HSC software have been carried out for every metal to estimate the energy required for their processing. HSC Chemistry [25] is specialized software where thermodynamic and mineral processing calculations can be carried out.

Fig. 3 shows the general flowchart for the mining, beneficiation, and refining of lead and zinc. It has been developed following guidelines found in technical reports: Prairie Creek mine in Canada [26] with a capacity converter of 87 tons per hour [tph], Platosa Silver–Lead–Zinc in Mexico [27] with a capacity converter of 83 tph, and Ying property mine in China [28], with a capacity converter of 74 tph. Additionally, essential data to elaborate the flowsheet has been taken from specialized mineral processing books [29], [30], [31], while specific details for every process for the particular metals analyzed along with this paper have been consulted from different references [30, 31]. The aim of this paper is to try to understand how it would be the behavior of a mine when the ore grade decreases. Therefore, twelve different scenarios will be created

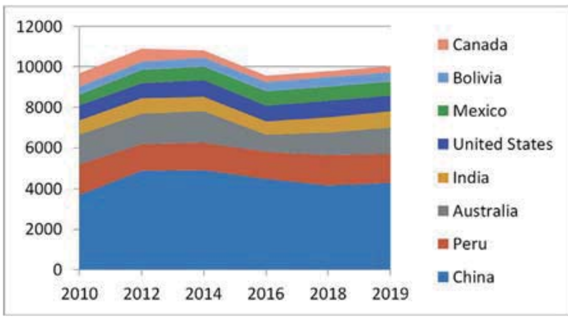

Fig. 2. Production of zinc by year [Mt] [19].

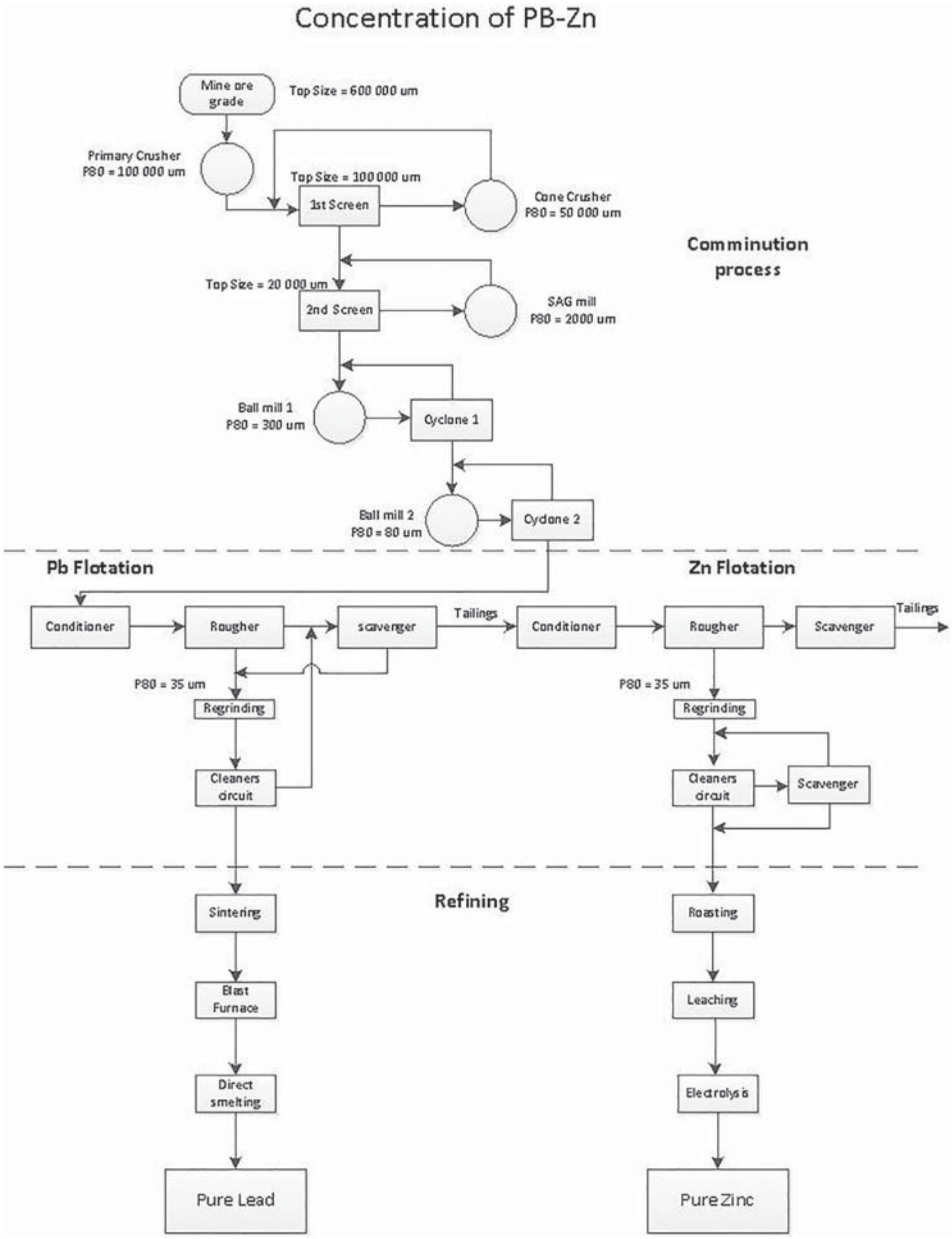

Fig. 3. Flowsheet of the beneficiation process for lead and zinc.

to calculate the energy needed to obtain a certain metal amount. The initial scenario will be carried out with the current ore grade, while the rest will be one-third of the previous, reaching very low values and simulating and predicting the problems that could appear in the future.

It should be stated from the outset that there are no similar mines, and therefore, the results obtained from every mine could be different. The results obtained for a generic mine can be used as a proxy for the rest, as the results show an estimation of the specific concentration energy when the ore grade decreases. In this paper, Ying property minerals have been chosen as a starting point for the simulation in HSC [28]. There are many minerals as lead and zinc sources [34]. However, not all of them are abundant, or the amount of Pb and Zn in them is very low and are not cost-effective to use [30, 32–35]. This is why we use galena as the main source for lead, while sphalerite for zinc, both sulfide minerals relatively abundant and wih high metal concentrations [38].

4. Methodology

4.1. HSC simulation

The feed chosen to introduce in the software is 800 tons per day [tpd], a rather high value since as the concentration is reduced, more amount of rock needs to be processed. This initial feed has a maximum particle size of 600 mm. Three main energy inputs have been considered in the analysis, which will then be validated with bibliographic data: ore handling, concentration, and refining.

Ore handling entails the diesel used for transportation, machinery, and electricity production. After ore handling, the first stage is comminution, carried out through crushing and grinding machines to reduce the particle size until the rock is small enough to proceed with the next stage [39]. As calculated in [8], [21], [22], the comminution was computed with well-known formulas such as Bonds equation [27, 34], which is applied to calculate the specific energy required for the different mills used along the comminution process.

$$W = 10\, W_i \left(\frac{1}{\sqrt{P_{80}}} - \frac{1}{\sqrt{F_{80}}} \right) EF_x \tag{1}$$

In Eq. (1), W_i is the work index, which is defined as the comminution parameter that expresses the resistance of the material to crushing and grinding, P80 is the diameter in microns through which 80% of the product passes, F80 is defined as the size through which 80% of the feed passes [31] and EF_x which is an efficiency factor, is an adjustment of the power calculated by utilizing efficiency factors dependent on the size of the mill, size, and type of media, type of grinding circuit, etc. [27, 36, 37].

The first stage (comminution process) aims to reduce the particle size down to 35 μm [27], using the flowsheet shown in Fig. 1. Comminution is divided into three main steps: Crushing, grinding, and regrinding. Crushing is carried out by a primary crusher, reducing the size to 100,000 μm, and then, the feed is sent to a screen, acting as a filter for particles higher than 100,000 μm. Any larger particle is diverted through a cone crusher, decreasing the size to 50,000 μm and passing through the same screen.

Once all the feed has passed through screen 1, another screen is introduced with a size filter of 20,000 μm, starting the grinding process. Particles, which do not pass screen 2, are sent to the SAG mill to reduce the size to 2,000 μm, crossing the filter applied. A ball mill is the next step when all the feed is out of screen 2. The mill is used to minimize it down to 300 μm, adding a cyclone just right after to assure that all particles satisfy the size requirements. Similarly, Ball mill 2 reduces the size to 80 μm and allows the feed to go to flotation. It is important to mention that the comminution process has been developed according to the reduction ratio [27, 34, 38]. Table 1 has been elaborated to summarize all the numbers and to recap every process with its details.

Sulfide metals are the main sources to produce lead and zinc also because they are separated from the rest of the minerals applying flotation [44]. At this point, the separation between lead and zinc is produced, because in the first unit of the flotation process there are two outputs: lead-rich feed and the tailings, which are recirculated to a different flotation process, to enrich zinc. [45]. The flotation process consists of a rougher circuit followed by several cleaners and a retreat circuit [46]. This stage aims to make the wanted metals float by adding additives. The rest of the minerals (unfloated) are vacated to the tailings [40, 41]. As two different metals are wanted, two different processes will be carried out, setting up the volume and the number of cells with common values obtained from manufacturers data [25, 42] and institutions specialized in flotation cells [48].

The process ends with the refining stage. When the feed contains the concentration desired, pyrometallurgy follows to obtain pure lead. In contrast, hydrometallurgy and an electrolytic process is used to obtain pure zinc [36]. Pyrometallurgy is composed of sintering and the use of a blast furnace [49].

5. Results

As was previously explained, the comminution process is common for both minerals. Hence, in this section, the modeling results regarding the specific energy required for every unit in the comminution

Table 1. Details of the comminution process.

	Primary crusher	Cone crusher	SAG mill	Ball mill 1	Ball mill 2	Re-grinding	
						Pb	Zn
Feed [tph]	800	512	578	1,569	1,406	474	250
P80 [μm][a]	100,000	50,000	2,000	300	80	35	35
F80 [μm][b]	245,631	219,277	38,163	3,164	138	50	48

[a] 80% of the passing size of the product [21].
[b] 80% of the passing size of the feed [21].

process will be shown. Subsequently, the section will be divided to explain the flotation and refining process for every mineral, highlighting the values obtained.

5.1. Comminution process

To start with the calculation of every unit, it must be noted that the Work Index (W_i) selected to introduce in Eq. (1) is the same for both minerals as their proximity is very close, and the difference between them in final results cannot be appreciated. Thus, the value chosen to introduce as a W_i is 11 kW h/t, which is obtained from [50]. Furthermore, different efficiencies must be added according to Rowland efficiency factors (EF_x) obtained from a literature review [43].

Table 2 is elaborated to determine the energy used for the comminution process. Eq. (1) has been used to calculate the specific energy for every unit, while the machines selected and settings come from references [27, 48], proposing units able to supply the power demanded. The results obtained are in line with the literature [27, 42, 48, 49], all of them in the same order of magnitude. It can be seen that there is a different regrinding for lead and zinc.

5.2. Flotation process

The flotation process is a concentration technique that uses the difference of the surface properties to separate minerals [38]. The flotation circuit is composed of three elements: roughers, cleaners, and scavengers. Roughers receive the pulp coming from the mills. Then, valuable sulfides float, obtaining a concentrate with many impurities [38]. Cleaners are commissioned to eliminate the impurities to obtain the concentrated mineral [38]. Scavengers are usually added right after the roughers in order to make the remaining sulfides that did no float in the rougher machine to float [38].

To simulate the behavior of a mine when the ore grade decreases, different scenarios will be created, reducing the initial concentration in the mine. This process will aim to increase the concentration until typical values required for the metallurgical process. Every scenario will contain a lower ore grade. This also means that more flotation units will be needed to obtain the same concentration.

The first scenario was developed with a typical value found in mines of 2.83 wt% and 6.29 wt% [26] for lead and zinc, respectively. The metal content needs to be increased to 45 wt% for lead and 52 wt% for zinc [36]. This is achieved through a rougher to start the separation. Due to their froth properties, galena floats in the surface while sphalerite is vacated through the tailings, starting a new flotation process.

The concentration stream from the rougher, containing galena, is passed through different cleaners and scavengers until the required concentration is reached. A regrinding process in between is used to make sure there are no particles larger than 35 μm. It must be mentioned that other tailings from flotation units are sent to the zinc flotation process to recover all possible minerals. Once all the sphalerite feed starts the flotation process, it is sent through a new rougher unit. After a regrinding and flotation process, the required pre-refining concentration is achieved.

More scenarios are created to simulate how each metal concentration's specific energy increases when the ore grade decreases. Scenario 1 represents the current ore grade, scenario 4 represents the tailings ore grade, scenario 8 represents the theoretical limit established by Sverdrup et al. [17], and scenario 12 represents a minimum concentration, very close to crustal concentrations.

Table 3 shows the results, highlighting that the last scenario created (12) entails the highest value of specific concentration energy as expected. It must be said that the flotation process for each mineral has been designed according to parameters obtained

Table 2. Power demand and energy required for the comminution process.

Equipment	Power demand [MW]	Specific energy [kWh/t-rock]
Primary crusher	0.60	0.75
Cone crusher	0.45	0.88
SAG mill	4.20	7.27
Ball mill 1	17.80	11.40
Ball mill 2	17.80	12.72
Re-grinding Pb	5.96	12.57
Re-grinding Zn	2.7	10.80

Table 3. Variation of the specific energy for concentration in flotation.

Scenario	Ore grade wt%	Lead, GJ/t-ore	Ore grade wt%	Zinc, GJ/t-ore
Scenario 1 (con. in mine)	4.55	10.85	6.5	50.90
Scenario 4	0.17	51.11	0.24	93.01
Scenario 8	0.002	3,220	0.003	3,579
Scenario 12	2.5×10^{-5}	267,407	3.6×10^{-5}	293,007

from literature review [26, 37, 40, 45, 51, 52], such as recovery ratio, residence time, the volume of the cell, etc.

5.3. Refining process

Refining is the last step to obtain pure metals [53]. In this case, the metals studied are not pure yet, so other processes are used to obtain the corresponding metal bullions. Pyrometallurgy is the treatment chosen for lead refining due to the high velocity of the reactions, the high production, and because it is the most common and developed process for obtaining pure lead [56].

There are several ways to obtain the bullion for the zinc refining process, being ISF (Imperial Smelting Furnace) and electrolysis the most common [36]. Although ISF experimented an important growth at the end of the 90's decade, the electrolytic process is the most applied since 1970, and it is expected to continue as it counts with 86 plants, 76 more than the second one [36].

5.3.1. Lead

There are several procedures to treat lead, being historically the most common based on the two-stage process for primary production [37]. Secondary lead production is derived from scrap and acid batteries due to the high proportion of lead they contain [57]. There is an alternative process to the two-stage process called direct smelting, which has advantages over the conventional treatment (e.g., more efficient process in terms of energy consumption), obtaining a high percentage of lead in the slag [37].

In this study, we consider direct smelting as is the most efficient and simplest process to obtain lead [49]. There are several direct smelting processes (Isasmelt, Kivcet, QSL, Outokumpu), and all of them hold different heat input, designs, and process control procedures [44, 51]. We use the QSL process; as it proceeds in one single step, the emissions are lower, and the feed range is very wide [49].

Fig. 4 shows the process applied to obtain the lead bullion. As it can be seen, a sintering machine and a blast furnace are the main units of the process. Although it is unnecessary to incorporate the sintering unit, it is useful to remove the pulp's remaining water. Coke is then introduced in the blast furnace as a fuel, limestone is introduced to react with the pulp, and the air is introduced to control the temperature of the blast furnace [44, 51].

The blast furnace outputs are related to the chemical reactions produced in it, achieving lead bullion with a lead grade of 99%, while sulfides mainly form matte. Further, speiss (a mixture of metal arsenides and antimonides) is composed of oxides, and the slag is composed of various metal oxides and a small percentage of lead.

5.3.2. Zinc

As it was already mentioned, pure zinc is obtained through an electrolytic process, which is shown in Fig. 5. This process consists of a roasting step to eliminate the sulphur of the feed and convert it into zinc oxide [36]. The following step is to prepare the solution, which involves different leaching stages. Electrolysis is then applied with a final melting step in a furnace to obtain pure zinc [36].

The feed contains a high amount of sulfides and must be converted into oxides to eliminate the pulp's impurities to prepare it for the following steps [45, 50]. The roasting process's significant impurities are Cu, Pb, Si, Ca, Na and K [58]. This process is carried out through the roasting furnace, where natural gas is introduced in order to react with the pulp and eliminate sulfurs. The oxygen input is controlled avoiding reaching temperatures higher than 960°C to prevent molten phases [58].

Once the feed is almost free of sulfides, it is sent to the leaching unit to dissolve zinc as selectively as possible to create a solution suitable for upcoming

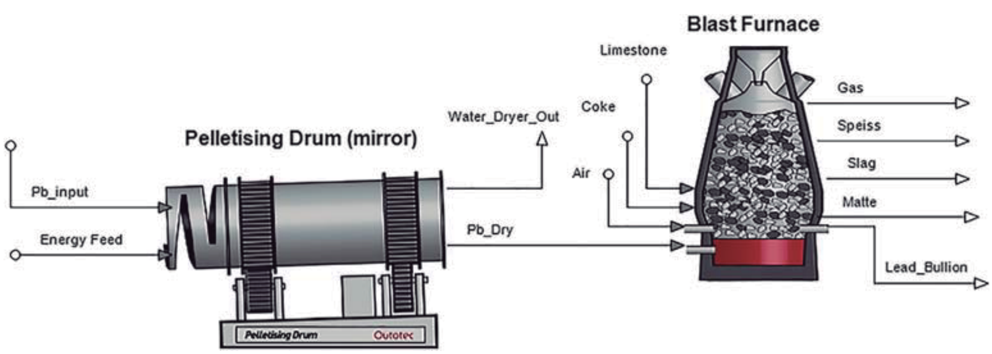

Fig. 4. Lead the refining process.

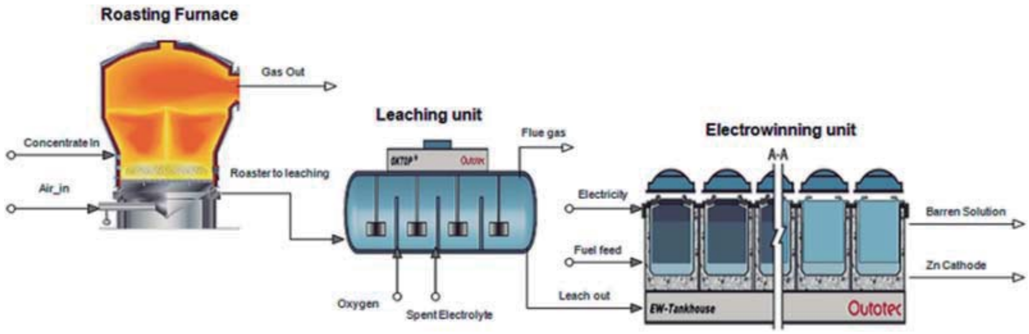

Fig. 5. Zinc refining process.

processes [45, 54]. Apart from other leaching agents, zinc oxide is usually leached by sulfuric acid due to its chemical properties and low cost [59], setting up the leaching rate according to temperature, time, pH, and particle size, among others [54, 55]. Leaching is carried out in two steps: the primary leaching where zinc sulfate and the high amount of zinc oxide will be dissolved by neutral leaching, and secondary leaching where zinc ferrites will be eliminated, although it could be challenging to leach the ferrite [45, 56].

To end up with the refining, the feed is introduced in the electrowinning unit, where zinc ions are discharged from a zinc sulfate solution with an open electrolytic cell [36]. It must be noted that gas treatment has been considered along the refining process. However, due to the low impact in the final results, it has been discarded.

6. Analysis

6.1. Specific concentration energy as a function of ore grade

As explained in the introduction, ore grades are expected to decrease in the future as mines become depleted through the increasing extraction.

Different scenarios were created, reducing the concentration in mines to estimate the corresponding energy consumption. Fig. 6 and Fig. 7 show the results obtained for lead and zinc, respectively. It can be seen that, as expected, the energy increases exponentially when the ore grade of the mine decreases. This can be explained by analyzing the comminution and flotation processes. The comminution process is applied to reduce the particle size with a specific concentration. Therefore, when ore grade declines, the specific comminution energy increases since less desired mineral is contained in the rock processed. On the other hand, the flotation process increases because more roughers, cleaners, and scavengers are needed to concentrate the mineral until typical values before sending it to the metallurgical process. With this concentration, flotation units require a high amount of specific energy since the concentration values must be decreased to a very low ore grade (close to 10^{-5} wt%).

Some authors [61–63] have designed different models trying to identify which is the lowest ore grade from which to extract metals. Some results show that this value is 5 × 10−5 wt-% [35] as an ore grade limit. Below that number, production costs

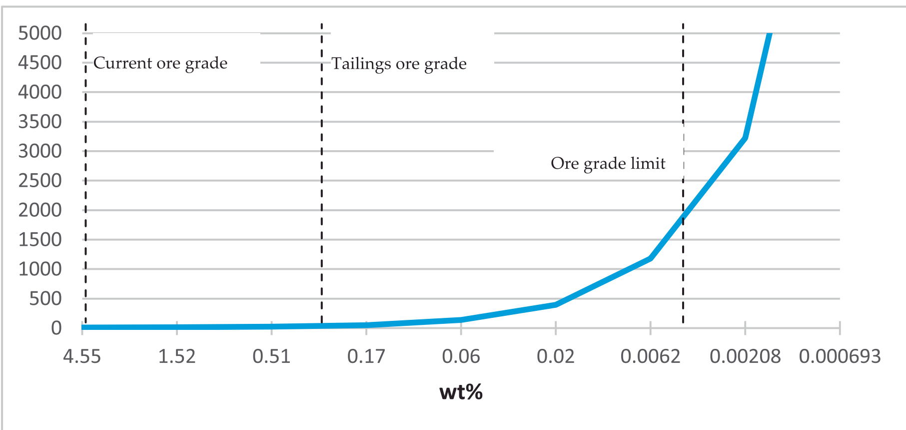

Fig. 6. Specific energy for concentration for lead [GJ/t-Pb].

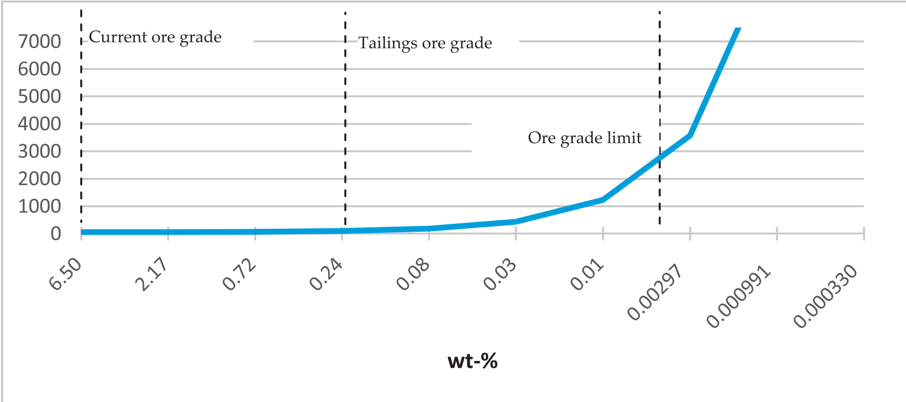

Fig. 7. Specific energy for concentration for zinc [GJ/t-Zn].

would be higher than the value of the ore, considering the best available technologies nowadays [17]. It is known that there are mines with an ore grade close to 0.xxx wt%, but are not economically profitable [62]. Additionally, it is demonstrated by the same authors that the lower the concentration, the smaller the recovery yield, being necessary to do the process many more times since this parameter goes down with small ore grade reductions [61–63].

Nowadays, the specific energy for concentration used for the beneficiation process for lead and zinc is 10.85 GJ/t-Pb and 50.90 GJ/t-Zn, respectively. According to the data obtained along with the study, these values would increase exponentially when the ore grade decreases. Table 4 has been elaborated to put into context the results, comparing the specific energy obtained and the tons of oil equivalent (toe) with meaningful concentrations to understand the order of magnitude that could be reached. The scenarios generated have been created by reducing the concentration one-third at any time until the theoretical limit is reached.

The first scenario has been chosen since it is a typical concentration found in mines, and it is the start point of this study. In this case, obtaining a ton of lead and zinc requires 0.259 toe and 1.22 toe, respectively. Scenario 3 for lead and Scenario 4 for zinc represent a concentration that is in the same order of magnitude that can be found in tailings [28]. It can be seen that obtaining a ton of lead from tailings would require 0.55 toe, which more than doubles current extraction energies. On the other hand, a ton of zinc would require 2.22 toe, which means an increase of more than 80% of the energy needed from the first scenario.

Scenario 8 is the last comparison since the concentration analyzed for both metals is just after the limit established by Sverdrup et al. [17], which affirms that it is not economically feasible to extract any metal from that concentration. At this point, the energy required to extract a ton of lead would increase to almost 77 toe, while 85.5 toe would be needed to obtain a ton of zinc. In other words, the energy to obtain lead would increase almost 300 times in comparison with the first scenario, while zinc would increase more than 70 times.

As a consequence, and after comparison with previous studies from the literature review, it has been stated that the values obtained are much higher, so the situation is even worse than what other authors thought. It must be mentioned that the procedure followed in this study can be considered more robust than those calculated by [19, 46]. This is because we have precisely modeled all units required to mine in this paper and beneficiate the minerals when ore grade declines. The data obtained is not based on trends but on simulated behaviors of what a real mine would eventually undergo. Thanks to the methodology used in this paper, we have calculated the energy required to extract minerals from tailings, finding a new source affordable in terms of energy and economy.

Table 4. Comparison of the specific energy obtained.

Pb			Zn		
Wt%	GJ/t-Pb	toe/t-Pb	Wt%	GJ/t-Zn	toe/t-Zn
Sce. 1 (4.55)	10.85	0.259	Sce. 1 (6.5)	50.90	1.21
Sce. 4 (0,2)	51.11	1.22	Sce. 4 (0.24)	93	2.22
Sce. 8 (0.00208)	3220	76.91	Sce 8 (0.00297)	3579	85.5

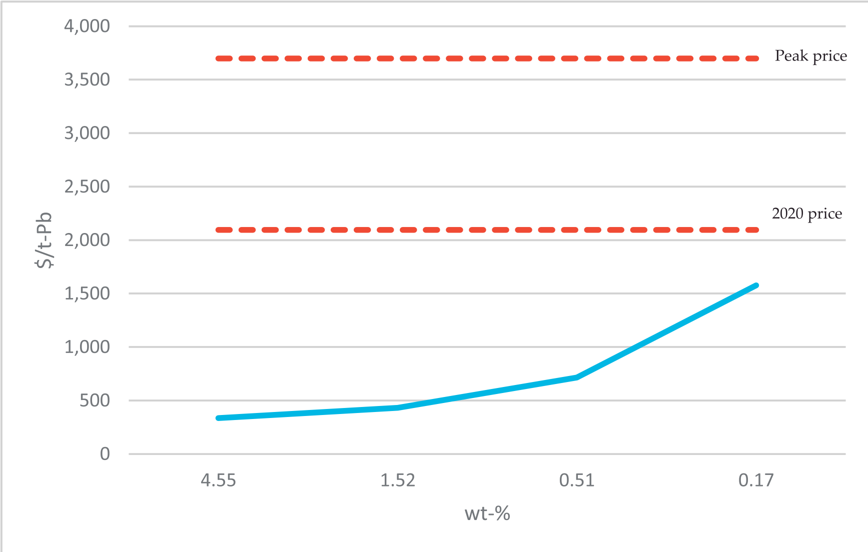

Fig. 8. Lead price range [$/t-Pb].

6.2. Cost assessment as a function of ore grade

Another analysis has been carried out, focusing on the price of the commodities and the expected value lead and zinc could reach in the future. Even if commodity prices are generated in the market, these should at least cover all associated costs, including energy, water and chemicals used to obtain the refined metal, and leave a profit margin for investors. Additional costs are related to investment, operation and maintenance costs, royalties, etc.

According to our calculations, the energy requirements considering a typical ore grade currently found in mines (4.55 wt%) is about 10.85 GJ/t. We can now transform this energy into monetary prices. To that end, we will consider that such energy is in the form of electricity. It should be mentioned that there are different types of energy involved in the process, such as diesel for waste rock transport, eventually natural gas, etc. Yet by considering that all energy is paid at the electricity price, provides us with an upper bound. Obviously this exercise only intends to provide orders of magnitude because uncertainties are very high. The electricity price chosen is that of the US in year 2020: 0.111 $/kWh [63].

With the aforementioned values, we can have an estimation of the energy costs associated to an average lead deposit: 335 $/t. Considering 2020 lead prices (2,095 $/t), energy costs contribute to about 16% of the price. In short, investment, O&M, royalties, profit, etc. would amount to 1,760 $/t.

With the models and the scenarios shown before, we can now estimate energy costs as a function of the ore grade, considering a constant energy price of 0.111 $/kWh. These are shown in Fig. 8. As ore grades decline, the margin left to other costs and profit significantly reduces. For an ore grade of 0.17 as could be found in tailings, the energy costs would amount to 1,576 $/t. If the rest of the costs plus the benefit would remain constant and equal to 1,760 $/t, the tailings price would increase to 3,336 $/t; which is close to the maximum historical lead price. This means that if commodity prices increased, tailings could eventually become a cost-effective source of lead. Table 5 has been created to spot all the figures mentioned for lead case in every scenario.

These values should be considered as a very rough approximation, because arguably, the other costs will also change when ore grades decline and commodity and electricity prices will fluctuate as well.

This same analysis has been created for zinc (Fig. 9). If energy cost and the rest of costs would remain constant, the maximum price for lead obtained from tailings would increase to 4,153 $ per t. This value is close to the historical peak, but it is lower, which

Table 5. Comparison of the specific energy obtained.

($/t)	Pb		Zn	
	4.55[a] wt%	0.17[b] wt%	6.5[a] wt%	0.24[b] wt%
Energy costs	334,46	1,576	1,569	2,855
Other costs	1,760	1,760	1,285	1,285
Total	2,095	3,336	2,855	4,153

[a] Current ore grade.
[b] Tailings ore grade.

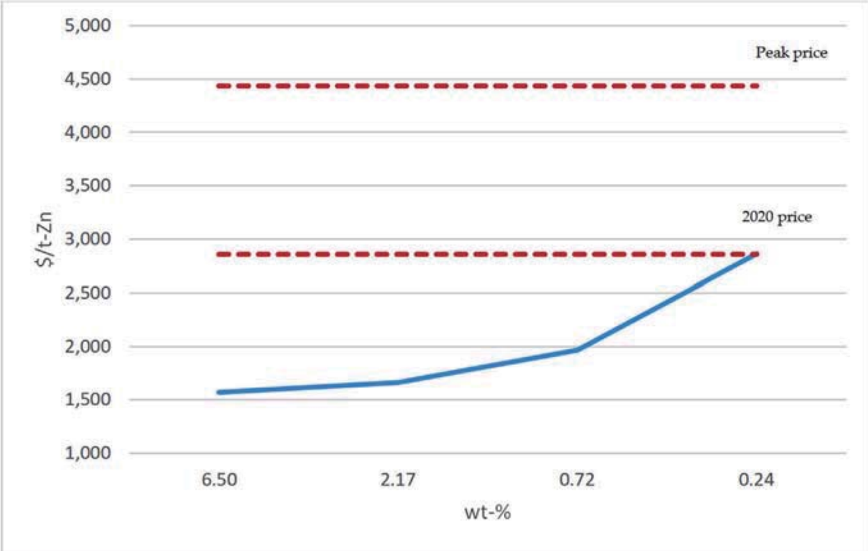

Fig. 9. Zinc price range [$/t-Zn].

means that at the moment tailings ore grade are reached, the new virtual price for a ton of zinc would remain below the historical peak. Thus, it could be considered as a viable source. Table 5 shows the results for both scenarios.

6.3. Considerations

Mines are composed of different minerals with different concentrations, and an important value of the data obtained is the comminution process. It must be noted that Bond's work index chosen for all the studies is 11 kW h/t [50], as it is typical for mines containing galena and sphalerite. However, this value can differ if the mine's concentration for galena or sphalerite is lower or these minerals are found together with others with a higher Bond index. This parameter is related to the reduction ratio (*Rr*). Then, it is essential to know the Bond Index of the rock to process because depending on the value applied, the specific energy for any unit of the comminution will be calculated.

Although the comminution process is the same for both metals, the energy allocation cannot be the same due to their properties and the concentration at the beginning of the process. In this way, according to the Ecoinvent Database energy consumption, the percentage assigned to lead and zinc is 37.4% and 62.6%, respectively [65]. Additionally, in the blast furnace (included in the refining process), a value of 31.4 MJ/l [66] has been considered as the High Heating Value (HHV) for carbon. Ore handling is considered for the processes of transportation, storage, feeding, and washing of the ore on route or during the different stages through the beneficiation process [31, 67], obtaining these data from the literature review [33, 60, 65].

While ore handling data has been taking from the literature review, refining both metals has been compared with other studies and reports [48, 66], obtaining small differences between the results and the bibliography, remaining in the same order of magnitude.

The results obtained show that the specific energy for concentration is higher for zinc than for lead. This could be explained by the cost allocation applied during the comminution process, which can reach more than 90% of the total value in low concentrations. These values could change if the cost allocation were different, thereby reducing the figure obtained. Different studies revealed [68, 69] that the specific energy required to extract zinc would decrease when the energy efficiency improves.

7. Conclusions

Through the methodology applied and HSC software, it has been possible to analyze the behavior of the specific extraction and beneficiation energy of lead-zinc deposits when ore grades decline. Such deposits serve as a proxy of what is likely to happen to the whole mining sector when mines become depleted through a probably accelerated extraction to meet increasingly higher raw material demands. As expected, the trend is not linear but exponential, which implies that much more GHG emissions will be generated as long as mining relies on fossil fuels. This means that the mining industry will arguably rank first among the most consuming and climate change contributing economic sectors.

Some authors consider that there is no limit to extraction because they trust in technology development. However, it is not possible to know how technology would evolve. In any case, the second law of thermodynamics cannot be overcome: the lower the ore grade, the greater the energy and other resources costs, and the associated environmental impact. Some limits of extraction must be considered. With current technology and the minimum concentration calculated in this paper, extracting a ton of lead and zinc would require 76.91 toe and 85.5 toe, respectively, needing to process millions of tons of ore, which would be, of course, economically unfeasible.

Since the demand is increasing and mines are being exhausted, the production will be reduced, and there will be a moment in time where the demand will be higher than supply. Thus, recycling becomes key. For the lead case, recycling ratio is higher than the 60%, which can be considered a high number in comparison with other metals. On the other hand, unfortunately, recycling ratio for zinc is around 15%, still far from an ideal figure (considering that 100% recycling is impossible to reach). In any case, more research must be carried out to try to increase recycling ratios to provide more share in the market and avoid the total depletion of mines.

Decreasing ore grades opens the opportunity to new extraction sources other than mineral deposits. As it has been seen in the paper, demand could be eventually supplied extracting minerals from tailings. However, this would entail that the energy would be multiplied by more than five times in the case of lead and almost two times in the case of zinc. Consequently, more emissions would be released into the atmosphere, even if this would preserve new unexplored regions and ecosystems to be potentially altered through mining. That said, the cost assessment carried out indicates that for both commodities, even if processing costs increase, there is still margin for profit. This is because the new costs assuming that O&M, investment costs, royalties and profit remain constant would all together remain below the maximum historical commodity's price peak. In summary, obtaining minerals from tailings would be arguably cost effective.

Another opportunity that opens up is what is called landfill mining. Many devices containing a high amount of minerals are sent to landfills, provoking serious environmental damage. As such, the concentration of many strategic materials in landfills is increasing year by year, even exceeding that of natural deposits. Landfill mining could become an important source of materials in the near future. That said, as long as consumption grows, relying on secondary materials will not be enough to satisfy the whole demand and natural mining will still be required.

Conflicts of interest

None declared.

Ethical statement

The authors state that the research was conducted according to ethical standards.

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PAPER II

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Limit of recovery: How future evolution of ore grades could influence energy consumption and prices for Nickel, Cobalt, and PGMs

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ABSTRACT

The unique properties of certain metals have made them indispensable in manufacturing advanced technological devices and for use in the green economy. However, these metals are not infinite, and the average ore grades in mines have been decreasing in recent decades. This study examines energy consumption as a function of ore grade decline for Nickel, Cobalt, and platinum group metals (PGMs), using simulations created with HSC Chemistry software. A limit of recovery (LOR) for each commodity was also defined. A comparative analysis of the evolution of ore grades, energy costs, and market prices was additionally carried out. According to the simulations, extracting nickel from sulfide ore tailings would be profitable if the price doubled. As for Cobalt, it would only be feasible if the market price increased considerably. For PGMs, even if the ore grade reached the LOR, it would still be profitable to recover them under certain circumstances explored in the paper.

1. Introduction

Nickel (Ni), cobalt (Co), and platinum group metals (PGMs) are highly valuable due to their diverse range of applications and significant role in the green economy (F. K. Crundwell et al., 2011). They provide specific technical details that are necessary to manufacture better and more efficient devices (Magistretti et al., 2020; Parasuraman, 2000; Wäger et al., 2011). Ni and Co are used in batteries, catalysts, medicines, and permanent magnets (Bao et al., 2019; Cárdenas-Triviño et al., 2017; Fernandes et al., 2013; Orefice et al., 2019), while PGMs are extensively used in catalyzers and catalytic converters of vehicles to reduce emissions (Mpinga et al., 2015; Saguru et al., 2018). This makes PGMs very strategic for the automobile sector. Additionally, PGMs are essential in rechargeable batteries and superalloys (Degryse and Bentley, 2017; Sverdrup and Ragnarsdottir, 2014; Wäger et al., 2011).

The primary deposits of Nickel, Cobalt, and Platinum Group Metals are not located within the boundaries of the European Union, which implies a high dependency on imports to support its industrial development. Specifically, the EU needs approximately 700 kton of these metals annually, but only 100 kton are produced within the region (Nickel Institute, 2012). As a result, two out of the three metals analyzed in this paper, considering PGMs as a single entity, are classified in the European Commission's critical raw material list (European Commission, 2023). Although Nickel does not meet the critical raw material (CRM) thresholds, it is listed as a strategic raw material under the Critical Raw Materials Act. On the other hand, Co is deemed critical due to its crucial properties essential for high-technology industries, and PGMs are considered critical because of their strategic economic importance, low recycling rates (Graedel, 2011; Wilburn and Bleiwas, 2004), and limited availability and scarcity in the crust.

According to the International Energy Agency, the demand for Nickel is expected to double by 2040 in a conservative scenario and almost triple in the worst-case scenario (International Energy Agency, 2021). However, the maximum production peak of current Nickel reserves is expected between 2025 and 2033 (Calvo et al., 2017b; Sverdrup and Ragnarsdottir, 2014).

Cobalt is primarily produced in the Democratic Republic of Congo (DRC), which holds more than 60% of the world's production (Farjana et al., 2019). The demand for Cobalt is expected to increase by 100% by 2040 in a conservative scenario, while in the worst scenario, this value could rise to 480% (International Energy Agency, 2021). The DRC has the highest Cobalt reserves, followed by Australia, which has one-third of the DRC's reserves (Shedd, 2020). However, mining production for Cobalt in the DRC is unregulated, and there is a history of political instability and armed conflicts, making it a high-risk business environment (Shedd et al., 2017). This could affect the future of Cobalt production in this country as processors and industrial consumers become more concerned with responsible sourcing of raw materials.

The demand for PGMs is continuously increasing (Schulte, 2020), which could put the availability of these resources at risk in the

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following decades. South Africa is the primary producer of Platinum, accounting for over 75% of the world's supply, with ores ranging from 7 to 10 g/t (Shaik and Petersen, 2017). Some authors have suggested that there could be enough PGM reserves for the next 200 years based on current production data and estimated reserves (Ndlovu, 2015). However, others have calculated that the maximum production peak for PGMs would occur in 2020 (Sverdrup and Ragnarsdottir, 2014). According to Valero et al. (2018) the demand for Co and PGMs could exceed their supply, creating a bottleneck.

The increasing demand for minerals are putting more and more pressure on the mining sector, which must face decreasing ore grades. As a thermodynamic fact, mining energy increases exponentially as ore grades decline (Calvo et al., 2016a). Consequently, extraction costs also increase, and mining may become unaffordable if prices remain low.

In this respect, global events directly influence commodity prices. For instance, following the onset of the war in Ukraine, the price of Ni doubled in just ten days. At present, the price of Ni remains higher than in the pre-war period. If this price increase persists over time and other metals experience similar increases, the mining industry may respond by activating lower-graded mines, which could affect total energy consumption.

Moreover, primary metal production carries massive environmental effects. As an example, up to 12 t CO2eq. per ton of ferronickel are sent to the atmosphere (Bartzas and Komnitsas, 2015). With the future demand and production expected for metals, the emissions sent to the atmosphere and the waste generated by the metal industry could be unaffordable for the future society unless some measures are taken (Spooren et al., 2020). In this respect, some studies have calculated the reduction of the environmental impact if certain metals were extracted from secondary resources. For instance, (Zhang et al., 2022) concluded that global warming associated with secondary copper extraction could be reduced sevenfold compared to primary production.

This study aims to examine the energy costs associated with extracting Ni, Co, and PGMs as ore grades in mines decrease. Previous research has explored the evolution of energy costs for gold (Palacios et al., 2019), copper (West, 2011), and lead and zinc (Magdalena et al., 2021b). For this study, a model was developed using specialized software, HSC Chemistry, which takes into account all the metallurgical processes required to refine each metal to the desired commercial grade (Outotec, 2020). The software enables thermodynamic calculations to be carried out, modeling different pyrometallurgical and hydrometallurgical flowsheets (Outotec, 2020). Moreover, cost allocation for Ni, Co, and PGMs was performed using various strategies to simulate how energy costs are associated with each metal. Lastly, several analyses were conducted to estimate the behavior of future mines during the beneficiation process and their future profitability considering metal market prices and energy costs.

2. Description of the metallurgical process

Co and Ni are typically co-mined, but Ni can be derived from two primary sources: laterites and sulfides. Approximately 70% of Ni resources are found in laterites, typically used for ferronickel production. However, the amount of Co present in laterites is typically too low to be economically feasible for extraction, so Co is usually obtained from Ni sulfides. PGMs, including Ru, Rh, Pd, Os, Ir, and Pt, can also be found in Ni ores, either dissolved or as distinct mineral grains (F. Crundwell et al., 2011; Xiao and Laplante, 2004).

Although laterite reserves are more abundant than sulfide reserves, this study will only focus on Ni sulfides, as they contain higher concentrations of Co and PGM than laterites (Piña et al., 2010). Furthermore, besides metal concentration in the ore, the specific energy required to extract Ni from laterites is also higher than the specific energy required to extract Ni from sulfide ores (Khoo et al., 2017; Mistry et al., 2016; Norgate and Jahanshahi, 2011).

After analyzing various Nickel-bearing minerals, it was decided to use pentlandite as the primary mineral ore (Alves Dias et al., 2018; Rao, 2000). Pentlandite has the highest Nickel concentration, implying lower specific energy when compared with other minerals. A standard concentration of pentlandite and other gangue minerals, such as quartz, has been established for an average mine to proceed with the simulation. Mineral composition and concentrations are also required to proceed with the simulation. Different scenarios can be created to simulate the future behavior and evolution of the mine once every mineral is set up with its concentration. Therefore, pentlandite concentration in the mine will be gradually reduced as the concentration of gangue minerals increases, simulating what could occur when the mine becomes exhausted.

Different specific energies have to be considered to carry out the simulation. For instance, ore handling involves using diesel for transportation, machines, and electricity for various units (Calvo et al., 2016a). Additionally, the increase in the concentration is achieved by increasing the g/t ratio of the metal (Nagaraj, 2005), starting from a low ratio at the beginning of the process. The purpose of the comminution process is to reduce particle size, which will increase the energy at this stage for low concentrations due to the embodied energy (Qin et al., 2022). Then, comminution is followed by a flotation process (Bulled and Mcinnes, 2005). The last stage is refining, where pure metal is obtained.

Fig. 1 represents all the main stages involved in the extraction of Ni, Co, and PGMs, highlighting the most important data introduced in the simulation. This diagram has been created following a literature review (Black et al., 2018; F. K. Crundwell et al., 2011; Metso, 2015; Napier-Munn and Barry, 2006; Rankin, 2011).

The beneficiation process is divided into three main stages: comminution, flotation, and refining. As seen, comminution and flotation stages are shared by all metals. After flotation, PGMs minerals are separated from pentlandite through gravitation (F. K. Crundwell et al., 2011). During the metallurgical stage, PGMs are refined to separate the six metals that compose PGMs (Cole and Joe Ferron, 2002; Kriek et al., 1995). Finally, pentlandite is refined to separate Ni and Co, obtaining these two metals in pure form at the end of the process.

In order to conduct the simulation, it is necessary to obtain concentration data before and after each of the main stages, including comminution, flotation, and refining. Average concentration values for each stage have been established based on various sources (Black et al., 2018; Cramer, 2007; Piña et al., 2010).

Table 1 displays the concentration of each metal at different stages of the beneficiation process. PGM is considered a single metal at this stage for simplification purposes, with a unique concentration in each step. It should be noted that the "in mined ore" figures are representative of the typical values found in literature references.

After inputting the data into the software, various scenarios were created by progressively decreasing the average concentration of each metal, as detailed in Table 2 and as supported by the consulted literature (Mills, 2022). In each scenario, the ore grade was reduced by one-third relative to the previous one, with Scenario 12 representing the lowest concentration of each metal, even falling below the crustal concentration (Valero and Valero, 2014). Currently, the lowest cut-off grade for metals is observed in gold, with a concentration of 2 g/t (2x10-4 wt-%), but technological advancements are expected to increase efficiency in the coming decades. As a result, scenarios involving values close to the crustal concentration were also investigated.

3. Simulation and results

The amount of feed at the beginning of the process significantly impacts the number and size of units required in the various processes, which in turn affects energy consumption. In order to standardize the study, a feed rate of 800 t/h has been chosen for all scenarios, which is appropriate for low-grade ores. The simulation involves considering three main energy sources, which correspond to the three stages described in the flowsheet. The first stage is comminution, where the

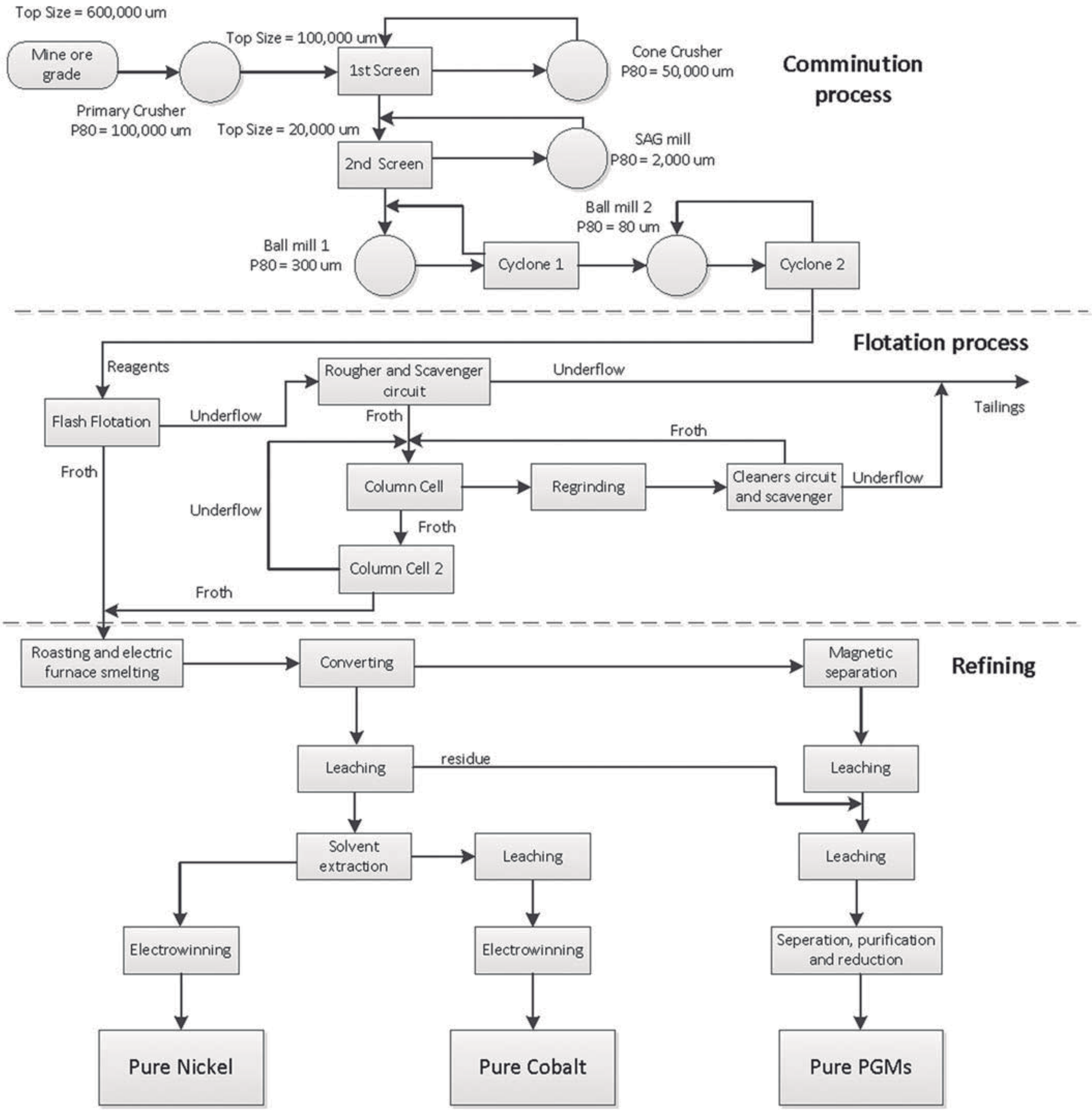

Fig. 1. Flowsheet for the extraction of Ni, Co, and PGMs.

Table 1
Concentration in different steps along the beneficiation process [data in %] (Black et al., 2018; F. K. Crundwell et al., 2011; Piña et al., 2010).

	In mined ore	After flotation	After smelting & converting
Ni	1.5–2.5	10–20	40–70
Co	0.05–0.1	0.3–0.8	0.5–2
PGMs	0.0004	0.01–0.02	0.2–0.4

size of the extracted rock is reduced to the required particle size for subsequent steps. As the ore grade decreases in each scenario, more rock must be processed to obtain the same amount of ore, resulting in an increase in embodied energy and specific energy consumption (Mudd, 2010, 2009; Norgate et al., 2010; Valero and Valero, 2012). The initial concentration at the beginning of the flotation process determines the design of the flowsheet. As the concentration decreases consecutively in the scenarios, more cleaners, column cells, roughers, and scavengers are required to achieve the desired concentration at the end of the process, increasing the specific energy of the flotation process. In contrast, the specific energy in the refining stage remains constant because the concentration at the beginning of this stage must always be the same across all scenarios.

After the simulation, the software provides data for the units used in the comminution process, including the primary crusher, cone crusher, SAG mill, ball mills, and re-grinding. Table 3 presents the specific energy consumption of each unit during the comminution process. These values

Table 2
Initial ore concentration for each scenario [data in wt-%].

	Ni	Co	PGMs		Ni	Co	PGMs
Sce. 1[A]	3	0.16	4x10^{-4}	Sce. 7	4.1x10^{-3}	2.19x10^{-4}	5.49x10^{-7}
Sce. 2	1	0.0533	1.33x10^{-4}	Sce. 8	1.37x10^{-3}	7.32x10^{-5}	1.83x10^{-7}
Sce. 3	0.33	0.0178	4.44x10^{-5}	Sce. 9	4.57x10^{-4}	2.44x10^{-5}	6.1x10^{-8}
Sce. 4	0.11	5.93x10^{-3}	1.48x10^{-5}	Sce. 10	1.52x10^{-4}	8.13x10^{-6}	2.03x10^{-8}
Sce. 5	0.037	1.98x10^{-3}	4.94x10^{-6}	Sce.11	5.08x10^{-5}	2.71x10^{-6}	6.77x10^{-9}
Sce. 6	0.012	6.58x10^{-4}	1.65x10^{-6}	Sce. 12	1.69x10^{-5}	9.03x10^{-7}	2.26x10^{-9}

A = concentration in mine (F. K. Crundwell et al., 2011).

Table 3
Power demand and energy required during the comminution process.

Equipment	Power demand [MW]	Specific energy [kWh/t rock]
Primary crusher	0.365	0.38
Cone crusher	0.477	0.88
SAG Mill	3.975	7.27
Ball Mill 1	22.92	12.05
Ball Mill 2	11.96	9.68
Re-grinding	3.73	10.46

will not be altered during the study as particle size reduction is required in all scenarios. The values obtained from this simulation have been compared with those reported in the literature (Latchireddi and Faria, 2013) and are within the same order of magnitude. As shown in Table 3, the highest energy consumption is from Ball Mill 1, followed by Ball Mill 2. The reduction ratio may explain this since these units aim to reduce particle size by two orders of magnitude. Interestingly, re-grinding requires less energy than SAG mills, despite having a higher specific energy. The reason for this is the particle size required for the final product. Re-grinding is introduced in the comminution process to decrease particle size considerably. Still, the efficiency drops as the process needs to be repeated more than once to achieve the desired size.

Using the Outotec Chemistry software, the energy demand for the flotation units involved in the process can be calculated, providing the total energy for the stage. Since the simulation includes multiple scenarios for the future behavior of the mine, more flotation units are required with each subsequent scenario to achieve the desired concentration. The process described in this article represents the current mining practice, but as mentioned, each following scenario will require additional roughers, cleaners, and scavengers, leading to an increase in specific energy for the entire process, as shown. Table 4 presents selected scenarios, along with the specific energy required for concentration during both the comminution and flotation stages of the beneficiation process, for comparative purposes.

The refining process is initiated once the desired concentration is achieved, and it involves various chemical processes to extract pure metals. As all the metals are initially present in the same feed, i.e., pentlandite, it needs to be sent to the metallurgical plant for further purification. Although the software can simulate the metallurgical processes, the values for the different metals are obtained from the literature for simplicity. The energy required for Ni purification is reported to be in the range of 60–100 GJ/T (Calvo et al., 2017a; Wei et al., 2020), while for Co purification, it is in the range of 72–129 GJ/T (Calvo et al., 2017a; Dai et al., 2018). In the case of PGMs, the value chosen for energy consumption during the refining stage is in the range of 315–566 GJ/T (F. Crundwell et al., 2011; Kingsbury and Thathiana Benavides, 2021).

Table 4
Specific energy for concentration in the comminution and flotation stages [data in GJ/t-ore].

GJ/t-rock	Comminution	Flotation	Both
Scenario 1 (conc. in mine)	5,526.37	2.29	5,528.66
Scenario 4	149,212	3,800.6	153,012.6
Scenario 8	1.21 x10^{7}	54,559.3	1.21 x10^{7}
Scenario 12	9.79 x10^{8}	3,098,853	9.82 x10^{8}

Note that PGMs are composed of six different metals.

4. Analysis and discussion

4.1. Energy share in the different stages of the beneficiation process

As mentioned earlier, the decreasing ore grade of certain minerals in mines may result in a capacity shortage to meet market demand (Calvo et al., 2016b; Northey et al., 2014). While it is impossible to predict the future of resource availability in each mine, it is possible to estimate the behavior of specific energy for concentration for each extracted metal. It should be noted that for the sake of simplicity, all six PGMs have been considered as a single metal in this analysis. Although the beneficiation process is the same for all metals, they are ultimately separated during refining. If the analysis had been performed for each PGM individually, it would not have affected the study's final outcome.

When the concentration of a metal is very low, ore handling becomes a critical process. The lower the ore grade, the more rock needs to be treated, processed, and transported, which in turn increases the amount of diesel required to transport the rock from the mine to the processing plant. For the three metals analyzed in this study, we consulted the Ecoinvent database for ore handling data (Ecoinvent, 2007). While the energy required for PGMs represents the lowest share of total energy, ore handling can still account for a significant portion of the energy consumption in the beneficiation process. It can vary widely depending on the metal being extracted. For example, in this study, the ore handling value for PGMs is 1,030 GJ/t-PGMs, while for Ni it is only 11.2 GJ/t-Ni. In the case of Co, it represents almost 40% of the total energy required for the rest of the stages. These differences can be attributed to the ore grade at the beginning of the process.

4.2. Cost allocation

Most mines are designed to extract more than one metal to maximize mine exploitation. During the extraction process until the end of the metallurgy process, there are common stages for all the metals extracted, which are needed to allocate different costs. Allocation is key when energy costs are being calculated since different results can be obtained depending on the type of allocation selected. Accordingly, different cost allocations have been reviewed to select the most accurate for this study. Hence, this analysis will focus on selecting Bond Index values and comparing different cost allocation systems, using: 1) metal market prices, 2) data from the Ecoinvent database, and 3) a thermodynamic allocation procedure explained below.

When the ore grade is very low, the comminution stage has the highest share of energy consumption. Therefore, Bond index is essential for calculating the energy at this stage since the energy calculated could be several times higher or lower depending on the value chosen, as demonstrated in previous studies (Magdalena et al., 2022; Palacios et al., 2019). Therefore, selecting an accurate Bond index that reflects the reality of the ore being treated is crucial. A wide range of Bond index values can be applied, from 2 kWh/t to 24 kWh/t, depending on the mineralogy of the rock in the mine. This study has chosen an average value of 13.65 kWh/t since it is a typical value for ores containing Ni (Michaud, 2015).

Efficiency factors are also considered in the data calculation, not just the Bond index. This is because the efficiency of the mills is never 100%, and it can increase the specific energy required by up to 10–20% for regular particle sizes (Rowland, 1999), applying an efficiency ranging from 90 to 95% as average in this study. Moreover, if the particle size required is extremely small, the efficiency decreases even further, requiring more energy to achieve the same result.

Regarding cost allocation, the first procedure (Fig. 2A) is based on the average metal prices between 2010 and 2020, as well as the production, as shown in Equation (1).

$$Allocation = \frac{P_i x M_i}{\sum_{i=1}^{n}(P_i x M_i)} \quad (1)$$

Where P_i is the market price, and M_i is mine extraction. This allocation is calculated by multiplying the annual production of each metal by the mentioned average price. The resulting values are then divided by the sum of the three metals, obtaining the share of each metal in the total revenue. These percentages can vary depending on the year chosen since metal prices can be very volatile. Using this approach, the cost allocation obtained for Ni, Co, and PGMs are 61%, 6%, and 33%, respectively.

The second option for cost allocation involves obtaining values from the Ecoinvent database (Ecoinvent, 2007), and the results are shown in Fig. 2B. This database provides allocation values for two different mines located in South Africa and Russia. The cost allocation is different in both mines as it is calculated based on the main metal sold. Therefore, allocation can vary depending on the metal sold and the by-products extracted. In the South African mine, the cost allocation for Ni represents 7%, while in the Russian mine, it represents 47%. The average of both mines has been calculated based on their respective allocation by mass and revenue, resulting in 50% for Ni, 30% for Co, and 20% for PGMs.

The proposed cost allocation based on Thermodynamic Rarity values of the metals (Valero and Valero, 2015) is shown in Fig. 2C. Thermodynamic Rarity is an index that assigns an average energy value to each metal based on its global scarcity, embodied energy, and energy replacement cost (ERC) according to the Second Law of Thermodynamics. The embodied energy of a metal refers to the total energy required to extract it from the mine to its use in the industry. On the other hand, ERC is the energy required to restore a mineral from a dispersed state to its initial concentration (Valero et al., 2013). Thermodynamic rarity values can be consulted in (Valero et al., 2021). The rationale behind this approach is that metals with a higher Thermodynamic Rarity require more energy to be produced, and therefore, their costs should reflect their scarcity. The annual production is multiplied by the Thermodynamic Rarity value for each metal to obtain the cost distribution, which is 40% for Ni, 29% for Co, and 31% for PGMs.

Table 5 summarizes the values obtained with each methodology used for cost allocation calculation. In the first case, the distribution provides a larger share to those metals with higher prices, although the amount of metals extracted may be lower. This allocation is not based on physical properties or sustainability conditions and can be very volatile, depending on political and demand factors. In the second case, using data obtained from Ecoinvent, the allocation in tons could differ depending on the mine and the primary metal extracted. These two approaches, however, do not adequately reflect the situation of these metals and their scarcity. The third approach, based on Thermodynamic Rarity, provides that cost allocation is not based on economic terms but rather on the scarcity of the planet's crust. More in-depth and complementary studies have analyzed different cost allocation strategies considering the market price, tonnage, and energy (Valero et al., 2015).

As shown in Fig. 2, cost allocation based on Thermodynamic Rarity and Ecoinvent can provide similar results. However, for the purpose of this paper and the analysis carried out, Thermodynamic Rarity has been selected as it places greater emphasis on metal scarcity, which is a physical indicator.

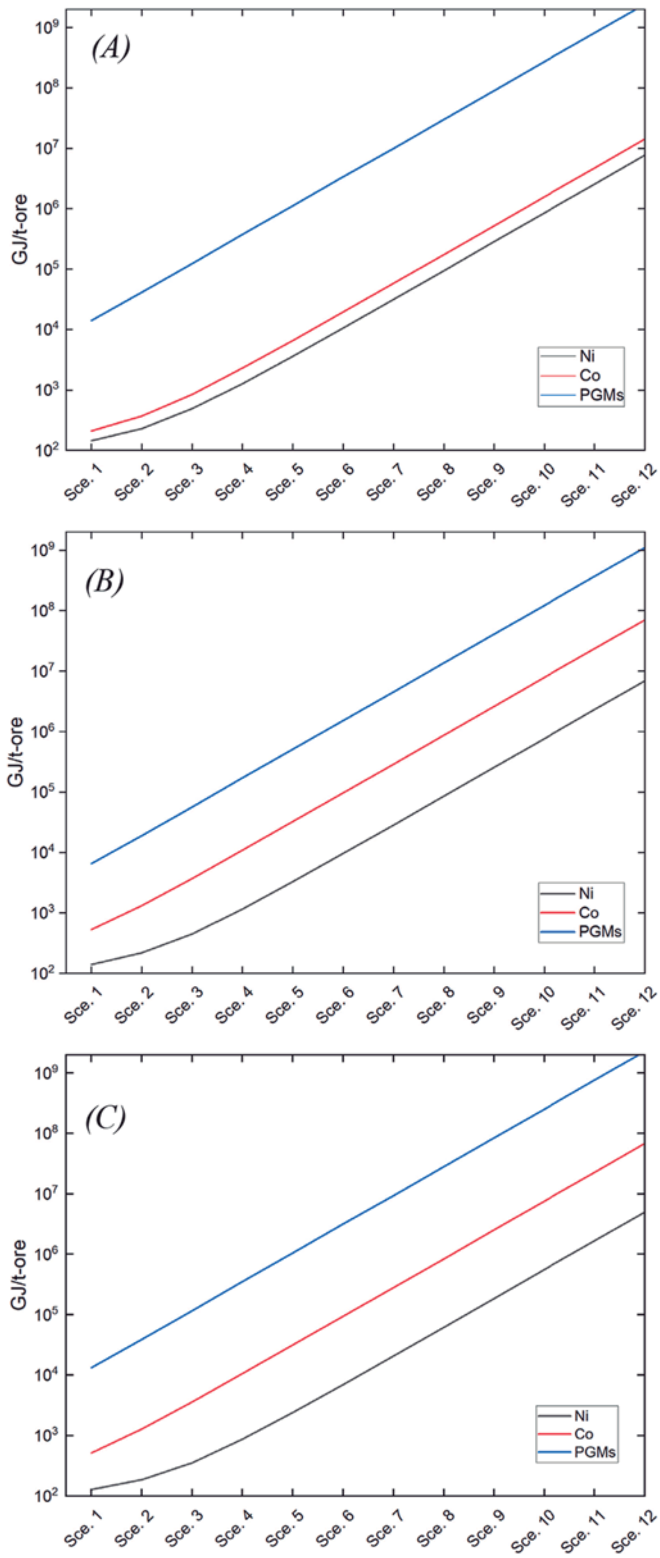

Fig. 2. Cost allocation for Ni, Co and PGM using different approaches. A) metal market prices, B) Ecoinvent database, C) Thermodynamic Rarity. Specific energy for concentration is in GJ/t-ore.

4.3. Limit of recovery

Different organizations and authors have made various estimates for

Table 5
Summary of the different types of cost allocations analyzed.

	Ni	Co	PGMs
Market price (2010–2020)	61%	6%	33%
Ecoinvent	50%	30%	20%
Thermodynamic Rarity	40%	29%	31%

the amount of Nickel resources. For example, the British Geological Survey (2008) estimated Nickel resources at 262 million tonnes (MT), while the Nickel Institute (2016) estimated it at 300 MT. However, not all of these resources are economically viable to extract due to technological constraints and other factors. Studies have been carried out to determine the grade limit for extracting minerals (Norgate et al., 2010; Rötzer and Schmidt, 2018; West, 2011). Some authors suggest that future mines will not be restricted by depletion but by dilution, as advances in technology may make it viable to extract elements that were previously not feasible (West, 2011). Others argue that the issue will be related to the price, as dealing with lower ore grade mines would require more energy for extraction, increasing prices and making these mines profitable (Rötzer and Schmidt, 2018).

In this paper, we have used the version proposed by Rötzer and Schmidt (2018) for analyzing the specific energy for the concentration of depleted mines, as it is not possible to predict how technology will evolve in the following years. Therefore, the best available technology has been applied to develop this model (Lenzen, 2008). In terms of ore grade, some authors (Sverdrup and Ragnarsdottir, 2014) mention that the limit of extraction for a mineral in any mine is 0.5 g/t, as there is currently no technology to lower concentrations, and it would not be economically viable.

We propose a new ore grade limit, the Limit of Recovery (LOR) to analyze the specific energy for concentration of depleted mines. We propose to use the energy needed to extract a ton of PGM from tailings as a baseline for setting the LOR. In this case, the concentration of PGMs in tailings comes from literature, which is set up at 2.4×10^{-6} wt-% (F. Crundwell et al., 2011). This concentration corresponds to an energy cost of 992,124 GJ/t-PGMs, as extracted from Fig. 3C. Therefore, it is possible to calculate which ore grade corresponds to 992,124 GJ for Ni and Co and set their corresponding LOR values.

Interestingly, the ore grade for Nickel that could be reached by applying the mentioned energy limit would be below crustal concentration, which makes little sense. This is why the chosen LOR for Nickel is assumed to be the average crustal concentration. Table 6 shows the final LOR values used in this study for the three analyzed commodities.

Fig. 3 depicts the expected trend for the beneficiation process obtained for Ni, Co, and PGMs after carrying out the simulation. Each black dot in the figure represents a scenario, and not all 12 scenarios are present in all the figures due to scale reasons. In this case, the cost allocation has been carried out using Thermodynamic Rarity. In addition to the dots representing the ore grade for each scenario, three other key points should be considered. Firstly, the current ore grade values have been obtained from the literature (F. K. Crundwell et al., 2011). Secondly, various studies have demonstrated that recovering metals from tailings can be profitable (Alfonso et al., 2020; Morin and D'Hugues, 2007) and could be critical to meet future metal demands, especially since the concentration in those tailings could be similar to the current ore grades in mines (Magdalena et al., 2021a). The concentration for PGM in tailings is 2.4×10^{-6} wt-%, 0.3% for Ni, and 0.014% for Co (F. K. Crundwell et al., 2011). The last key point is the LOR, which corresponds to the first column in Table 6. In the case of Ni, the LOR value is equivalent to the crustal concentration, as mentioned previously.

In the case of Ni, the primary energy share corresponds to the refining process in the first scenario (Fig. 3A). However, as the ore grade decreases, comminution becomes more relevant, which can be observed in the curve shifting towards an exponential trend. The metal content in

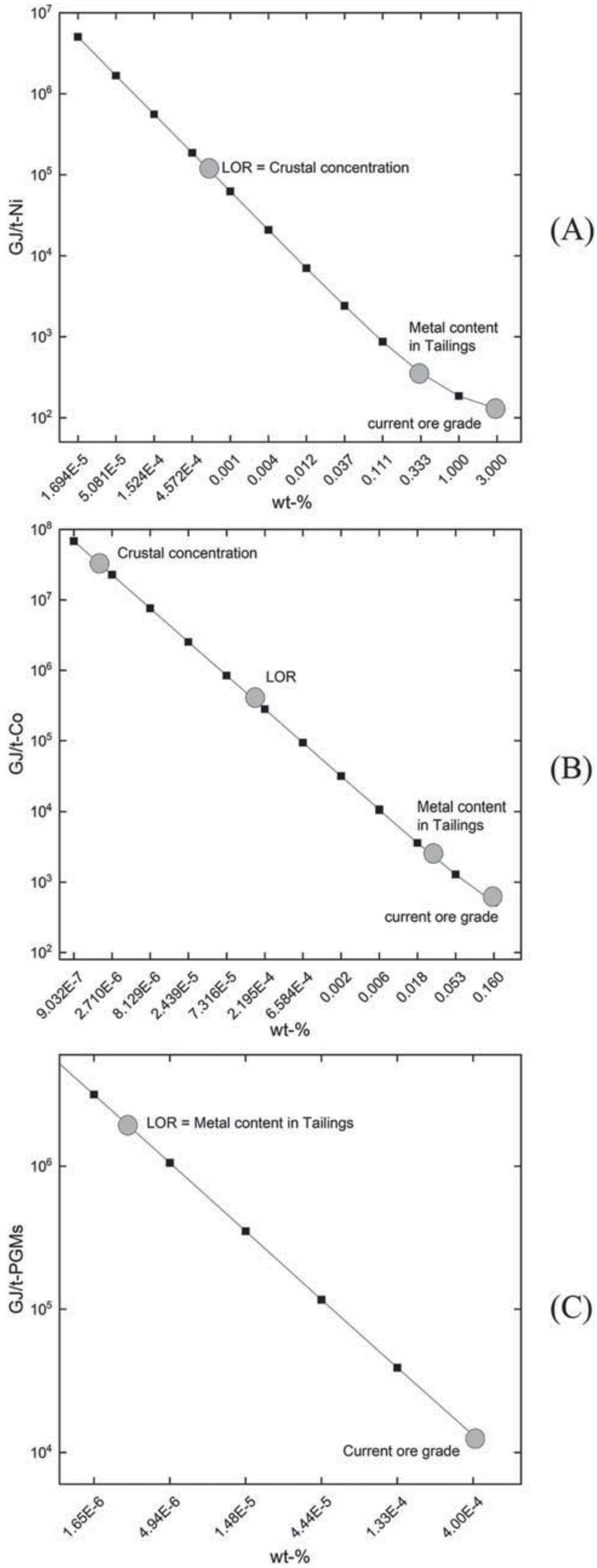

Fig. 3. Estimation of the specific energy for concentration for Ni (A), Co (B), and PGMs (C) [GJ/t-ore] with cost allocation carried out using Thermodynamic Rarity.

Table 6
Limit of recovery (LOR) as proposed in this study and average crustal ore grade [wt-%].

Metal	LOR	Crustal concentration (Valero et al., 2011)
Nickel	4.00 x10^{-4}	4.00x10^{-4}
Cobalt	6.89 x10^{-5}	5.15 x10^{-7}
PGMs	2.40 x10^{-6}	3.95 x10^{-8}

tailings (0.3 wt-%) is reached around Scenario 3, which could be very relevant in the near future as current tailings still contain a significant amount of Ni that could soon become economically viable to recover if the average ore grade in the mines decreases to that extent. A similar situation can be seen for Co (Fig. 3B), where the metal content in tailings is reached before Scenario 3. However, the metal content in tailings for Co is one order of magnitude lower than that for Ni. In both cases, the LOR is still several orders of magnitude lower, and as stated before, in the case of Ni, the LOR value is equivalent to the crustal concentration. As for PGMs (Fig. 3C), the current ore grade in the mines is considerably lower. As explained, since the limit for LOR was established using the energy needed to extract a ton of PGM from tailings, in this case, LOR is equivalent to the ore grade in tailings. Comparing these values, it can be seen that LOR is only two orders of magnitude lower than the current ore grade. This situation could create potential supply problems in the future if all mines start becoming depleted.

4.4. Analysis and implications of energy consumption

An estimation was made to observe how the specific energy for concentration (in GJ/t of metal) changes as the ore grade decreases until it is almost 0 wt-%. Three values have been used for comparative purposes: current ore grade in mines, metal content in tailings, and LOR (minimum concentration). To put these results into perspective, they have been converted into tons of oil equivalent (TOE) per ton of metal. Table 7 summarizes the values obtained for each scenario and metal.

In 2020, the global production of Ni was 2,510,000 tons, 142,000 tons for Co, and 383 tons for PGMs (U.S. Geological Survey, 2022), equivalent to an energy consumption of 9.56 MTOE (scenario A). This represents over 31% of the total Australian mining energy consumption in 2019 (Australian Government, 2020). If, for instance, all PGM reserves were to be extracted, which according to the U.S. Geological Survey (2022) are estimated at 70 kT, more than 22 MTOE of energy would be needed, representing 16% of the total energy consumption in Australia in 2019 (Australian Government, 2020).

Energy consumption dramatically increases when the metal content reduces until the tailings concentration (scenario B). For Ni, energy consumption increases almost three-fold, while for Co, this value increases seven-fold when compared to scenario A (current ore grade). A more drastic increase can be seen when comparing scenarios B and C.

4.5. Economic assessment

The simulation and the specific energy data obtained can now be used to conduct an economic evaluation to assess the energy costs for each metal and compare them to their current market prices. Comminution and flotation primarily rely on electricity, while diesel is used during the ore handling phase, and natural gas and coal are used during different metallurgical processes. Therefore, since all previously obtained values are in energy terms, converting them into monetary terms using energy prices is straightforward. The electricity market is very volatile and depends on many factors. Therefore, electricity prices are very variable, directly affecting the energy cost to mine and refine metals and, ultimately, the final price of metals.

Australia has a significant mining industry and one of the world's largest mineral reserves, so its electricity and energy prices are used in this study. The Australian Government publishes more reliable electricity and energy prices than other main-supplying countries. According to the Australian Energy Regulator, the average prices for electricity, natural gas, and coal in 2020 were 0.29 USD/kWh, 0.073 USD/kWh, and 62 USD/ton, respectively, while the diesel price was 1.22 USD/l (Australian Government, 2021). Combining this information with the specific energy previously calculated, we can obtain the energy costs for the simulations for each metal as a function of the ore grade's evolution (Fig. 4).

Additionally, an economic assessment can be carried out by comparing the energy costs of each metal in each scenario and simulation with their current market prices. According to USGS statistics, the average Ni price was 10,403 USD/ton in 2022, while for Co it was 55,731 USD/ton, and more than 29,580,000 USD/ton for PGMs (U.S. Geological Survey, 2022). The PGMs price was calculated as an average of the six metals included in the PGMs group. Since metal market prices can be volatile and change considerably over time, the analysis in Fig. 4 includes three prices: 1) 2022 price, 2) maximum historical price, and 3) current price multiplied by ten. Using the energy costs calculated for scenario 1, the share of the metal price that corresponds to the energy costs can be obtained. For Ni, the current energy costs represent 63% of the metal price, while for Co, this number is 67%. In contrast, for PGMs, the energy costs only represent around 3% of the metal price. Electricity and diesel prices are subject to fluctuations due to economic and political issues. For example, in Australia, the electricity price increased by 100% at the beginning of 2022 (Australian Government, 2021). Therefore, different scenarios have been created considering: 1) the aforementioned energy prices, 2) a two-fold increase in energy prices, and 3) a five-fold increase in energy prices.

Analyzing the relationship between energy and metal market prices, the case of Ni is particularly representative because the striped area covers situations where extraction from tailings could become profitable given the current energy price and even if this price were to double. A different situation can be seen if the energy price increases fivefold. In this case, extracting Ni from tailings would not be economically beneficial, even with a severe increase in the metal market price. Regarding Co, the striped area would cover the first two energy price scenarios (current price and price multiplied by a factor of two) when considering the current ore grade in mines. Still, in the case of tailings, the situation is different and could only be profitable under certain conditions while maintaining current energy prices. Even a slight increase in energy price could make this process unaffordable. if the metal market price remains within the striped area. However, if the Co price increases, it would be viable to recover the metal from tailings and even from materials with an even lower concentration. All the numbers are listed in Table 8.

The energy costs associated with tailings processing would be significantly higher for PGMs as it would be necessary to process a larger amount of rock. However, due to the scarcity and high market prices of PGMs, the current energy cost represents only 3% of the metal price.

Table 7
Comparison of the specific energy for each metal for three scenarios: A) current ore grade, B) metal content in tailings, C) LOR.

	Ni			Co			PGM		
Sce.	wt-%	GJ/t-Ni	TOE/t-Ni	wt-%	GJ/t-Co	TOE/t-Co	wt-%	GJ/t-PGMs	TOE/t-PGMs
A	3	128.39	3.06	0.16	514.86	12.29	4x10^{-4}	13,210.65	315.53
B	0.3	355.49	8.49	0.01	3,601.84	86.02	2.4x10^{-6}	992,124	23,696
C	4x10^{-4}	992,124	23,696	6.9x10^{-5}	992,124	23,696	2.4x10^{-6}	992,124	23,696

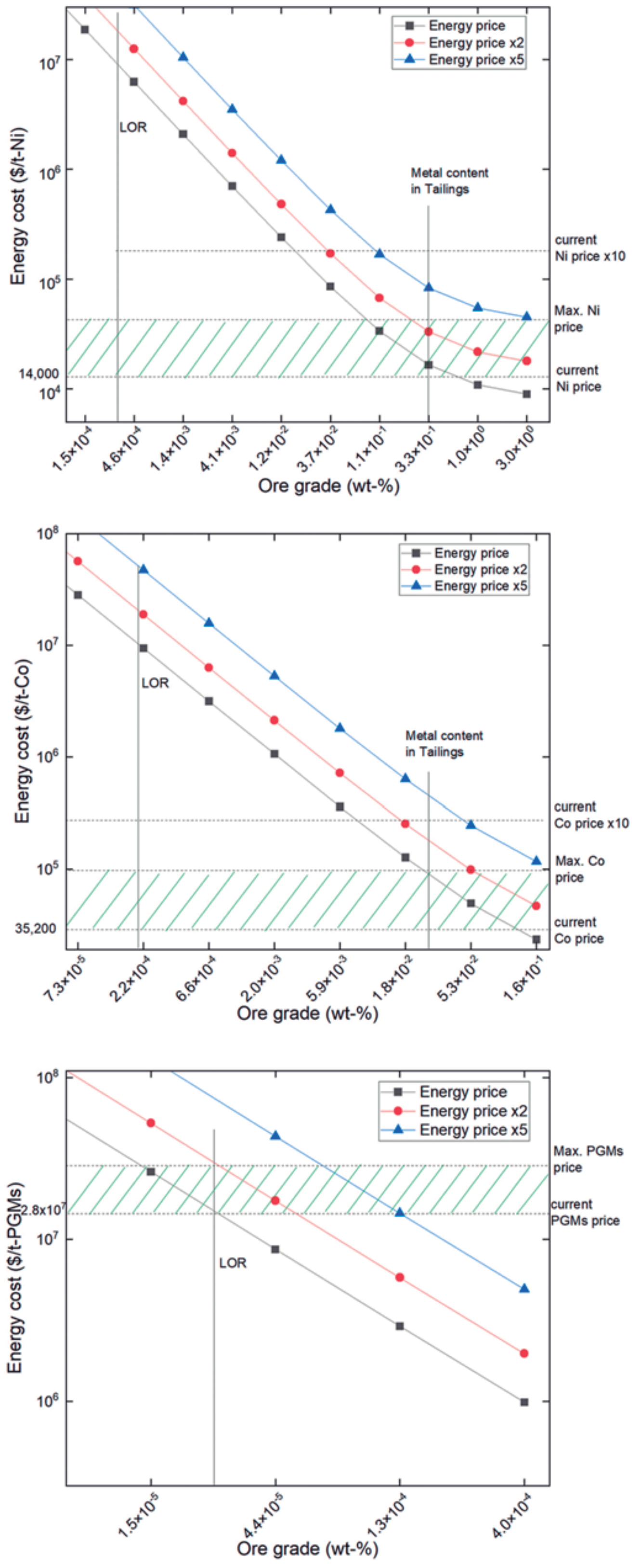

Fig. 4. Energy cost as a function of the ore grade for Ni, Co and PGMs. The striped area represents the area between each metal's current and maximum historical price.

Table 8
Energy cost with different ore grades and different energy prices [$/t-ore].

	wt-%	Current	x2	x5	Commodity price[1]
Ni	3	9,340	18,680	46,700	10,403 $/ton
	0.3	114,429	2.39E + 04	5.98E + 04	
	$4x10^{-4}$	25,754,851	3.96E + 04	9.90E + 04	
Co	0.16	23,738	47,476	118,690	55,731 $/ton
	0.016	130,746	261,492	653,730	
	$6.9x10^{-5}$	29,291,647	58,583,294	146,458,235	
PGMs	$4x10^{-4}$	489,170	978,340	2,445,850	29,580,000 $/ton
	$2.4x10^{-6}$	113,996,791	227,993,582	569,983,955	

[1] (U.S. Geological Survey, 2022).

Consequently, the striped area representing profitable scenarios for tailings processing is much larger with respect to the current ore grade compared to the other two elements analyzed. The high price of PGMs can only be compared to that of gold, which explains why the profitability threshold is so low. In this study, the metal content of PGMs in tailings was used to determine the minimum energy required to extract any metal. If the ore grade decreases until that point and energy costs remain constant, it would still be possible to recover PGMs. A two-fold increase in energy costs would be required to make the recovery unviable. However, other costs such as operation, maintenance, and management must also be factored in, and energy costs from other metals could reduce the initial share, making the process more feasible.

Finally, PGMs present a unique situation due to their scarcity in the crust and their high market prices. As previously mentioned, the current energy cost represents only 3% of the current PGMs price. This explains why the striped area is so high with respect to the current ore grade, compared to the two previous elements. The high price of PGMs, which can only be compared to that of gold, justifies this situation. In this case, the PGMs metal content in tailings has been chosen as the LOR to obtain the minimum energy needed to extract any metal. Even if the ore grade decreases to that point, it would still be possible to recover PGMs if the energy costs are maintained. The energy costs would have to increase by more than two-fold to make the recovery unprofitable. However, the price could hold some energy costs coming from the other metals, reducing the initial share, obtaining more benefits. Other costs apart from energy must be added to these prices, such as operation, maintenance, and management.

It is important to note that mines are designed to be economically feasible, which means that cost allocations are crucial to maximize metal extraction. As a result, it is common for the metal that generates the maximum profit to receive a higher cost allocation since its market price is higher (Magdalena et al., 2022). Conversely, companion metals with a lower market price receive less allocation to obtain more benefits when metals are sold. Although there are no common criteria for cost allocation, economic assessment is widely used since mining companies need to make a profit from extracting minerals. Therefore, an analysis was conducted to determine what would happen if allocation changed. Since Ni is the most extracted metal out of the three studied in this paper, a larger share of the total cost allocation was considered, ranging from 40% to 70%. Table 9 summarized the results of this analysis. In this example, different allocations have been provided for the three metals studied, obtaining different costs depending on the allocation procedure used.

Based on the results of this analysis, the main conclusion is that by increasing the cost allocation for Ni, the costs for Co and PGMs reduce considerably (almost 50% in the case of PGMs), while Ni prices increase only slightly. This can be easily seen if the energy costs are compared with current metal prices. As mentioned, the energy cost for Ni, Co, and

Table 9
Energy costs calculated according to different cost allocation procedures and energy prices [$].

	Current energy price			Current energy price x2			Current energy price x5		
	Ni	Co	PGMs	Ni	Co	PGMs	Ni	Co	PGMs
Ni 40% Co 29% PGMs 31%	8,985	23,292	983,960	17,970	46,583	1,967,920	44,925	116,459	4,919,799
Ni 50% Co 24% PGMs 26%	9,223	21,063	829,338	18,446	42,125	1,658,676	46,115	105,313	4,146,690
Ni 60% Co 19% PGMs 21%	9,461	18,833	674,716	18,922	37,667	1,349,432	47,305	94,167	3,373,580
Ni 70% Co 14% PGMs 16%	9,699	16,604	520,094	19,398	33,208	1,040,188	48,495	83,021	2,600,470

PGMs represents 63%, 67%, and 3%, respectively, of the current price. However, if this comparison were made with the highest allocation for Ni (70%), the energy cost associated with this metal would be 69% of the current Ni price, while for Co, it would change to 47% and 1.5% for PGMs. Mining companies can use these different allocations to determine the price of the metals they are extracting, as it can lead to significant differences in some metals.

5. Conclusions

Metals have become increasingly critical due to their expanding usage in technological devices and industries, and this demand is expected to persist in the future. This study scrutinized Nickel, Cobalt, and Platinum Group Metals from diverse viewpoints, taking into account key factors such as the energy cost of extraction, the limit of recovery (LOR) for each commodity, and the impact of price variation in the mining sector. These approaches allowed for the evaluation of outcomes in various scenarios.

HSC Chemistry software was employed to simulate the energy consumption behavior in a mine as the ore grade declines. For this purpose, the specific energy for concentration was calculated for various processes carried out during the beneficiation process, including comminution, flotation, and refining stages. The amount of energy required to extract a ton of different metals was determined by considering current concentrations in mines, in tailings, or when an ore grade limit (LOR), as specified in this paper, is reached. Energy costs would increase more than 250% for Ni, 700% for Co, and 7,500% for PGMs if they were extracted from tailings. In these cases, for extraction to be viable, the market price of Ni should at least double, and that of Co and PGMs should be more than two and three times higher, respectively.

The economic evaluation also underscored the importance of cost allocation. Currently, the energy cost represents 63%, 67%, and 3% of the price of Ni, Co, and PGMs, respectively. However, if the cost allocation changes, it may be feasible to extract a specific metal, despite a reduction in the ore grade.

As demonstrated in this paper, the cost to extract and refine these commodities will become unaffordable as the ore grades approach the limit of recovery. Environmental impacts will also tremendously grow, putting ecosystems at risk.

Therefore, it is crucial to work on postponing the depletion of mines as much as possible. Recycling could be an excellent solution in this regard. However, the recycling rates for some of the metals analyzed in this study, including many others critical for the green economy, are considerably low. Even if millions of devices containing those metals are manufactured daily, their dispersive use makes it challenging to recover them. Currently, it is still more profitable to resort to primary extraction than to try to recover these small quantities, but this may not always be the case in the future.

CRediT authorship contribution statement

Ricardo Magdalena: Conceptualization, Methodology, Software, Data curation, Writing – original draft. **Alicia Valero:** Supervision, Validation, Writing – review & editing. **Guiomar Calvo Superivision:** Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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PAPER III

geosciences

Article

The Energy Cost of Extracting Critical Raw Materials from Tailings: The Case of Coltan

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Abstract: Niobium and tantalum are mainly produced from columbite–tantalite ores, and 60% of their production is nowadays located in the Democratic Republic of Congo and Rwanda. The concentration of supply, the scarcity, the wide range of use in all electronic devices, and the expected future demand boosted by the clean and digital transition means that Nb and Ta have high supply risks. In this context, extraction from rich Ta and Nb tailings from abandoned mines could partly offset such risks. This study analyzes the energy cost that the reprocessing of both elements from tailings would have. To that end, we simulate with HSC Chemistry software the different processes needed to beneficiate and refine both metals from zinc tailings as a function of Nb and Ta concentration. At current energy and metal prices, tantalum recovery from rich Ta-Nb tailings would be cost-effective if ore-handling costs were allocated to a paying metal. By way of contrast, niobium recovery would not be favored unless market prices increase.

Keywords: niobium; tantalum; coltan; mineral production; extraction; specific energy; tailings

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1. Introduction

Several authors have defined the 21st century as the Technological Age [1]. The number of connected devices has risen exponentially in the last few years. An increase of around 3–5% in the production of electric and electronic equipment (EEE) is expected [2]. From around 2 billion devices (primarily personal computers and smartphones) sold in 2000, the world has progressed to more than 22 billion in 2018. According to some estimations, this number could even reach 38 billion by 2025 [3]. The type of technologies in use has also changed, incorporating many different devices such as tablets, smart TVs, wearables, and the internet of things.

The penetration of advanced technologies implies using a more-significant number and variety of raw materials [4,5]. Specifically, two metals are of extraordinary relevance in this context: niobium and tantalum, which have a wide range of uses. Their main applications are the fabrication of smaller and more effective condensers, which allow smaller, more efficient devices to operate at higher performance levels [6,7]. Ta and Nb are also becoming key metals in the green energy transition, being present in large amounts of electric vehicles. This is why both elements are present in the list of the so-called critical raw materials of several studies (i.e., Calvo et al. [8] and Moss et al. [9]) and institutions, such as the list of Critical Raw Materials developed by the European Commission [10] and the report of the Critical Defense Materials of the United States Government [11], among others.

Niobium and tantalum are mainly produced from columbite–tantalite ores, also known as coltan. The importance of both metals is such that some authors have claimed that we live in the Coltan Age, rather than in the Technology Age [12].

Although coltan is vital for our society, various issues related to its extraction and production must be considered [13,14]. Coltan extraction is mainly concentrated in the Democratic Republic of Congo (DRC) and Rwanda. Two countries that arguably do not respect human rights and whose extraction processes have been questioned many times by international organizations [13]. The United Nations has published several reports asking for governments, markets, and companies to monitor the supply chain of these metals [15,16]. A similar movement is also led by the Group of 8 (G8). With the promotion of a voluntarily certified trade chain (CTC) in mineral production, the aim is to prevent poverty and encourage political stabilization. The use of materials from countries in conflict, where the chain of custody is not assured, could be reduced and those suppliers who focus on using "blood free" materials rewarded [17].

Given that it is related to the use of new technologies, the global extraction of Nb and Ta has increased in the last decades [18]. Australia has been the largest producer of these elements for several years, with more than 60% of the total share in 2005 [19]. In 2008, there was a noticeable reduction in Australian production. This was mainly because one of its main exploitations, Sons of Gwalia, had to close, reducing to almost zero Australia's coltan production in 2010 [13,19]. More recently, the Wodgina mine, also located in Australia, ceased production in 2017 as Ta concentration was too low to be cost-effective [20]. This is why, from 2010 on, African countries have notably increased their world coltan production, particularly the Great Lakes Region, accounting for more than 50% of the total share. Nonetheless, this figure must be taken very carefully, as not all the mining production is always reported in official sources of the country, and the amount extracted could be even higher [21].

Although Central Africa has been the main producer of Ta in the last decade, the largest reserves are not located in that region. According to Nikishina et al. [22], South America holds 41% of the total Ta reserves of the world, followed by Australia with 21%. As for Nb, reserves are mainly concentrated in Brazil, with 16,000,000 tons, and Canada, with 1,600,000 tons [23].

Still, there is a limited amount of these two elements in the Earth's crust. Some authors state that the Ta maximum-production peak occurred in 2005 [24], while others locate it in 2039 [25]. As for Nb, the expected maximum-production peak could be around 2030 [24]. Even if the difference between all these estimations might seem significant, the truth is that the order of magnitude is very similar, and even an increase in reserves might not postpone it much farther in time [25]. This, combined with the Nb and Ta expected growing demand, means that the supply of these metals could be at risk in the medium term.

There is another issue that is not being sufficiently addressed in the literature. With increasing extraction, high-grade mines become depleted. Consequently, it is necessary to resort to lower-grade mines, which entails an increase in energy consumption and the generation of waste rock if no additional measures are taken [26]. With declining ore grades, a new source of coltan may become competitive: mining tailings.

Certainly, some mine tailings may contain concentrations of metals that were discarded when the mine was in operation [27]. This can be explained due to technological limitations at the moment of extraction or to low prices of the commodities, among others. Accordingly, waste rock that, in the past, was considered non-profitable might even have a higher metal content than currently operative mines [27]. Such is the case of a mine in Kasese, Uganda, where cobalt-rich tailings generated during the primary extraction of copper are now being reprocessed years after the mine ceased its operations [28]. Another case is the Penouta mine, located in the north west of Spain, which was one of the most important tin mines in Europe [18]. In the 21st century, new studies were carried out, identifying a significant amount of tantalite concentrate in Penouta [29]. For the Balsa Grande tailings area, estimated resources add up to 4.8 Mt of residue containing 48 ppm of Ta and 39 ppm of Nb, while for the other tailings area (Balsa Pequeña), resources are estimated at around 0.22 Mt with 42 ppm of Ta and 34 ppm for Nb.

Valero et al. [5] carried out an analysis to calculate the cumulative expected material demand from 2016 to 2050 in green technologies, including wind energy, solar photovoltaic, solar thermal power and light-duty vehicles, estimating that the amount of Ta and Nb required could be around 54.60 ktons for Ta and 2287.95 ktons for Nb. This means that, if the whole tantalum present in Penouta mine tailings could be recovered, it would account for more than 43% of the total required from 2016 to 2050. As for Nb, this value would reach 1%.

That said, is it feasible to recover all such resources with available technology? What would be the energy cost to recover them? The Second Law of Thermodynamics states that energy costs spiral with declining ore grades [30], meaning that not only quantity but the concentration of both elements in the tailings are key to determining whether they are recoverable.

The main goal of this paper is to analyze the evolution of the specific energy needed to concentrate Nb and Ta as a function of ore-grade decline. This way, it will be possible to estimate the point at which tailings become a viable alternative to current mines from an energy point of view. Some studies in the literature follow a similar approach, recovering gold through a unique beneficiation process [31]. In the particular case of Nb and Ta, as they are both recovered during the beneficiation and refining stages as by-products of tin ores, the complexity of the process is higher, and the consequences of ore-grade decline are worth studying in more detail.

The analysis presented in this paper was carried out using specialized software called HSC Chemistry, modelling all the mining and metallurgical processes required to obtain pure Ta and Nb as a final product. The software includes different modules providing chemical/thermodynamic data for mining and metallurgical operations. For the simulation, 12 different scenarios were created.

2. Ta and Nb Processing

Ta and Nb often occur together in different minerals and in combination with oxide impurities [32]. As these two metals have similar chemical and physical properties, it is difficult and costly to separate them and obtain a high metal concentration [33]. Ta and Nb sources can be divided into three main groups: pyrochlore, alkaline, and granites [34]. Within these sources, many minerals contain Ta and Nb. Still, only two are currently cost-effective: titano-niobates and tantalum-niobates [35]. However, if the ore grade decreased to a point where the process were no longer cost-effective, it would be necessary to look for alternative sources for these metals [18,36]. In this case, tin slags could be considered another viable source of Nb and Ta, for their relatively high concentrations [35].

Figure 1 shows a general flowsheet for the extraction of Ta and Nb from tin tailings [37–41]. There are three main steps in this process: (1) comminution, (2) flotation and (3) refining.

2.1. Comminution

The first step, comminution, seeks to reduce the particle size to facilitate the separation of the minerals [42,43]. This stage can be divided into three steps: crushing, grinding, and regrinding.

Minerals have different chemical and physical properties that influence the power demand in the units to reduce their particle size. The Bond work index is the most widely used parameter to measure ore hardness. The amount of comminution energy depends on the Bond index of each metal and it is calculated through Equation (1).

$$W = 10\, W_i \left(\frac{1}{\sqrt{P_{80}}} - \frac{1}{\sqrt{F_{80}}} \right) EF_x \tag{1}$$

For the case study, the major component of the mine is tin (Sn). The Bond index for this metal ranges from 10–14 kWh/t [38,44]. Thus, an average value was chosen for the simulation (12 kWh/t).

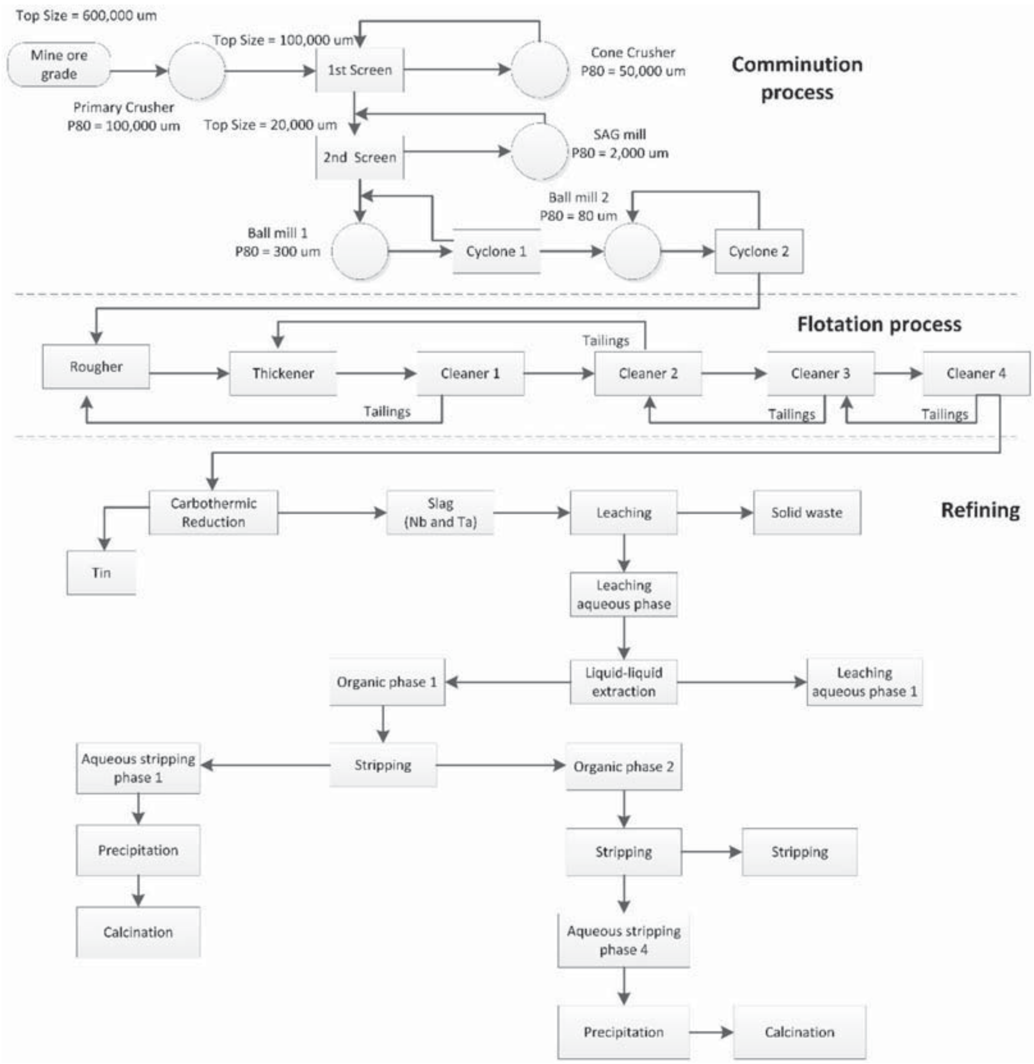

Figure 1. Flowsheet for the extraction of Ta and Nb from tin tailings.

It must be noted that efficiency factors must be considered, as they can reach up to 20% of the final energy. Still, other authors have considered this factor as zero to simplify calculations [31,45]. As these factors modify the power depending on the size of the mill, the feed, circuit, etc. [38,39,46], efficiency factors were included, after a literature review, to approximate the power calculated to an actual process.

Equation (1) depends on the Bond index (W_i); the diameter in microns (P_{80}), meaning that 80% of the product passes; and the size of the feed (F_{80}), meaning that 80% of the feed passes [40]. The last term of the equation is the efficiency factor (EF_x), which depends on the mill, and the particle size, among other factors.

The reduction ratio (P_{80} and F_{80}) is one of the main factors in the equation. The units in the comminution process can treat a wide range of reduction ratios, which were selected after a literature review [35], considering the feed introduced and other factors such as the number of units.

2.2. Flotation

During flotation, the minerals are concentrated using additives and flotation cells. The particle size is already small at this stage, so flotation circuits are needed to concentrate Ta and Nb. These flotation circuits are mainly composed of conditioners, roughers, and cleaners, and, in this case, a thickener is also needed [47,48]. The feed from the comminution process is introduced in a rougher and then in a thickener. After the thickener, there are four cleaners in a row, where the concentrate stream goes to the following cleaner. At the same time, all tailings are recirculated to the previous cleaner to try to recover as much Ta and Nb as possible. For that reason, residence time, volume cell, recovery ratio, and pH were introduced in the simulation [47,48].

2.3. Refining

After flotation, the feed is sent to the final step, refining, where the targeted metals are separated from the rest of the metals. This last process can be carried out using a combination of hydrometallurgy and pyrometallurgy.

At this point, the feed must have a specific concentration to make purification feasible. Since Nb and Ta are being recovered as by-products of Sn, two different metallurgical processes are needed to obtain the three metals individually. Accordingly, the feed goes through carbothermic reduction, obtaining a Sn concentrate and slags with a high concentration of Ta and Nb. Then, the Sn stream is introduced in an electrolysis step (and then purified) while the slags are introduced in a leaching and precipitation circuit. Subsequently, Ta and Nb are separated in a leaching unit, applying calcination at the end of each process, obtaining pure Ta and Nb separately [35,36].

3. HSC Simulation

An extensive literature review was carried out to obtain reliable data to run the simulation: the ore grade in the mines, concentration needed before refining the feed, number of cleaners and roughers needed to concentrate the mineral, power used in the comminution process, etc.

The average coltan concentration in the crust is around 2 ppm (parts per million) [13,35]. Obviously, in the mines, this concentration is higher. For the simulation, cassiterite-columbite mineral bearing was chosen as a reference, with a global average in a mine of 0.2 wt-% [34,49]. This value is similar to the one found in the Penouta Mine (Spain) [50,51]. However, although the global average concentration is 0.2 wt-%, the initial concentration must be set up for Ta and Nb individually in the simulation. Accordingly, based on the literature review, it is possible to find a range of concentrations for Ta and Nb in mined ore, as reflected in Table 1 [50].

Table 1. Concentration along the beneficiation and refining process (%).

	In Mined Ore [50]	After Flotation [36]	After Refining [33,36]
Ta_2O_5	0.51–3.7	8.45	79.67
Nb_2O_5	0.16–2.22	5.40	98.45

Table 1 also shows the concentration along the beneficiation process for both elements. The concentration gradually increases in the first steps. After the flotation process, the Ta concentration must be 8.45 wt-% for Ta and 5.40 wt-% for Nb, something that is achieved using additives or repeated concentration. Then, the purification of each metal is carried out during the refining process, with a final concentration of 79.67 wt-% and 98.45 wt-% for Ta and Nb, respectively.

The ore grade and energy consumption evolution were analyzed using twelve different scenarios. The initial concentration was calculated as the average between the lowest and highest concentration values, 2.1 wt-% and 1.2 wt-% for Ta and Nb, respectively. Accordingly, this concentration decreased consecutively by one third in each scenario. This way, the future behavior of mines can be simulated, estimating the specific energy for concentration for each metal from current mines to the worst-case scenario.

The specific data used in the simulation for the different steps of the extraction of Ta and Nb are described next.

3.1. Comminution

In the simulation, Nb and Ta were extracted from Sn ores, specifically, cassiterite. Thus, it was necessary to set up a feed for the comminution process to proceed with the calculations. Twelve different feeds were defined, as shown in Table 2, to analyze the evolution of energy consumption.

Table 2. Feed for every scenario created.

Scenario	Feed [t/h]	Scenario	Feed [t/h]
1	400	7	800
2	450	8	1000
3	500	9	1400
4	550	10	1800
5	600	11	2400
6	700	12	3000

As stated before, the Bond index is an important factor for the calculations in the comminution process (which holds the highest energy share for low ore grades). We selected a value found in the bibliography (12 kWh/t) according to certain parameters, such as the bearing mineral and the concentration of metals in the mineral. Considering a different Bond index would affect the results obtained at the end of the model.

If the ore grade decreases, it is necessary to process more rock to obtain the same amount of ore. For this reason, the as wis increased by 50 t/h until the fifth scenario. Then, it was increased from 100 t/h up to 600 t/h, reaching the top feed for the last scenario, 3000 t/h. This last scenario considers a very low ore grade in the mine, close to depletion.

With this increase between scenarios, the software could reach the concentration goals established along the different stages during the simulation, avoiding any lack of feed.

Different studies were conducted to determine the optimal particle size for the comminution process as it could affect the whole process [48,52]. A too-large particle size could negatively affect further steps and lead to a less-efficient flotation process. On the other hand, a too-small particle size could decrease the efficiency of the additives.

The comminution process starts with the crushing stage (Figure 2). Following a literature review [38,53], the particle size is reduced from 600 mm to 50 µm in the regrinding unit, which was incorporated at the beginning of the flotation process. With a top size of 600 mm, the feed is introduced to the jaw crusher to reduce the particle size to 100,000 µm. Some particles will have a final smaller or larger size, so a screen is applied to separate them. Larger particles are sent to the cone crusher unit, reducing its size to 50,000 µm to accomplish the requirements. Another screen is applied to filter the feed with a top size of 20,000 µm, sending larger particles to be reduced in a SAG Mill. When the feed of the second screen is filtered, the grinding stage starts, which is composed of a ball mill circuit followed by cyclones. In the first unit, the size is reduced to 300 µm, while in the second ball mill, the size is decreased to 80 µm. Cyclones are incorporated after every ball mill to avoid larger particles in further steps. The last step in the comminution process is regrinding. This step is applied at the beginning of the flotation process, reducing the particle size to 50 µm.

Table 3 summarizes the power demanded in every unit and the specific energy in kWh per ton of rock for scenario 1. The grinding process has the highest power demand. This could be easily explained due to the small particle size required for further process steps. The smaller the particle size, the lower the efficiency, and, therefore, the more energy is needed to reduce the size to these values. These numbers are within the same order of magnitude as those obtained by Latchireddi et al. [54].

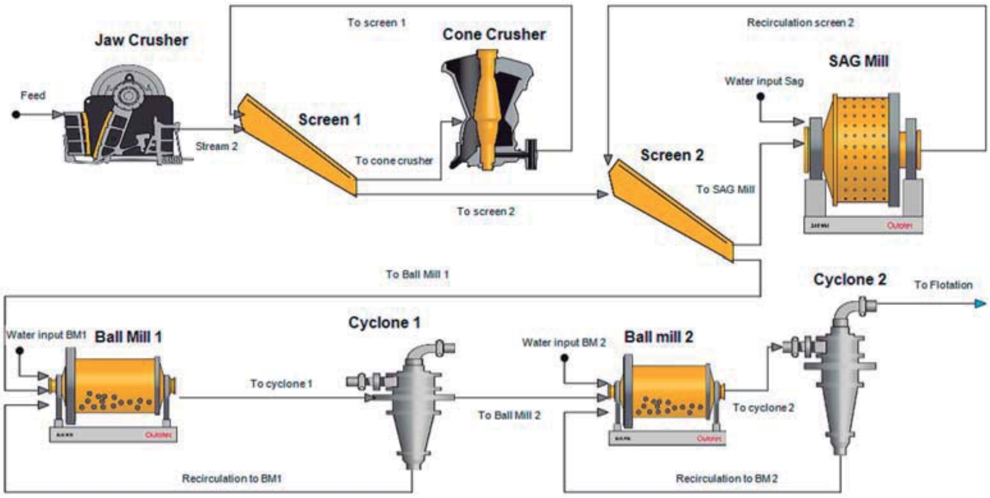

Figure 2. Comminution process.

Table 3. Detail of the units of the comminution process for scenario 1.

Equipment	Power Demand [MW]	Specific Energy [kWh/t Rock]
Primary crusher	0.365	0.38
Cone crusher	0.477	0.88
SAG mill	3.975	7.27
Grinding—Ball mill 1	22.927	12.05
Grinding—Ball mill 2	11.960	9.68
Re-grinding	3.735	10.46

3.2. Flotation

After the comminution process, the feed is introduced in a rougher where it is diverted into two outputs, the concentrated feed, and the tailings. The concentrated feed is sent to the last ball mill and, subsequently, to a thickener to separate the pulp. Then, several cleaners are applied to increase the feed concentration before sending it to the metallurgical process. While the kinetics is not being considered, every cleaner was designed considering the residence time, volume cell, the power demanded, etc., using bibliography data [47,48].

The lower the ore grade in the initial feed, the more cleaners have to be introduced before the flotation process, and the more specific energy is required to obtain the concentration required at the end of the process.

3.3. Refining

Metallurgical processing requires an organized and coordinated arrangement of unit operations designed to provide physical and chemical changes to purify certain raw materials and leave them ready for use in the industry [55]. This process was divided into two steps: (1) Sn recovery, (2) Ta and Nb recovery [56].

For the recovery of Sn, the feed is sent to the refinery so carbothermic reduction can be applied. After this process, Sn with a concentration higher than 96 wt-% is obtained. Then, electrolysis is applied to obtain pure Sn. High amounts of water and sulphuric acid are needed to reach the desired concentration (99.99% Sn).

As the slags generated during this process have a high Ta and Nb concentration, they are further processed to obtain pure Ta and Nb. First, leaching is applied, introducing different additives to change the pulp mix. Then, another unit transforms part of the pulp from an aqueous into an organic phase. The next unit is the first stripping, where Ta and Nb are separated. While Nb is converted into the aqueous phase, Ta remains in the organic phase and is sent into a new stripping unit. After the first stripping, Nb is diverted to the precipitation unit, where it reacts with certain chemicals and is then sent to the last step, calcination, to eliminate the excess water.

On the other hand, Ta is sent into a new organic phase where more ammonium fluoride and ammonia are poured, sending the feed to an aqueous stripping process. Subsequently, Ta feed is precipitated and sent into a calcination process to obtain pure Ta. Table 4 summarizes the reagents needed to purify the three metals analyzed in this study.

Table 4. Summary of the inputs introduced in the metallurgy process for a ton of rock (data in t/h).

Reagents	Electr. [1]	Casting	C. Tower [2]	Leaching	Liquid. Extra.	Stripping	Pre. Nb [3]	Calc. Nb [4]	Stripping [2]	Pre. Ta [5]	Calc. Ta [6]
H_2O	10.24	0.08	0.13	1.97	-	4.05	-	-	3.94	7.67	-
HF	-	-	-	0.49	-	-	-	-	-	-	-
H_2SO_4	0.88	-	-	1.59	-	-	-	-	-	-	-
Cyanex	-	-	-	-	4.2	-	-	-	-	-	-
NH_4F	-	-	-	-	-	0.04	-	-	0.17	-	-
NH_3	-	-	-	-	-	0.01	0.60	-	0.03	-	-
KF	-	-	-	-	-	-	-	-	-	0.76	-
Natural gas	-	-	-	-	-	-	-	0.0038	0.022	-	0.0063

[1] electrolysis; [2] cooling tower; [3] precipitation Nb; [4] calcination Nb; [5] precipitation Ta; [6] calcination Ta.

It is important to highlight that almost 40% of the total water needed in the process is introduced during electrolysis to obtain pure Sn.

Table 5 summarizes the mass balance of the three metals (Sn, Ta and Nb) at the beginning and at the end of the beneficiation process. More than 92% of Sn, 95% of Ta, and 67% of Nb are recovered, reaching, thus, high recover yields. However, more than 40% of the inputs end up as waste rock along the process. Additionally, this material is usually contaminated with chemicals and additives applied during the flotation and the refining process, entailing other consequences during waste management.

Table 5. Summary of the mass balance for the three metals studied using a ton of rock as input in the metallurgy process.

	Beginning of the Process		End of the Process		Recovery Yield
	t/h	wt-%	t/h	wt-%	%
Sn	0.54	54.35	0.50	99.99	92
Ta	0.06	6.51	0.06	79.67	95
Nb	0.04	4.68	0.03	98.45	67

4. Results and Discussion

Increasing demand, the corresponding rise in commodity prices, and potential technological improvements could make lower-grade mines profitable [57]. Beneficiation processes would undoubtedly improve with technological development [57,58]. More-efficient machines and units could be developed and used to maintain the energy for the beneficiation process within the same order of magnitude. This is in line with other studies that state that, as reserves partially rely on economic factors, they could increase in the next two centuries for both metals, thus eliminating any possible risks of supply or bottlenecks [59]. That said, the question now is whether the recovery of key elements from low-grade deposits such as niobium and tantalum would be cost-effective with current technology.

To answer that question, we created twelve scenarios to calculate energy consumption as a function of ore-grade decline.

4.1. Specific Energy for Concentration

Ore-grade values of Ta range from 2.1 wt-% in Scenario 1 to 0.000012 wt-% in Scenario 12, and from 1.2 to 0.000007 wt-% for Nb. Comminution and flotation processes are common for the three metals to be recovered: Sn, Ta and Nb. A cost allocation based on the metal output was applied, with the following share: 80% for Sn, 12% for Ta and 8% for Nb.

Table 6 shows the evolution of the specific energy for the concentration stage for Ta and Nb applied during the flotation process for the 12 scenarios.

Table 6. Evolution of the specific energy for concentration obtained during the flotation stage (data in GJ/t-ore).

	Ta	Nb
Scenario 1 (con. in mine)	0.68	1.21
Scenario 2	1.14	2.17
Scenario 3	2.12	4.26
Scenario 4	6.11	12.23
Scenario 5	17.30	21.16
Scenario 6	45.89	48.25
Scenario 7	136.57	178.23
Scenario 8	328.41	360.23
Scenario 9	703.33	768.15
Scenario 10	1729.44	1974.79
Scenario 11	4495.87	5280.51
Scenario 12	13,135.13	16,192.05

4.2. Specific Energy for Refining

Ta and Nb are extracted as by-products of Sn, as the slag generated during the beneficiation process of this metal contains a very high concentration of both elements. Therefore, a fair allocation must also be applied. At this stage, since both elements share the same processes, Ta and Nb each account for 50% of the costs.

It is important to note that the metallurgical processes for both metals remain the same in all the scenarios. This is so because the concentration at the beginning of the metallurgical stage is always the same, and, hence, the same processes apply to all scenarios.

With all the processes simulated in HSC and the considered allocation procedure, the values calculated for the Ta and Nb total refining process are 13.69 GJ/t-Ta and 13.21 GJ/t-Nb, respectively. These data are within the same order of magnitude as those found in other studies [60].

For these calculations, 31.4 MJ/kg was chosen for the high heating value (HHV) for all the calculations where coal is required [61]. Additionally, natural gas is introduced in the calcination process at the end of the refining process; the value used in this case was 42.2 MJ/kg [62].

4.3. Total Energy

Figure 3 shows the evolution, in logarithmic scale, of the total specific energy for Ta and Nb, including the comminution, the flotation and the refining stages.

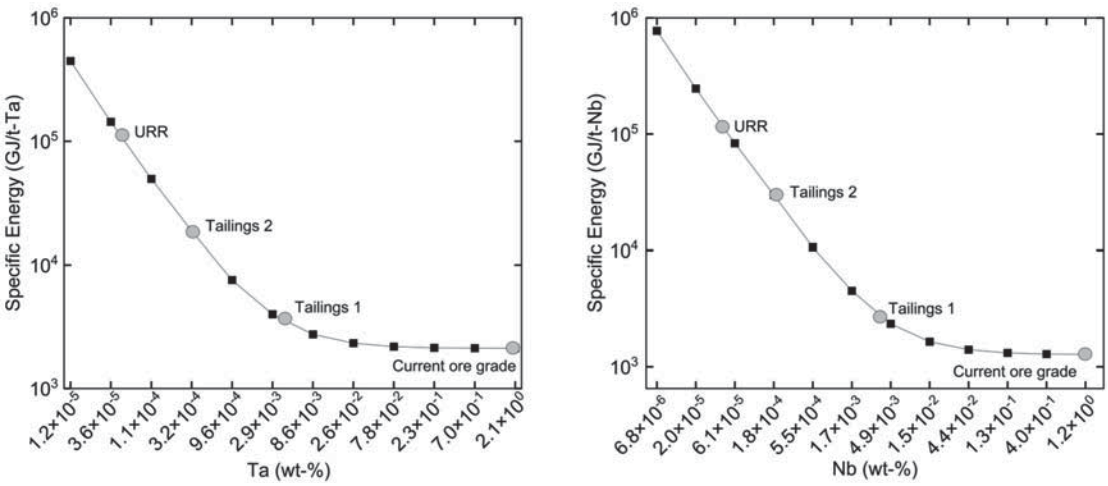

Figure 3. Specific energy for concentration for Ta (**left**) and Nb (**right**). In both cases, the *Y* axis is in log scale. For the sake of clarity, the points representing the scenarios have been joined to form a continuous line.

As observed, the specific energy experiences significant growth in both cases as the ore grade declines. It is important to note that the results are on a logarithmic scale, which means that the curve becomes exponential when the ore grade is drastically reduced or, in other words, when the mine approaches depletion. This is in line with other studies, where the evolution of the energy consumption as a function of the ore grade in different mines was analyzed [63]. Tailings 1 and 2 and URR are three relevant points with a particular concentration, explained in the next section.

In the current case study, several reasons can explain this growth. First of all, the amount of rock that has to be processed in each scenario grows considerably [64–66]. As the ore grade decreases at the beginning of the beneficiation process, the feed that reaches the flotation circuit is less concentrated, implying that more units are needed to concentrate the feed. Alternatively, more time is required to obtain the desired grade for further processing, which results in more specific energy for the flotation stage. Unlike in the comminution and flotation processes, the specific energy for concentration for the refining stage is always the same, as stated in the previous section.

It must be noted that ore-handling costs should also be considered, including transportation, feeding, and washing [67]. Ore-handling costs can be as high as those for beneficiation and refining or even higher, depending on the ore concentration [31]. All such costs are assigned in this paper to tin production, as it is considered the paying metal.

4.4. Tailings Ore-Grade Analysis

After carrying out the simulation, the energy requirements of very depleted mines can be appropriately assessed. Two situations are compared: extraction from current mines and extraction from tailings.

Current ore grade in mines has already been established and is represented by Scenario 1, being 2.1 wt-% and 1.2 wt-% for Ta and Nb, respectively. The average values considered for "Tailings 1" are 4.4×10^{-3} wt-% for Ta and 3.6×10^{-3} wt-% for Nb, corresponding to those of the Penouta mine in Spain (considering Balsa grande and Balsa pequeña) [29]. Tailings 2 is an even lower value, which has been arbitrarily reduced one order of magnitude with respect to Tailings 1, i.e., 3.2×10^{-4} wt-% for Ta and 1.83×10^{-4} wt-% for Nb.

Table 7 shows the energy requirements obtained. As can be seen, with current ore grades, the energy required to recover Ta and Nb is around 900 GJ/ton for Ta and 80 GJ/ton for Nb. Reducing the concentration to the Tailings 1 grade would increase energy costs to about 2140 GJ/ton of Ta and 1550 GJ/ton of Nb. Going beyond and considering Tailings 2 concentration would increase that energy to 17,540 GJ/ton of Ta and 28,700 GJ/ton of Nb. All such figures can be compared with energy requirements for the beneficiation of gold, one of the commodities for which ore grades are very low. As seen in Table 7, extracting Ta and Nb from Tailings 1 or 2 entail energy costs that are well below the current energy cost for the recovery of a ton of gold, which, according to Calvo et al. [63], is 145,000 GJ/t-gold. Accordingly, extracting Ta from Tailings 1 and Tailings 2 grades would have an energy cost equivalent to 1.48 and 12.09%, respectively, regarding gold beneficiation energy. For Nb, the figures would be 1.07 and 19.79%, respectively. Such high energy costs for gold are only justified by its elevated market price, which in 2021 reached an average price of 58,000 USD/kg [68]. Comparatively, the price of Ta was 160 USD/kg and for Nb 20 USD/kg that same year, i.e., 0.28 and 0.03% of gold market price, respectively [68].

Nonetheless, some authors state that there is a minimum concentration value from which beneficiation could be still profitable [24,69]. Hence, we could even go beyond and analyze the extraction energy costs of the so-called ultimate recoverable resources (URR), which are defined as the total amount of a certain mineral that could ever be recovered and produced [70]. Sverdrup and Rangnasdottir [24] proposed this limit grade at 5×10^{-5} wt-% for any metal. These authors' limit is based on the well-known Hubbert's peak model [71]. Considering the URR concentration of 5×10^{-5} wt-%, the energy costs would increase to 3401 toe/t for Ta and 1956 toe/t for Nb, reaching similar energy costs as for current gold extraction (Table 7).

Table 7. Comparison of the specific energy and % of the energy compared with the gold beneficiation process.

	Ta				Nb			
Ore Grade	wt-%	GJ/t-Ta	toe/t-Ta	% Compared with Gold [1] [63]	wt-%	GJ/t-Nb	toe/t-Nb	% Compared with Gold [1] [63]
Current	2.10	916.70	21.89	0.63%	1.20	78.47	1.87	0.05%
Tailings 1	4.4×10^{-3}	2144.8	51.22	1.48%	3.6×10^{-3}	1552.6	37.08	1.07%
Tailings 2	3.2×10^{-4}	17,541.8	418.97	12.09%	1.83×10^{-4}	28,709.7	685.70	19.79%
URR	5×10^{-5}	142,413	3401	98.21%	5×10^{-5}	81,912	1956	56.49%

[1] % compared with the average energy requirements for gold beneficiation.

To put these values in context, considering the worst-case scenario from a production perspective, some authors estimate the production of 6.5 kt of Ta in 2050 [72]. Regarding Nb, the expected demand for 2050 could increase to up to 250 kt [59]. If all this amount had to be extracted from mines that have reached this limit grade, the energy needed would represent almost 20% of the renewable energy generated that same year [73].

4.5. Economic Assessment

Knowing that the expected energy increases due to the reduction of mine grades, we can economically evaluate the extent to which these elements' extraction in tailings could become profitable. High energy costs with low commodity prices are decisive factors for reclaiming tailings materials. It is thus essential to consider both aspects.

The primary energy source applied during the comminution process is electricity. For the refining process, natural gas and coal also come into play. Energy values can be transformed into monetary values through energy prices. For the study, the average price for electricity in 2021 in Spain has been chosen as 0.25 USD/kWh according to Eurostat [74], and for natural gas and coal, 0.086 USD/kWh and 123 USD/ton, respectively. It should be remembered that ore-handling energy costs (most of them in the form of diesel) are not considered here, as they are entirely allocated to the paying metal Sn.

Accordingly, the estimated energy costs for Ta and Nb in Scenario 1 (i.e., considering current ore grades) are 1861 USD/t and 1984 USD/t, respectively, which constitute 1.16 and 9.92% of the average price for Ta and Nb in 2022 [68] (Ta: 160,000 USD/t, Nb: 20,000 USD/t). This leaves wide room for manoeuvre, even if many other costs need to be added, including investment costs, wages, water and chemical costs, emission abatement costs, etc. Figure 4 has been elaborated, considering different scenarios with rising energy costs. For instance, electricity prices increased from 0.14 USD/kWh to 0.31 USD/kWh from January 2021 to January 2022 in Spain [75]. Triggered by the soaring demand and supply-chain disruptions, commodity prices also increase. For instance, nickel and lithium recorded an increase of around 30% and 110% in the last year, respectively [68].

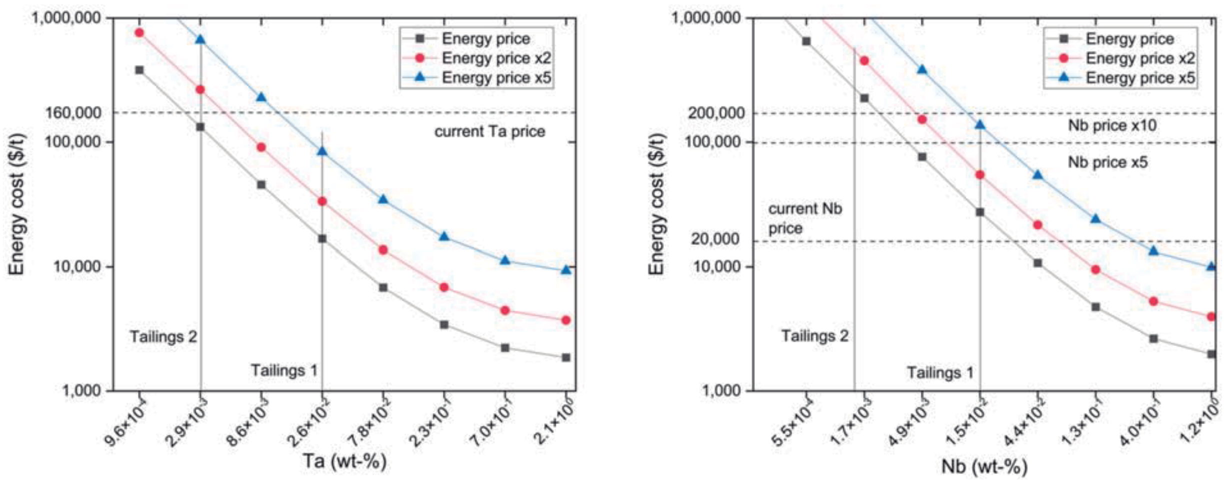

Figure 4. Evolution of energy costs as a function of ore-grade decline for different scenarios.

As shown in Figure 4, for the Tailings 1 scenario, with constant energy prices, energy costs rise by a factor of 10. For tantalum, energy costs still represent only a small fraction of current commodity prices (10%). If energy prices were to double, energy costs would represent 50% of current commodity prices, putting the viability of its extraction at risk. Tailings 2 scenario would be unfeasible even at current energy prices.

The case of niobium is slightly different, since the current Nb price is eight times lower than the Ta price, yet energy costs are similar due to their production routes. This means that Nb recovery from Tailings 1 is not cost-effective, even considering low energy prices. If Nb price were to increase fivefold, its recovery would likely be profitable if energy prices doubled. However, this would not be the case if, at the same time, energy prices increased fivefold. In that case, Nb extraction would only be likely viable if its market price increased tenfold. Extraction from Tailings 2 would be unfeasible in any analyzed scenario.

These results need to be interpreted with caution, as they are particularly sensitive to the metallogenesis of the ore and the allocation procedure. Niobium extraction is unfavored due to its low market price. A higher cost allocation towards tantalum would improve its viability. Similarly and as stated before, ore-handling energy costs were entirely assigned to the paying metal tin. Allocating part of such costs to tantalum or niobium would radically change the picture, questioning their profitability even at current ore grades.

5. Conclusions

Tantalum and niobium have become essential elements for the current society, as they are used in millions of electric and electronic devices and renewable technologies. The concentration of supply of both commodities, their scarcity, meagre recycling rates and soaring demand make these two metals very critical. This is why a new source of niobium and tantalum resources comes into play: tailings.

This paper analyzed the energy costs associated with the recovery of both elements as a function of their concentration in tin tailings. With the help of a simulation software, HSC Chemistry, we simulated the specific energy in every stage: comminution, flotation and refining.

Specifically, four situations were analyzed. The first corresponds to the current ore grade of both metals. The second one is based on the composition and concentration of current tailings in Penouta (Tailings 1). The third is a hypothetical situation with a concentration of one order of magnitude lower than that in Penouta (Tailings 2). The fourth is an extreme situation where the concentration reached is that of the so-called ultimate recoverable resources (URR).

As expected, it was found that the amount of energy required to extract a ton of Ta and Nb would considerably increase when ore grade declines, even if the best available technology were applied. However, for the first three scenarios, energy costs would still be significantly lower than current gold energy requirements and comparable with the URR scenario.

A preliminary economic assessment shows that, at the current commodity and energy prices and considering that ore-handling costs are allocated to tin in its entirety, the recovery of tantalum in the Tailings 1 scenario would be cost-effective, even if energy prices were to double. On the contrary, the recovery of niobium would not be favored because of its current low market price. If Nb prices increased or if most energy costs were allocated to tantalum, the situation would change.

There are many metals in abandoned mines and tailings that could be recovered in the future. Similarly, mountains of waste from electric and electronic equipment, with high concentrations of valuable metals, are filling worldwide landfills and are creating serious environmental problems. The time has come to recognize this waste as an opportunity, yet much more research needs to be undertaken to assess its recoverability.

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PAPER IV

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Article

Simulation to Recover Niobium and Tantalum from the Tin Slags of the Old Penouta Mine: A Case Study

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Abstract: Demand for niobium and tantalum is increasing exponentially as these are essential ingredients for the manufacture of, among others, capacitors in technological devices and ferroniobium. Mine tailings rich in such elements could constitute an important source of Nb and Ta in the future and alleviate potential supply risks. This paper evaluates the possibility of recovering niobium and tantalum from the slags generated during the tin beneficiation process of mine tailings from the old Penouta mine, located in Spain. To do so, a simulation of the processes required to beneficiate and refine both elements is carried out. After carbothermic tin reduction, the slags are sent to a hydrometallurgical process where niobium oxide and tantalum oxide are obtained at the end. Reagents, water, and energy consumption, in addition to emissions, effluents, and product yields, are assessed. Certain factors were identified as critical, and recirculation was encouraged in the model to maximise production and minimise reagents' use and wastes. With this simulation, considering 3000 production hours per year, the metal output from the tailings of the old mine could cover around 1% and 7.4% of the world annual Nb and Ta demand, respectively.

Keywords: coltan; niobium; tantalum; critical raw materials; technological metals; mineral processing; tailings

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1. Introduction

The 20th century has been characterised by a drastic increase in global material extraction, and this trend is far from changing in the 21st century [1,2]. In the last decades, we have seen a considerable increase in the demand for certain metals, especially intended for the manufacture of electric and electronic components [3,4].

Electric and electronic equipment (EEE) allow for increased efficiency and better experiences in technological devices, the Internet of Things (IoT), Machine Learning (ML), or Artificial Intelligence, among others [2]. They are also crucial in the development of clean technologies. Indeed, digital technologies need to be combined with clean technologies to mitigate climate change. In the "Mission Innovation" signed in Paris in 2015, 20 countries agreed to promote the acceleration of innovation on clean energies to make them more affordable and accessible to all, and achieve the goals of the Paris Agreement and pathways to net-zero [3]. This, in turn, increased the investment of governments and deployment of renewable energies, a type of technology that requires a considerable amount of critical materials in the manufacturing process [4,5].

In short, the use and applications of electric and electronic equipment (EEE), both in renewable energies and in other fields, is steadily growing as innovation has made devices more efficient [6,7]. This development usually implies an increase in the number and variety of the metals used [8,9], improving the capabilities of electronic devices [10].

The abovementioned is the case of niobium (Nb) or tantalum (Ta), both crucial for EEE and renewable energies. Niobium is an essential metal for manufacturing ferroalloys, such as ferroniobium, containing between 60%–70% niobium [11]. It also forms part of high-strength low alloy (HSLA) steels [12]. Tantalum is used almost entirely in electronic devices, specifically in capacitors and in different parts of smartphones such as lenses, batteries, microprocessors, etc. Both metals were discovered centuries ago; still, they have only begun to be used in the last decades. However, even if they are included in small quantities on each device, the total amount used at the world level is considerable. Moreover, their future availability could be dangerously compromised as the primary sources, meaning the places where they are mined are limited [13]. They are considered critical by many countries and institutions, as their current and future availability, or the concentration of supply, could put many economies at risk [14–16].

Therefore, securing a stable supply of certain raw materials including Nb and Ta is essential for many governments, such as the European Union, which promotes the so-called circular economy [17]. Unfortunately, current technologies are not designed to recover all the components and valuable metals from the waste of electric and electronic equipment (WEEE) [18]. This could be eventually solved following eco-design guidelines [19].

Alternatively, a stable supply of raw materials can be secured by resorting to domestic production. Yet, this is not free of difficulties, as there is much opposition to the opening of new mines due to the social and environmental issues that this may entail [20].

In this respect, the long mining tradition has left many abandoned facilities and discarded materials such as tailings, which are also a source of concern. If the remediation process is insufficient, it can cause a series of environmental impacts. Tailings can contain certain elements whose mobility and dispersion may pose an environmental hazard for soils, water, ecosystems, and people [21,22].

That said, particular mining wastes may include considerable amounts of valuable elements discarded during the initial mining process for not being economically profitable at the moment of exploitation. These wastes could become a relevant source of raw materials in the future, thereby increasing the domestic supply of metals that are currently almost only imported. However, the metallurgical processes to recover valuable metals from tailings usually involve the use of toxic substances. Therefore, the processes that can be applied have to be studied in depth, analysing how the use of reagents could be minimised to avoid further impacts.

This paper explores the potential recovery of niobium and tantalum from the zinc tailings of an abandoned mine in Spain. To that end, a virtual pilot plan modelled with HSC chemistry was set and optimised to maximise its efficiency and identify costs of chemicals, water, electricity, and emissions.

2. Niobium and Tantalum Production and Availability

According to the United States Geological Survey (USGS), Brazil is the largest niobium producer at the world level, and this trend has been maintained over the last few decades (Figure 1). Only in 2020, this single country was responsible for 91% of the niobium world production, followed by Canada (8%) [23]. Niobium reserves are also mainly concentrated in Brazil (95%) and Canada (3.5%), while the remaining are located in Angola, Australia, and South Africa, among others [24].

As for tantalum, one of the most valuable ores from which this metal is extracted is coltan. Coltan is a mixture of two minerals: tantalite, where tantalum predominates, and columbite, where niobium predominates. For this reason, coltan is also an important source of niobium.

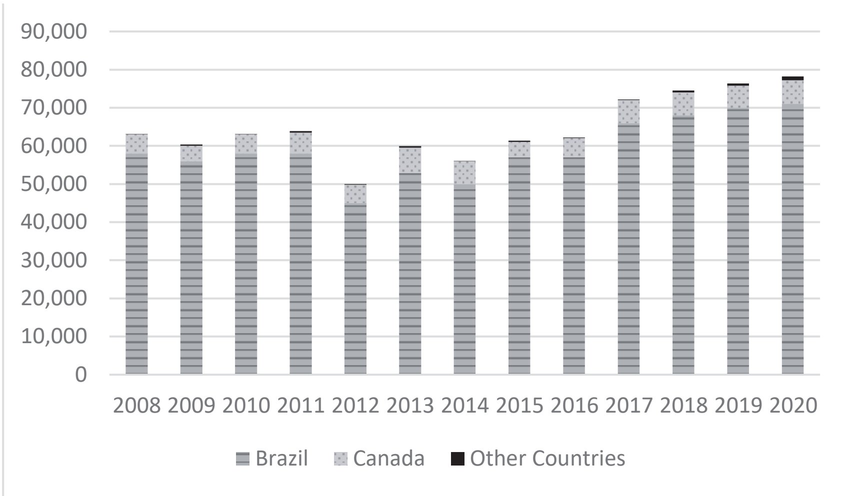

Figure 1. Historical production of niobium in metric tons, adapted from [23].

More than 60% of tantalum reserves are hosted in the Democratic Republic of Congo (DRC), while the remaining are in Brazil and Australia [25]. DRC alone was responsible for 40% of the total world production in 2020 [23]. Historical tantalum production can be seen in Figure 2, clearly showing the predomination of Africa over other regions of the world.

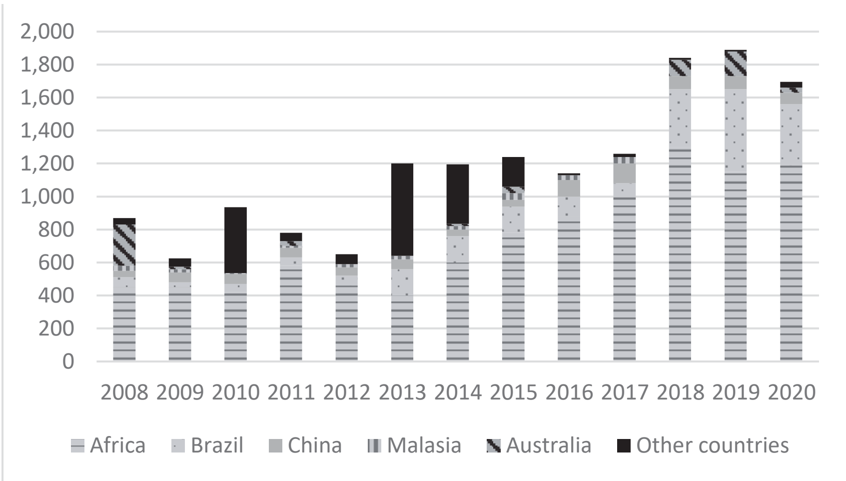

Figure 2. Historical production of tantalum in metric tons, adapted from [23].

Africa plays, thus, a key role in tantalum production since it has been responsible for more than 60% of the global production on average in the last years. Before 2008, Australia had an important market share, reaching almost 50% of the total world production [26]. However, with the worldwide crisis that occurred in 2008, some of the biggest mines in Australia suspended their activity due to financial difficulties, reducing their production share in the global market in the following years [27].

The concentration of supply in DRC and Rwanda, countries that arguably do not respect human and work rights, is a global concern [28,29]. Some of the most powerful companies agreed to obtain every metal used in their devices from a trustworthy resource [30]. To that end, a certificate can be provided to the end-user, claiming that the device has been manufactured by companies that respect human and work rights, from the extraction of the mineral until the device is sold [28].

Another alternative to overcome this situation of supply concentration is to find new ways to obtain niobium and tantalum or new sources. For this endeavour, the slags generated during the tin beneficiation process in the Penouta mine (located in Spain) will be analysed as a future source for both metals. Different geological studies were carried out, but the mine ceased its activity in the 1980s due to a decrease in tin price and depletion of higher ore grade zones.

Penouta Mine

The history of the Penouta mine goes back to the beginning of the 20th century when the area was first exploited, and small amounts of cassiterite were extracted. Mining activity was then resumed in the 1960s and until 1971, becoming one of the most important tin mines in Europe. During the last years of activity, around 1,600,000 t of rock were extracted, containing around 640 t of cassiterite and 170 t of tantalite concentrate [31]. This deposit consists of a greisenised, altered and kaolinised granite mass enclosed in metamorphic rock, with disseminated cassiterite and columbo-tantalite [32]. In the 21st century, new studies were carried out. Between the two zones analysed, estimated resources add up to 11,910,402 t of ore, with a Sn and Ta content of 428 and 35 ppm, respectively. In 2020, Strategic Minerals Spain resumed the mining activities in the area, becoming again the only mine in Europe in which concentrates of Nb and Ta are recovered, but not yet refined.

3. Methodology and Data Availability

Model for Recovering Nb and Ta from Slags

The aim of this study is to analyse the possibilities of the recovering process of Nb and Ta from tin slags using a simulation of a metallurgical plant. Similar simulations using the same software to recover metals from common rocks, such as iron, lead, zinc, and gold, have been carried out in previous studies [33–35].

As stated before, the Penouta tin mine was selected for the case study. Tin was initially obtained from cassiterite (SnO_2), containing important concentrations of Nb and Ta that could be economically profitable to recover [36]. The slags obtained after the first metallurgical process still have an important concentration of Nb and Ta. Until now, they had remained in the tailings as they could not be beneficiated when the mine was operating, yet they constitute a valuable source of such commodities.

The processes required for niobium and tantalum recovery were already studied by different authors in previous studies, establishing the initial concentration for the three metals considered [36–39]. As niobium and tantalum have similar chemical and physical properties, their separation and purification processes are considerably difficult [38]. Still, they can be recovered from the slags generated after a carbothermic reduction [39,40]. Additionally, recent investigations driven by research groups at CSIC developed a process at lab scale to recover Nb and Ta by solvent extraction from Sn-Ta-Nb mining tailings which has also been the seed of this study [40].

Figure 3 shows the flowsheet of the processes used to recover the three metals generated with HSC Chemistry. The process starts with the tailings coming from a particular mine with Sn-Nb-Ta, in our case, Penouta. It is important to mention that before the beginning of the process, comminution is needed to reduce the rock coming from the tailings; for this, jaw crushers and ball mills are used. The particle size is then reduced to 200 μm and sent to the feed of the metallurgical process. Next, it is necessary to proceed with pre-concentration in the industrial plant. After mixing the minerals of the feed with some additives, they are sent to the carbothermic reduction to start the purification of metals [39]. Carbothermic reduction is applied to separate Sn from other oxides.

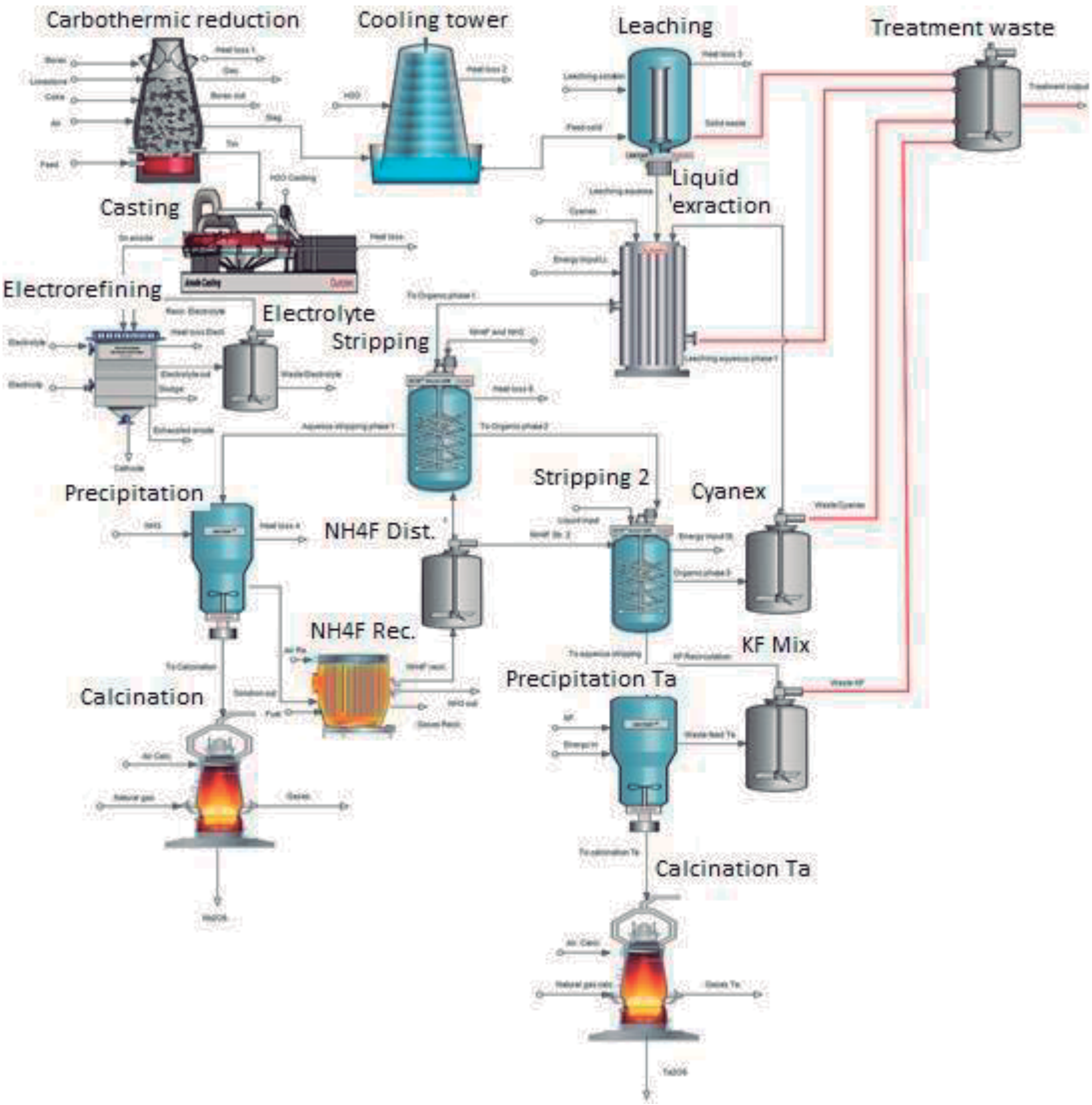

Figure 3. Flowsheet of the process used to recover Sn along with Nb and Ta from the slags.

At this point, Sn is obtained with a concentration higher than 96%, while the slags contain a significant concentration of Ta and Nb, 25% and 21%, respectively [39]. As the final product should be 99.99% Sn, it is necessary to apply an electrorefining process in order to increase its concentration. To that end, an electrolyte of H_2SO_4 is prepared in order to separate impurities from Sn, increasing its concentration to the desired value [39].

On the other hand, slags are sent to different units to extract Nb and Ta. The feed is first sent to the leaching unit, obtaining solid wastes and another output in an aqueous phase, which ends in the liquid-liquid extraction unit. It is then mixed with organic additives, discarding the leaching aqueous phase and redirecting the organic phase output into the stripping unit. Additionally, NH_3 and NH_4F are added since this is the unit where Nb and Ta will be separated. By using these additives, a new enriched Nb aqueous phase is formed, finishing in the precipitation unit. Meanwhile, the other output, still in the organic phase, is sent to a new stripping unit to convert it into an aqueous phase, too. It follows precipitation for both feeds, aiming at eliminating any impurities before continuing with the last phase of the process, calcination. Calcination is used to eliminate the undesired water and humidity, recovering at the end of the whole process, Nb with a concentration close to 99% and Ta with a concentration of 78%.

It is important to mention that there are also several recirculation units and that a vast number of reagents are needed for this whole process. To reduce the total use of chemicals, feeds are recirculated and introduced again in the units when possible. One example is the "mixing Cyanex 923" unit, where 95% of the total Cyanex 923 is recirculated in order to maximise its use. Another one is the "mixing KF" unit. It is not possible to use 100% of this reagent due to the conditions needed in the extraction of tantalum. For that reason, a recirculation of 65% is assumed, thereby re-using it as many times as possible.

This process has been widely studied by different authors [41,42] as coltan has become one of the most important minerals in industry. Additionally, its scarcity and concentration of supply are also well known. Hydrometallurgy processes used to recover these two elements are based on strong acids, which are economically and environmentally challenging. One of these studies considers a greener approach for the selective dissolution of the amorphous slag matrix, obtaining a concentration similar to commercial grade [41]. This same study reflects the high mass losses produced by sequential acid and alkaline leaching, while the sequential Acid-Basic-Acid leaching is the most favourable, with concentrations of 63% [41]. One of the main disadvantages of this process is the high amount of chemicals needed to purify the metals. Another study analyses the availability to purify Nb and Ta from tin slags with a very low ore grade [42]. Although the recovery ratio of the metals is very high and the results are very promising, a vast number of processes, time, and a high amount of chemicals are required [42]. As a result, the environmental impact is very high, and with the reagents applied, it makes this process less cost- efficient compared with the process proposed in this paper.

In this study, alternative chemicals as those proposed in the literature are used during the leaching process, thereby reducing material losses as well as increasing the metal yields. In that same line, in our case study, the aim is to reuse reagents as much as possible to decrease the environmental impact of the whole process.

Once the initial model of the treatment plant is ready, a preliminary analysis of the different inputs needed to purify the three main metals present in this mine (Sn, Nb, Ta), as well as a thermodynamic analysis for a future set up of the metallurgy plant, is undertaken.

4. Results

The process validated at lab scale, is upscaled with a specialised software called HSC Chemistry. This software allows to assess costs and optimise processes [43]. In particular, for this paper, it has been applied for thermodynamic and mineral processing calculations, such as mineral extraction, beneficiation, and mineral refining [33].

The first step is to determine the amount of rock per hour to be treated, selected as 1 ton per hour (tph). This number is in accordance with the size and capacity of the mine. After setting up all equipment, flows, and reactions taking place, the amounts of reagents needed for the whole process (and for each unit) as well as outputs of metals and electricity used, among other factors, were obtained, as described in the next sections.

4.1. Reagents and Water Used

Table 1 shows information about the flow rates of the different reagents introduced in the system.

Table 1. Amount of reagents introduced (in t/h).

Borax	Limestone	Coke	HF	H_2SO_4	Cyanex 923
0.14	0.20	0.23	0.49	2.03	0.07
Solvesso	**NH_4F**	**NH_3**	**KF**	**Natural gas**	
0.12	0.11	0.66	0.03	0.03	

A significant number and amount of chemicals are used in the aforementioned process to recover Sn, Nb, and Ta. Nonetheless, sulphuric acid is the most used reagent, with 2.03 t/h. This is something that is consistent with the beneficiation process used, as an electrolyte is needed to process more than 0.5 t/h of Sn in order to increase its concentration to 99.99%.

The type of reagents used in each metallurgical unit have also been analysed (Figure 4). This way, it is possible to compare which reagents are used on each specific part of the whole process and their share with respect to the total use on each unit.

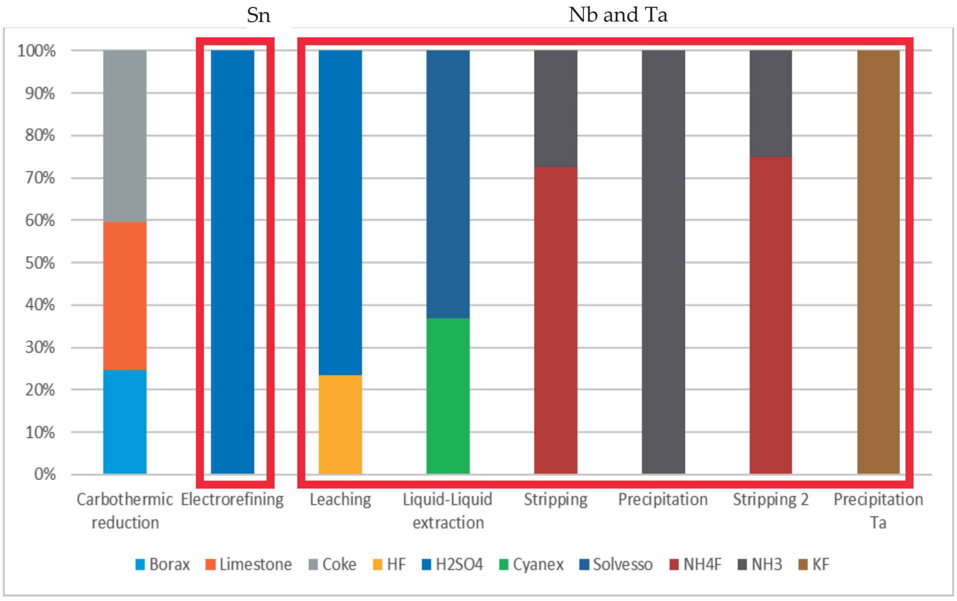

Figure 4. Share of reagents needed in each unit of the treatment and beneficiation process of Sn, Nb, and Ta.

In this case, it is also possible to see how the carbothermic reduction is the unit where a greater number of different reagents are introduced (borax, limestone, and coke). Moreover, the liquid-liquid extraction process also stands out as a crucial unit since the phase changes from aqueous to organic. Specifically, it is the only unit that uses Solvesso (solvent) and Cyanex 923(extraction agent). Additionally, HF is only used in the leaching unit and KF in the precipitation of tantalum, while NH_3 is used in three different units, stripping 1 and 2, and precipitation.

Among the materials used during the beneficiation process, water is the largest input in the system with almost 12 t/h, which is a common rate used in metallurgical processes [44].

Of these 12 t/h of water needed, almost half (5.12 t/h) are used in the electrorefining unit (Figure 5). The second unit, where more water is required, is in the stripping because of the high volumetric relation between the organic and the aqueous phase.

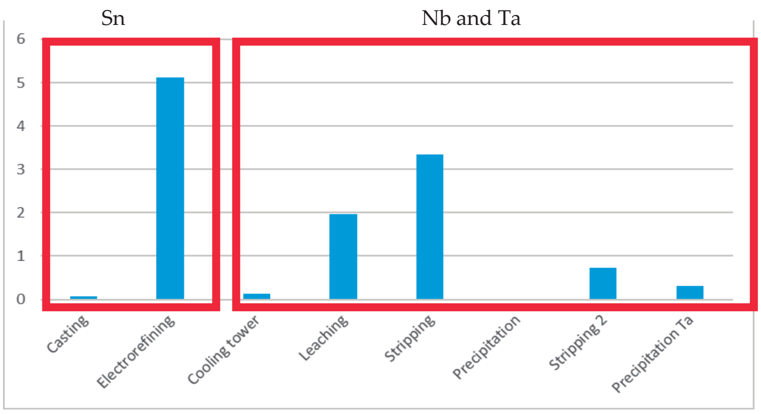

Figure 5. Water requirements in the beneficiation process of Sn, Nb, and Ta (in t/h).

4.2. Metal Output

At the end of the process, the metals obtained are tin, niobium, and tantalum. Table 2 shows how much metal is recovered with a feed of 1 t/h of ore. The main difference between these metals is that tin is recovered after two metallurgy processes using a very small number of reagents. A total of 0.50 tons of tin are recovered per hour and considerably lower amounts of Nb and Ta. Besides, niobium and tantalum are recovered as by-products. Their initial concentration is very small, and a higher number of processes and chemicals are needed to purify them.

Table 2. Metal output (in t/h).

Metal	Amount
Sn	0.45
Nb	0.03
Ta	0.05

4.3. Electricity Consumption and Gas Emissions

The electricity required for the hydrometallurgy processes, as well as the gases generated during them, are also considered in the study.

Electricity is needed during the process to move the blades that are in charge of mixing the reagents with the feed [45]. During the simulation with HSC, it is not possible to directly obtain figures on electricity consumption as this parameter is related to the feed introduced and the size of the units. However, some authors state that an average value could be between 0.05 and 0.1 kW/m^3 [46].

Since the volume of every hydrometallurgy unit is known, it is then possible to calculate the electricity needed for our process, choosing the highest electricity consumption value (see Table 3).

Table 3. Electricity needed on each unit.

Unit	Electricity (kW)
Electrolyte mix	1.062
Leaching	0.416
Liquid-Liquid extraction	0.842
Stripping	0.959
Precipitation	0.515
Mixing reagents	0.428
Stripping 2	0.858
Mixing Cyanex 923	0.421
Precipitation Ta	1.31
Mixing KF	1.301

The highest energy values correspond to the units that precipitate and recirculate Ta. This is in line with the results obtained during the simulation since the volumetric relation between H_2O and the reagent used to precipitate Ta is very high. Consequently, recirculation units must be similar to the previous units since the amount of feed introduced is within the same order of magnitude, and therefore, it will have a high energy consumption.

According to some studies, the electricity needed to send tin to electrorefining could be between 150–200 kW/t/tin [47]. Therefore, with the amount of pure Sn obtained in our simulation, the electricity needed would be in the range of 75–100 kW.

As for gaseous emissions, mainly CO and CO_2 are generated predominantly in three units: carbothermic reduction, Nb calcination, and Ta calcination (Table 4). In the carbothermic reduction, as it is necessary to increase the temperature to 1200 °C so that the process can occur, 0.23 t/h (around 24% of the feed) of coke is introduced, producing 0.84 t/h of CO_2 emissions to the atmosphere. Additionally, both Nb calcination and Ta calcination also need a temperature of 1200 °C to eliminate the humidity from the feeds. In these cases, 0.02 t/h and 0.01 t/h of natural gas are introduced in the Nb calcination unit and Ta calcination unit, respectively. Compared to the emissions of the carbothermic reduction, they have almost negligible gas emissions to the atmosphere.

Table 4. Gases emissions per unit (in t/h).

Output Gases	Carbothermic	Calc. Nb	Calc. Ta
CO	0.06	0.003	0.005
CO_2	0.84	0.05	0.013

4.4. Analysis of the Results

After processing one ton of ore coming from the Penouta mine, around 0.5 tons of metals are recovered, the vast majority corresponding to tin.

As mentioned, several metallurgical processes are needed to purify Nb and Ta from that ore. Various reagents must be mixed with the feed to produce changes in the phases and separate them so that they finally end up precipitating in the form of almost pure metal. At the end of the simulation, to obtain 30 kg of Nb and 50 kg of Ta, more than 3000 kg of chemicals were used to reach full separation. Moreover, the amount of water needed in the process is not negligible either. Around 12,000 kg of water has to be used to process one ton of ore, of which around 6000 kg are needed in the electrorefining process to purify tin. The rest is used in the remaining processes to concentrate Nb and Ta.

As seen in Figure 3 and after analysing the costs associated with the reagents, it was determined that different recirculation units should be incorporated. Particularly, we introduced five units that recirculate reagents and water. These units are crucial as the requirements of chemicals could increase up to 50% if there were no recirculation.

Additionally, a final unit named "treatment waste" was included in the simulation. All the undesired outputs are recirculated to this unit to proceed with further treatment and decrease the overall environmental impact of the plant. Table 5 shows the most abundant reagents that reach this unit. This can be used to better understand the importance of waste treatment as more than 8000 kg/h of water is discarded and mixed with other substances.

Table 5. Certain reagents that end in the treatment waste unit (in kg/h).

Variable	Amount
H_2O	11,510
HF	370
H_2SO_4	2030
CaF_2	80

According to the results obtained during the simulation, the percentage of recovery at the end of the process from the rock is 45%, 3%, and 5% for Sn, Nb, and Ta, respectively. However, if only tin slags are considered, values for Nb and Ta increase significantly, reaching values close to 50% for niobium and more than 56% for tantalum. These values are considerably higher than those that can be found in the literature [48].

5. Discussion and Conclusions

The results obtained from the simulation are very promising since the recovery of niobium and tantalum after tin beneficiation has been demonstrated to be possible. Furthermore, even if the Penouta mine was mainly aimed at obtaining tin, both metals could also be extracted from the slags as by-products with currently available technology. Considering that the current demand of pure Nb in 2017 was 6400 tons while the demand of Ta was 2079 tons, according to our simulation, the metal output from the mine could represent more than 1% and 7.4% of the annual market share for Nb and Ta, respectively, assuming 3000 production hours in a year. These values represent a moderate scenario since the input introduced could be higher than 1 t/h of rock, depending on the capacity of the mine and ore quality. Additionally, this 3000 production hours in a year could also increase, depending on different factors such as different working shifts, working days in the year, etc.

The main disadvantage found in the simulated process is the number of chemicals that are required, as well as the use of water in the process. This issue could affect the cost-effectiveness of a future processing plant. Additionally, the environmental impacts related to all the reagents discarded should also be closely monitored and find ways to reduce or mitigate them. An example is the Ta precipitation unit. Despite water humidity and KF being recirculated at a 65% rate, high amounts of water are still needed, and a large part of this humidity is discarded and hence lost. The "Liquid-Liquid extraction" unit is also a critical one. This is because an organic phase is introduced in this unit, and an important amount of water and other elements in the water phase end up being discarded.

Until now, in Penouta, Nb and Ta ended up in tailings, but we have proved that there are ways to recover a very significant amount of these elements annually. Looking for new and more sustainable paths to get the most out of the mines and recover metals more efficiently could be a way to overcome future shortages of elements, mineral depletion, and decreasing ore grades without compromising the environment.

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PAPER V

Eco-credit system to incentivise the recycling of waste electric and electronic equipment based on a thermodynamic approach

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Abstract: The use of electric and electronic equipment has been increasing dramatically in the last years and entails an important amount of waste containing many valuable metals which could constitute an important source of raw materials if appropriately recycled. In this paper, an expression has been developed to value waste of electric and electronic equipment that are sent by users to an appropriate recycling plant. The user obtains in turn eco-credits, which can be later exchanged through different incentives. The eco-credit expression is based on the raw material content of the given device, assessed through an indicator called thermodynamic rarity, which rates minerals according to their scarcity in the crust and the energy required to mine and refine them. Additionally, the state of the device, lifetime and recyclability of the materials are considered in the equation. The expression has been applied as a case study to a working tablet and an LED lamp.

Keywords: raw materials; reuse; recycling; exergy; eco-credits; rarity; waste electrical and electronic equipment; WEEE.

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This paper is a revised and expanded version of a paper entitled 'Ecocredit system for incentivizing the recycling of waste electric and electronic equipment based on a thermodynamic approach' presented at ECOS 2019, Wroclaw, 23–28 June 2019.

1 Introduction

The quantity of waste generated from electric and electronic equipment (WEEE) has increased considerably in the last decades due to the rise of new generation devices and technologies (Ikhlayel, 2018). For instance, 1.5 billion smartphones were sold in 2017 (Nair, 2018) and almost 140 million tablets in 2018 (Lui, 2019). According to a report of the United Nations Environment Programme (UNEP), in 2019, the world's production of e-waste was 50 million tonnes, 90% of which ends up illegally traded or dumped. Unfortunately, this number is expected to increase rapidly as the production of EEE has a growth at a rate of 3% per year, which could lead to a production of 120 million tonnes of e-waste in 2050 (Nijman, 2019). In fact, according to the 'Global E-waste Monitor Report 2017' (Ku and Hung, 2014), 44.7 million tonnes of e-waste were generated in the world of which only 20% was recycled through proper channels. Additionally, Europe was the second largest generator of e-waste per inhabitant with an average of 16.6 kg/inh.

On the other hand, the demand of critical raw materials is expected to rise due to the increase of the production of these technological products and green and efficient technologies, including the 24 raw materials labelled as critical (21 elements plus heavy rare elements, light rare earth elements and platinum group metals) by the European Commission due to their high economic importance and supply risk (EC, 2019). As a big share of the elements used in EEE is not recovered, new amounts need to be mined from Earth to cover the demand.

This problem is in turn linked to the limited availability of material resources on Earth, some of which are facing or will soon face serious restriction issues when demand exceeds supply (Valero et al., 2018). There will come a time when the demand of some of these elements used in EEE will be higher than the supply due to the scarcity of certain of those materials on Earth and the difficulty of the extraction and beneficiation process (Calvo et al., 2016). Not only the lower concentration of minerals in the mines will make them harder to extract and process, but also the price will arguably increase as it will imply a higher energy consumption and therefore, higher costs. This issue could in fact boost and encourage the correct management of waste electrical and electronic equipment (WEEE).

According to Kumar and Dixit (2018), there are several barriers that can possibly hinder the adoption and implementation of WEEE management; these barriers include government policies, consumer attitude, technological gaps, stakeholders role, globalisation and economic consideration between formal and informal sector. Besides, there is now a widespread consensus that current human consumption and production practices are having a detrimental effect on environmental quality, social equity and long-term economic stability (Anand and Sen, 2000; Charles and Linda, 2007; Millar et al., 2019). As stated by Jayaraman et al. (2019), the Kohlberg's stage of moral development theory disposes three levels of moral development to create awareness in people: pre-conventional, conventional and post-conventional moral developments. This theory and global concern have led to promote the so-called circular economy (CE).

CE is defined as closing loop material flows in the whole economic system in association with the so-called 3R principles (reduction, reuse and recycling), taking into account economic aspects without restricting economic growth (Lieder and Rashid, 2016). With this definition, CE can serve as a tool for sustainable development and to better understand how its long-term effects differ from those of the 'linear' economy (Millar et al., 2019).

Particularly for WEEEs, there are several directives trying to promote CE in Europe by means of regulating WEEE flows and trying to achieve higher collection rates (35%) (Islam and Huda, 2018). In this region, the first Directive related to electrical and electronic equipment (EEE) was approved in 2002 (Directive 2002/96/CE), recognising the responsibility of producers once the product becomes a waste. In 2012, the Directive 2012/19/EU entered into force to try to reduce the environmental impact of WEEE acting through all the different stakeholders involved. Among all the stakeholders, producers have the main responsibility as they should finance at least the collection from collection facilities and the treatment, recovery and disposal of WEEE.

A key aspect to promote CE practices and improve the collection of WEEE is to provide accurate information regarding the consequences of not acting. This is an important goal, informing the users about the material composition and recyclability of every product and raising awareness about risks of material supply in the future. It is necessary to be prepared for that moment and the reusability of materials and recyclability must increase to be able to compensate that rise in demand.

With the aim of raising awareness about the importance of EEE recycling, this paper proposes an eco-credit system to incentivise users when old devices are sent to appropriately collection point. The methodology is based on a thermodynamic approach, which accounts for the physical value of materials contained in it. The eco-credits proposed in this study are calculated using three parameters, and unlike the studies of Kitajima et al. (2015) and Szargut and Stanek (2008), who proposed also methods to assess the environmental burden of WEEE, lifetime and state of the device are included with an equal weight in the equation compared to the composition, trying to foster the reuse of the device, which actually comes before recycling in the hierarchical sequence of the 3 R principles mentioned before. Nonetheless, our study, as well as these two other approaches, aim for a greener economy, penalising the misuse of non-renewable sources, stockpiling and encouraging properly recycling.

Two case studies are going to be used for this matter, tablets and LEDs.

2 Methodology

2.1 Thermodynamic approach

As stated before, the amount of minerals and elements that can be extracted from Earth is limited by their availability in the crust. The evolution of technology is triggering the use of certain materials which are considered critical by many economies, such as rare earth elements, gallium or indium, although the percentage in mass in electronic devices is small in comparison with other base metals or plastic. These elements are, in many cases, considerably scarce in the crust or have mining and beneficiation processes that require large amounts of energy. Second Law of Thermodynamics can be used to develop an indicator that is able to measure the physical value of those critical materials, the so-called thermodynamic rarity (Valero and Valero, 2014), which, contrarily to a mass-based approach, it gives more weight to valuable and scarce raw materials.

One could think that a price-based approach would also allocate more weight to scarcer materials. However, price is volatile and depends on many factors alien to the physical reality of the material itself, and it cannot be considered as a universal numeraire. On the other hand, using a thermodynamic rarity approach, the weight of every material is strictly based on physical aspects of the resource and is therefore stable and universal. Moreover, as well as the price-based approach, it reflects the social perception of 'value'. Therefore, thermodynamic rarity allows assigning numerical values to measure the availability of scarcer minerals such as platinum, niobium or gold compared to other minerals with higher availability such as silicon, iron or lead.

The methodology applied, called thermodynamic rarity, is based on the assumption of a physical value for minerals, according to their chemical properties and the availability on Earth. In this way, the scarcer a mineral, the higher its embodied exergy and therefore, the higher the cost of extraction and production (Valero and Valero, 2014). This is explained because when the ore grade decreases, the amount of rock to treat to obtain the same concentration is higher and as a consequence, the energy used is higher too (Mudd, 2009).

Thermodynamic rarity is composed of two parts. The first one is referred to the embodied exergy cost, which accounts for the energy needed to extract a mineral from the mine until this mineral is treated and processed to be converted into a pure metal (cradle-gate approach). The second term in the methodology is referred to a hypothetical cost, related to the savings we have for having minerals concentrated in mineral deposits and not dispersed throughout the crust. This term is accounted f through the so called exergy replacement costs (ERC) and represent the exergy needed to concentrate a given mineral from a completely dispersed state (i.e., a hypothetical grave) until the state of composition and concentration found in the mines (i.e., the cradle), with current technology. As such, the methodology considers the exergy to obtain the metal from a mine with the efficiency of the process and the reposition exergy of the metal once this reaches its end of life (Valero and Valero, 2012).

A baseline must be set up in order to obtain the state of maximum dispersion and hence the corresponding average concentrations of each mineral in the upper crust. For that purpose, Thanatia, a model of resource-exhausted Earth, was defined as a total dispersed planet, with no high grade deposits and composed by more than 300 of the most abundant minerals at crustal concentrations (Valero et al., 2011; Valero et al., 2012). In this way, with equations (1), (2), (3) and (4) developed in the work of Valero et al. (2013), ERC can be calculated.

$$b_{ci} = RT_0 \left[\ln x_i + \frac{(1-x_i)}{x_i} \ln(1-x_i) \right] \tag{1}$$

$$\Delta b_{ci} = b_{ci(x=x_c)} - b_{ci(x=x_m)} \tag{2}$$

$$ERC = k \cdot \Delta b_{ci} \tag{3}$$

$$k = \frac{E_{Realprocess}}{\Delta b_{mineral}} \tag{4}$$

where b_{ci} is the concentration exergy needed to separate an element from a substance. R is the universal gas constant (8.314 kJ/kmol K), T_0 is the temperature of reference and x_i is the concentration of the given mineral measured in grams of mineral per gram of ore. 'replacement exergy', named as Δb_{ci}, is the difference between the concentration exergy calculating x_i with the concentration of Thanatia (x_c) and x_i with the ore grade of the mine (x_m).

Additionally, exergies must be multiplied by a k factor which is a constant, being defined as the ratio between the total exergy required to extract a mineral from a mine and the minimum exergy to carry out the same process. Then, with the methodology explained, the rarity (R_i) of a mineral (i) is calculated through equation (5).

$$Ri = ERCi\,(grave - cradle) + Embodied\ exergyi\,(cradle - gate) \tag{5}$$

With this methodology, Table 1 was generated assessing the value of the rarity of the different elements. It is important to stress that thermodynamic rarity does not consider the distribution of materials in specific components. Materials can be homogenously spread throughout a whole system or found in almost a pure form in several components. This fact would certainly affect the recyclability of a device, which is not the object of this paper, but the rarity would remain the same (Ortego et al., 2018). This way, to calculate the thermodynamic rarity of a device or specific component, equation (6) should be applied, once the composition in terms of elements contained (m_i) in device (A) are known:

$$R(A) = \sum_{i=1}^{n} m_i R_i \tag{6}$$

Table 1 Rarity values for different elements analysed

Rarity	*Ag*	*Al*	*Au*	*Cr*	*Cu*	*Fe*	*In*	*Mg*
kJ/g	8,937	661	654,683	41	348	32	363,918	146
Rarity	*Mn*	*Ni*	*Pb*	*Pd*	*Sb*	*Sn*	*Ti*	*Zn*
kJ/g	73	758	41	2,870,013	488	732	203	197

Source: Valero and Valero (2014)

2.2 Composition of the devices

For the purpose of this study, the composition of the following devices has been analysed: LEDs, tablets, laptops and smartphones. These devices have been selected because of the expected increase in sales and the criticality of the materials contained in them. Additionally, an increase in the number of certain key materials included in such technologies is expected due to technological improvements. This is because certain elements can confer specific features to the devices, improving their functionality. This can be implemented to increase and improve the battery life, efficiency of the device, screens, etc.

According to Directive 2012/19/EU of the European Union, from 2016 onwards, the minimum collection rate shall be 45%, calculated from the total weight of WEEE collected in a given year in the Member State concerned, expressed as a percentage of the average weight of EEE placed on the market in the three preceding years in that Member State. From 2019 onwards, the minimum collection rate shall be 65% of the average weight of EEE placed to the market in the preceding years in the Member State concerned (EC, 2018).

Table 2 Material composition of every device [g]

Element	*Iphone 6*[1]	*Element*	*Tablet*	*Element*	*Laptop*	*Element*	*Bulb LED*[8,9]
Al	31.14	ABS	166.92[10]	ABS	373[6]	Ag	0.003
As	0.01	PMMA	22.5[10]	PC	406[6]	Al	17.49
S	0.44	Silicon	61.92[10]	Other plastic	343[6]	Cu	2.31
Bi	0.02	Ag	0.022[5]	Glass	300[6]	Fe	1.28
Ca	0.44	Al	0.47[3]	Epoxy	244[6]	Ga	0.009
C	19.85	As	0.03[5]	Cu	270[6]	Ni	0.74
Cl	0.01	Au	0.01[5]	Al	512[6]	Pb	0.000071
Co	6.59	Cd	0.0002[5]	Steel	871[6]	Au	0.004
Cu	7.84	Co	12.67[4]	Au	0.36[6]	Sn	2
Cr	4.94	Cr	0.076[2]	Ag	0.92[6]	Ti	0.01
Sn	0.66	Cu	5.56[3]	Pd	0.05[6]	Ce	0.000071
P	0.03	Fe	2.322[2,3]	Ni	0.99[6]	Y	0.003
Ga	0.01	Hg	0.0001[2]	Zn	0.1[6]	Polycarbonate	14
H	5.52	In	0.02[2]	Nd	1.06[6]	Polyester	17.61
Fe	18.63	Li	4.43[4]	Sn	9.3[6]	Polyamide	6.15
Li	0.87	Mg	0.28[3]	Pb	6.1[6]	Others	9.3
Mg	0.65	Mn	14.31[3]	Co	65[7]		
Mn	0.29	Ni	12.403[3,4]	Ta	1.7[7]		
Mo	0.02	Pb	0.54[3]	Pr	0.27[7]		
Ni	2.72	Pd	0.0001[5]	Dy	0.06[7]		
Au	0.014	Sb	0.07[3]	In	0.04[7]		
O	18.71	Sn	0.91[2]	Pt	0.004[7]		
Pb	0.04	Ti	0.19[3]	Y	0.002[7]		
K	0.33	Zn	0.61[2]	Gd	0.00001[7]		
Si	8.14	Other	93	Ce	0.00008[7]		
Ta	0.02			Eu	0.00013[7]		

Source: [1]Brian Merchant (2017), [2]Zhang et al. (2017), [3]Zhang et al. (2018), [4]Brian Merchant (2017), [5]Meng et al. (2017), [6]Deng et al. (2011), [7]Buchert et al. (2012a), [8]Panasonic (2020), [9]Cenci et al. (2020), [10]Lin et al. (2009). Information for printed card boards, screens, batteries have been also consulted in Buchert et al. (2012a, 2012b), Jayaraman et al. (2019), Giegrich et al. (2012), since the information was in percentage and other cases in grams

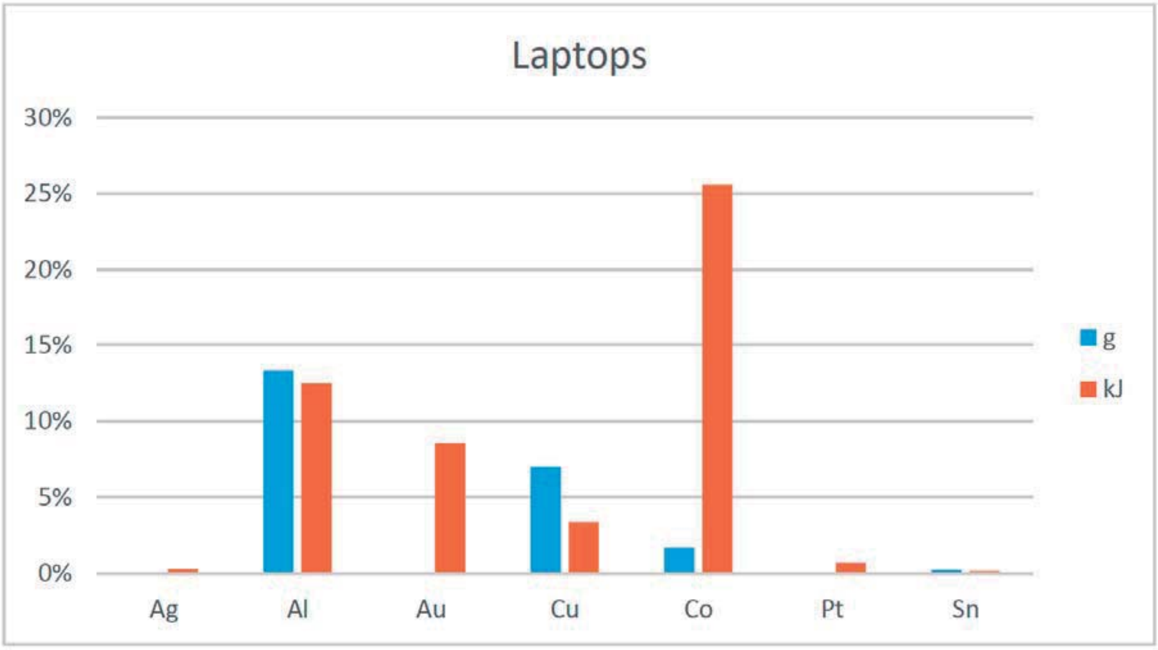
Table 2 Material composition of every device [g] (continued)

Element	*Iphone 6*[1]	*Element*	*Tablet*	*Element*	*Laptop*	*Element*	*Bulb LED*[8,9]
Ti	0.3			La	0.00011[7]		
W	0.02			Te	0.00004[7]		
V	0.04			Other	442[6]		
Zn	0.69						
TOTAL	129		405		3,847		71

Source: [1]Brian Merchant (2017), [2]Zhang et al. (2017), [3]Zhang et al. (2018), [4]Brian Merchant (2017), [5]Meng et al. (2017), [6]Deng et al. (2011), [7]Buchert et al. (2012a), [8]Panasonic (2020), [9]Cenci et al. (2020), [10]Lin et al. (2009). Information for printed card boards, screens, batteries have been also consulted in Buchert et al. (2012a, 2012b), Jayaraman et al. (2019), Giegrich et al. (2012), since the information was in percentage and other cases in grams

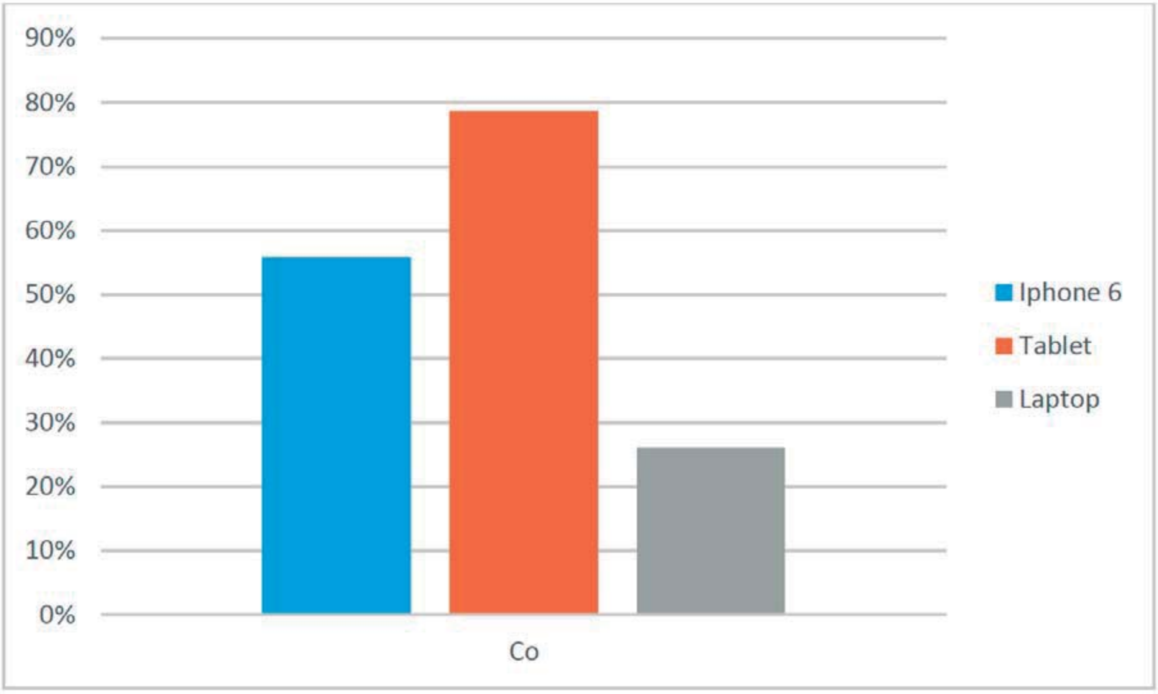
Following the methodology explained before, thermodynamic rarity will be used to identify which devices of those studied in this paper have a higher impact in terms of raw material depletion. To proceed with the evaluation, an extended literature review has been performed to determine the material composition of each product. Table 2 shows the material composition for tablets, LEDs, smartphones and laptops, information has been compiled and compared using several reports and papers.

Figure 1 Contribution in weight (g) and exergy (kJ) for different elements present in a laptop (see online version for colours)



To better understand why this methodology based on thermodynamics has been applied, Figure 1 shows the contribution, in percentage, for some elements present in laptops both in grams (mass terms) and in kJ (rarity). As it can be seen, the contribution of copper in weight is higher than 7% while in rarity decreases until 3%. This becomes even more evident with the case of cobalt. Cobalt represents only 1.5% in weight, but when this value is transferred into rarity, it represents 25% of the total. Therefore, its rarity is higher when compared to other abundant elements, such as iron for instance. This can be explained due to the scarcity of cobalt in the crust, consequently, its ERC is higher.

Figure 2 Rarity share of cobalt in three different devices (iPhone 6, tablet and laptop) (see online version for colours)



We can also compare the amount of cobalt that each one of these devices contains in terms of thermodynamic rarity (Figure 2). Cobalt is an element widely used in batteries and not surprisingly it is considered strategic or critical for different regions, such as Europe or the USA. In the case of the devices analysed, the iPhone 6, tablet and the laptop, cobalt rarity represents 56%, 79% and 29%, respectively, of the total thermodynamic rarity, as it is a key metal in the batteries. The demand of these products will increase the following years but also in electric vehicles, where cobalt demand is expected to grow exponentially, as vehicle batteries are composed by more than 65% of this metal and therefore can be considered a strategic element for the vehicle sector (Iglesias-Émbil et al., 2020; Ortego et al., 2020). On the recycling side, total recovery rates for cobalt in e-waste are currently around 30%, which cannot cover this increase in demand. Still, with existing technology, it could be possible to recycle up to 95% (World Economic Forum, 2019).

As shown in Table 3, a laptop presents the highest thermodynamic rarity value among all the devices analysed. This is a consequence of the number of materials included in it, as its size is much larger than the rest of the devices and therefore it needs more elements. In a general way, it can be said that the more electronic components in a device, the higher its thermodynamic rarity, as every component contains small quantities of minor but very valuable metals.

Table 3 Thermodynamic rarity of the metals in different electric and electronic equipment [kJ][1]

Element	*Iphone 6*	*Tablet*	*Laptop*	*LED bulb*
Ag		194.8	8,222	31.7
Al	21,228	317.8	349,035	11,925
As	4.3	9.6		
Au	9,286	9,816	238,790	2,825
Bi	10.9			
Cd		1.3		
Ce			0.05	0.04
Co	72,556	139,553	715,658	
Cr	202	3.1		
Cu	2,731	1,937	94,083	808.3
Eu			0.00	
Fe	593.9	73.9		40.9
Ga	7,548			6,967
Gd			0.04	
Ge				
Hg		2.9		
In		6,623	14,556	
K	219.9			
Kr				
La			0.04	
Li	851.1	4,340		
Lr				
Mg	378.9	163.9		
Mn	21.2	1,048		
Mo	21.1			
Nd			710.3	
Ni	2,384	10,871	867.7	648.5
P	0.16			
Pb	1.6	22.3	248.9	0.00
Pd		956.7	478,335	
Pr			235.8	
Pt			19,133	
Sb		34.4		
Si	630.4			
Sn	298.9	414.7	4,212	909.5

Note: [1]It must be noticed that not all elements have been included due to the small amount included in the devices and the lack of information of those elements.

Table 3 Thermodynamic rarity of the metals in different electric and electronic equipment [kJ][1] (continued)

Element	*Iphone 6*	*Tablet*	*Laptop*	*LED bulb*
Ta	9,718		826,062	
Te			113	
Ti	79.9	50.2		3.2
V	62.9			
W	160.5			
Y			2.4	
Zn	1,161	1,032	168.3	
TOTAL	130,153	177,469	2,750,437	24,159

Note: [1]It must be noticed that not all elements have been included due to the small amount included in the devices and the lack of information of those elements.

It should be stated that all the numbers included in this paper are calculated for a single device. A different situation could be observed if these calculations were carried out considering all the sales of each device (mobile phone, tablet, laptop) sold in a given year.

2.3 Lifespan: average lifetime and lifetime usage

In addition to the material contents of WEEE, an important parameter to be considered when promoting CE principles is the average lifetime of devices in the technosphere. Moreover, lifespan is an essential parameter to estimate WEEE generation. It can be considered as a fixed parameter that represents an average value and gives an expectation of the time that an equipment is going to work properly without becoming obsolete. It is a crucial parameter to be analysed when reuse and recycling is considered, as a big number of devices are being thrown away even if they are still functional, just because a new model of device is available on the market. This means that there are many devices ready to be reused but are not because there are no systems that facilitate a proper collection. Moreover, the lifetime parameter is important to avoid incentivising the 'throw away culture', as the main goal is to promote the use of the given product during its whole lifetime.

To determine this parameter, a literature review has been carried out (see Table 4) highlighting the lifetime for the devices assessed in this paper.

Table 4 Average lifetime for some of the analysed devices

	Tablets	*Laptops*	*Smartphones*	*LEDs*[2]
Lifetime	36 months	102 months	21.75 months	54.8 months
Reference	Pires et al. (2017)	RDC-Environnement (2008)	Hira et al. (2018), Maragkos et al. (2013)	LUZFIN (2016)

Note: [2]It is considered that the LED is turning on once and leave it on for the rest of the lifetime.

An alternative system to make the lifetime parameter more accurate is through the application of the Weibull distribution. Weibull distribution function can represent a probability distribution that considers the different lifespans between individual owners and the dynamic nature of product obsolescence. In addition, it has been demonstrated to best fit the lifespan of most products (Wang et al., 2013; Balde et al., 2015, 2017; Parajuly et al., 2017). In fact, this is the formula included in the Commission Implementing Regulation (EU) 2017/699 of 18 April 2017 that establishes a common methodology for the calculation of the weight of EEE placed on the market of each Member State and a common methodology for the calculation of the quantity of WEEE generated by weight in each Member State.

The Weibull distribution is defined by a time varying shape parameter $\alpha(t)$ and a scale parameter $\beta(t)$ as is shown in equation (7):

$$EL^{(p)}(t,n) = \frac{\alpha(t)}{\beta(t)^{\alpha(t)}}(n-t)^{\alpha(t)-1} e^{-\left[(n-t)/\beta(t)^{\alpha(t)}\right]} \tag{7}$$

Due to social and technical factors (Magaline et al., 2014), lifespan can differ between products and countries, so it is a time dependent term in the eco-credit equation. Some countries have this information available through consumer surveys, stock levels and during certain time periods, as well as from sorting and sampling of the waste stream. However, it is difficult to find governments that collect and openly publish this information and when they do so, it is normally out of date.

Lifespan data from France, Italy, Netherlands and Belgium have been obtained using consumer surveys (Wang et al., 2013; Balde et al., 2015; Balde et al., 2017). In the absence of more recent and detailed data, they have been included in the calculations performed in the present paper for tablets and LEDs (Figures 3 and 4). Note that if data were updated later, it could be easily incorporated in the methodology.

Figure 3 Discarding probability for tablets with Weibull distribution (see online version for colours)

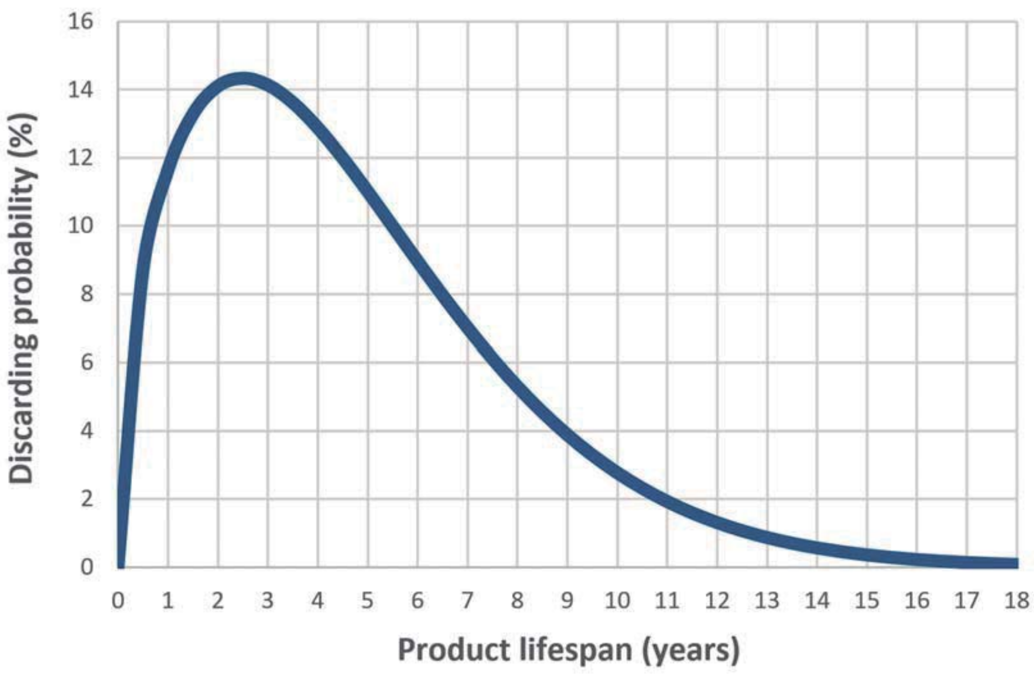
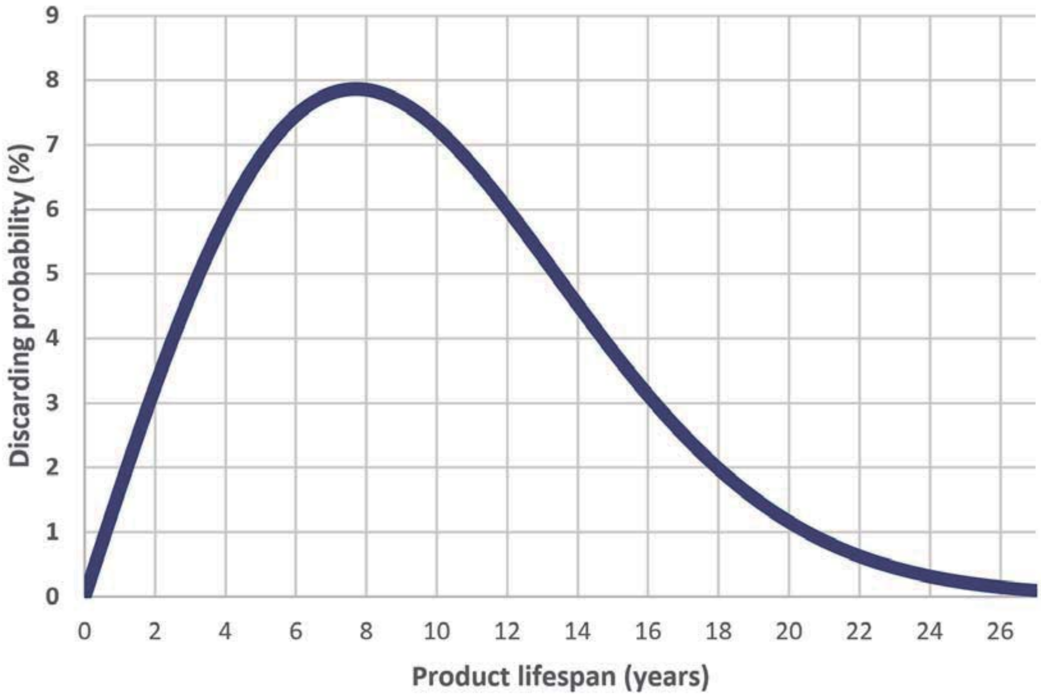


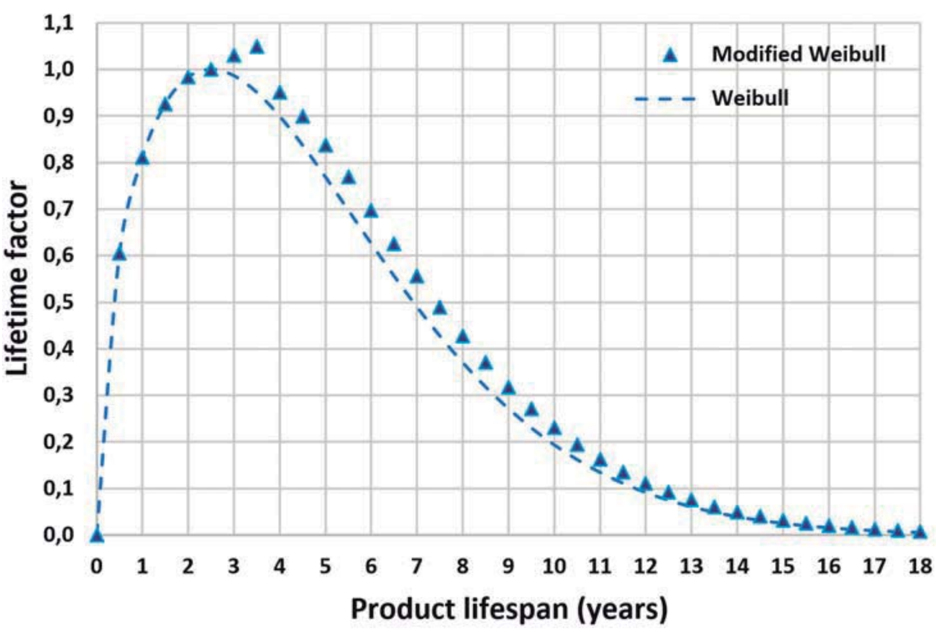
Figure 4 Discarding probability for LEDs with Weibull distribution (see online version for colours)



As it can be observed from Figures 3 and 4, the maximum peak use for tablets is around 3.5 years, then, the function decreases until reaching 17 years. In the case of LEDs, the peak is found at 8.5 years and decreases until reaching 27 years.

In both cases we can observe that the peaks are extended for a long period, the reason behind is that the lifespan reported covers the interval between the purchase and shipment of the new product and the final discard of the device, including both the period of use and hibernation (Wang et al., 2013). Data including only the period of use have not been found in bibliography.

Figure 5 Lifetime factor calculation for the case of a tablet (see online version for colours)



One of the main goals of the collection system is to avoid the storage of WEEE that are no longer used, rewarding its deposition in collection points as soon as possible as its value decreases with its age. On the other hand, CE principles are in line with the extension of the lifetime of products, so less energy and resources are needed. Thus, the aim with the methodology presented in this paper is to incentivise the extension of the lifetime of a product and the fastest deposition once the product is no longer used, avoiding its storage in houses. Still, it is impossible to determine if a five-year-old tablet has been used during its whole lifetime or it has been used during three years and then stored the last two years.

In summary, the lifetime factor of the expression (7) is going to be calculated by means of the Weibull distribution according to the following procedure. First, the Weibull distribution is obtained for the given WEEE. Then, this distribution is normalised between 0 to 1. Last, the normalised value is assimilated to the lifetime factor in the expression (7). This is shown in Figure 5. Note that if the aim is that consumers lengthen as much as possible the use of EEE, the maximum of the Weibull curve could be extended for several years. Thus, a user that extends the lifetime of a tablet or a mobile phone beyond its lifetime during a certain period of time, is not penalised. On the other hand, a user that returns the devices before the expected lifespan is penalised, still, this penalty is less if the return is closer to the expected lifespan. However, this extension cannot be kept forever, as this would be encouraging the stockpiling of non-used equipment, a practice that should be avoided.

3 Eco-credits index

As stated before, society needs to understand the importance of recycling and handling WEEE properly. Knowing the physical value in terms of materials that a given device contains can be the first step to contribute to that purpose. To that end, the idea proposed in this paper is to develop an expression to evaluate WEEE, obtaining as a result the so-called eco-credits, which are granted through a mobile application once a certain device is sent to a specific recycling point.

According to the requirements established in the WEEE directive, the recycling rate should increase yearly in order to achieve the goals set. One of the activities that could improve recycling ratios could be the use of monetary incentives directly given to device users when they actively participate in the recycling process (currently this is already being tested in pilot experiences).

This methodology should be able to evaluate the composition of different devices as all of them contain many critical raw materials. However, the methodology needs to consider the point of view as well of the stakeholders involved in the recycling process. Thus, the equation that is going to be used to calculate the eco-credits, which eventually could be converted into economic benefits or alike, has been developed using thermodynamic rarity (already explained) as well as input from recycling and repairing companies and other stakeholders involved. In order to reach an equilibrium among the different factors, the eco-credit formula includes three terms as shown in equation (8):

$$EcoCredits = A \cdot \sum_{i=1}^{n} a_i rarity_i + B \cdot EoL\ state + C \cdot lifetime\ factor \tag{8}$$

When a device is being analysed, not only the physical value and the materials is evaluated but also other parameters which would identify the device as potentially reusable or not. This way, apart from the physical value, the state of the device is considered (whether it is working or not) as well as its total lifetime (months since the device was bought). Summarising, the expression (8) will consider the following parameters:

- *Rarity:* This first term of the equation provides the physical value related to materials contained in the devices, with the methodology explained in Section 2.1. This is combined with the recyclability of the materials. Unfortunately, not all materials used in the devices can be recycled with current End of Life (EoL) technologies. In order to take this into account, for each raw material included in a device, its rarity needs to be multiplied by a factor that considers its recyclability, α_i, which will be equal to its recyclability ratio whenever it can be recycled (a value that will vary from 0 to 1) The value will be between 0 if it is not recyclable at all and 1 if it can be recycled completely. These values correspond to recycling processes provided by the recycling company and they can be updated in the future if those processes are improved. This way, the eco-credit formula can be also applied using new values, just by changing the given factor.
- *EoL state:* The state of a product is going to determine its reusability. This is included in the second term of equation (7). The EoL state value will only account for three different values: 1 if the device works perfectly, 0.5 if it is not working but can be repaired and 0 if it is not possible to fix the product.
- *Lifetime:* The third term of equation (7) is related to the average lifetime expected for each specific device and the real usage.

Accordingly, when a user takes the device to a WEEE collection point, the device is checked. Several parameters have to be introduced by the user and then verified by a technician: type of WEEE and whether it can be directly reused, repaired or recycled. Then, the aforementioned expression is used to obtain the final number of the so-called eco-credits, which will then appear on the mobile phone of the user through an app. Afterwards, these eco-credits can be exchanged in the form of different incentive schemes.

As it can be observed, in equation (7) the three different terms are preceded by a weighting factor (A, B, C) that give the adequate importance to each term and that can be allocated based on the preferences of the managing entity. The first factor, A, presents values that have from three to four orders of magnitude higher than the second and third term. The second parameter (B) ranges from 1 to 10 due to the values that can present EoL (0 to 1). Setting the exact values for A and B is an arbitrary process and they can be fixed by entities who will provide the incentives associated to eco-credits (depending on their interest in weighting the three terms of the equation) or be set under another criteria. These parameters, A and B, are multiplying terms that do not depend on time so their values will only define the cross with the ordinate axis in a figure where eco-credits against time are represented.

Once A, B and C are set for a reference device, any other equipment will be related to it. In this study, the tablet has been chosen the reference to normalise any other EEE. The normalisation factor is linked to the rarity parameter, which arguably is the most prominent factor indicating the value of the device. In order to calculate these parameters for another device, such as a LED, the values A, B and C are multiplied by a factor that accounts for the ratio between the rarity of the given device and that of the reference (the tablet) as shown in equation (9).

$$\frac{Rarity\ LED}{Rarity\ Tablet} = \frac{25{,}144}{184{,}807} \approx \frac{1}{7} \tag{9}$$

Accordingly, A, B and C for the LED bulb will be multiplied by 1/7 as shown in Table 5. This same methodology can be applied to all devices after a rarity assessment.

Table 5 A, B, C factors for tablets and LEDs

	Tablet	*LED*
A	10^{-4}	$10^{-4}/7 = 1.43 \times 10^{-5}$
B	10	10/7 = 1.43
C	15	15/7 = 2.14

It should be stated that other studies have been carried out trying to evaluate the environmental burden of WEEE proposing a resource efficiency index (Kitajima et al., 2015). In their expression, the concept of ‘total material requirement’ (TMR) is used, defined as the total amount of crude metals, ores, soils, removed surface soils, etc. needed to obtain a unit amount of refined metals. A large TMR value means that a huge amount of ore has to be extracted from earth’s environment to get the material. However, in the expression proposed in this paper two other parameters have been considered apart from rarity: state and lifetime of the device (Kitajima et al., 2015) to obtain the resource efficiency index.

Another study where the methodology applied can be compared to the present paper can be found in Szargut and Stanek (2008). This study proposed to replace the value added tax (VAT) with a new one based on the composition of the device and the cumulative consumption of non-renewable exergy. The VAT suggested is based on an equation developed through the extraction of the minerals and fuel, being the VAT depending on the impact to the environment of manufacturing each device.

Once we know how we can estimate the eco-credits corresponding to each device with equation (7), in the next section two case studies are going to be developed, first a tablet and then a LED bulb.

4 Case study: eco-credit calculation

4.1 Tablet

Around 11 million tablets are sold each year and as there are different manufacturers and several formats and sizes of tablets, in this study we have used an average composition for a 10.1’ tablet that can be seen in Table 2 (in g) and in Table 3 (in kJ).

To obtain the eco-credits, equation (7) is applied. For the first term of the equation, and according to the composition provided in Table 2, the thermodynamic rarity corresponding to the metals of our average tablet accounts for 177 MJ. Additionally, plastic components and glass from screen account for a representative mass share (22.5 g of PMMA, 165 g of plastics, considered as ABS and 62.02 g of silicon) that needs to be additionally included in the rarity calculation. The rarity value for silicon is 1.4 kJ/g (Valero and Valero, 2014). For PMMA and ABS thermodynamic rarity can be considered equal to their corresponding HHV, 26.75 kJ/g and 39.84 kJ/g, respectively (Walters et al., 2000). Considering those data, the final thermodynamic rarity value for an average tablet is equal to 184 MJ.

From the perspective of reuse, if the user provides to the recyclers a working or a reparable tablet, it would entail avoiding the extraction of raw materials and the manufacturing process needed to build a new one so the rarity for a working and reparable tablet will be equivalent to 185 MJ, since all the metals are being reused.

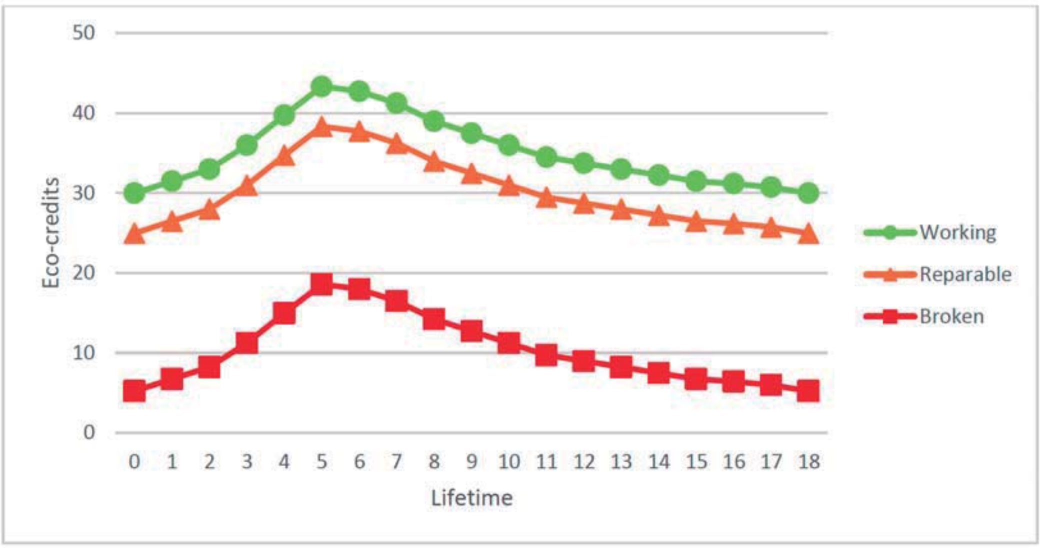
From the perspective of recycling, if the user provides a device that is neither working nor reparable, the only possibility left is to recycle its components. According to a WEEE recycling company in Spain, only PMMA (100% recyclability), plastics (95% recyclability) and some metals (aluminium 85%, iron, 100% and copper 100%) can be recycled. For these materials, a recyclability value of 1, 0.95, 0.85, 1 and 1 are respectively assigned for a_i. Additionally, palladium, platinum, gold and silver could be extracted together (even if mixed) so a value of 0.5 is assigned for a_i. The rest of the raw materials are considered as non-recyclable so their a_i value is 0.

Summarising and according to these estimations, the first term of the equation (7) will be equal to 185 MJ when the tablet is working or reparable and 37 MJ whenever the tablet is not reusable. For the second term, as explained before, the EoL state will be equal to 1 if the tablet is reusable, 0.5 if it is reparable and 0 if it cannot be fixed. Finally, for the third term, depending on the lifetime of the tablet, the values shown in Table 6 will be assigned.

Table 6 Normalising process for lifetime factor for tablets

Time (years)	*0*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Factor	0.1	0.2	0.3	0.5	0.75	0.99	0.95	0.85	0.7	0.6
Time (years)	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	
Factor	0.5	0.4	0.35	0.3	0.25	0.2	0.18	0.15	0.1	

Figure 6 Eco-credit evaluation for tablets (see online version for colours)



Finally, Figure 6 shows a case study of the eco-credits granted to a user that sends his/her old tablet to a proper recycling point, depending on the average lifetime and EoL state. In the case study, the following values have been assumed: $A = 10^{-4}$, $B= 10$ and $C = 15$. This way the rarity term can have a similar weight in the equation than the rest of the terms of the equation.

As it can be seen, a working or reparable device provides comparatively a higher number of eco-credits than a broken one, therefore, the EoL state has a very high importance in this case study.

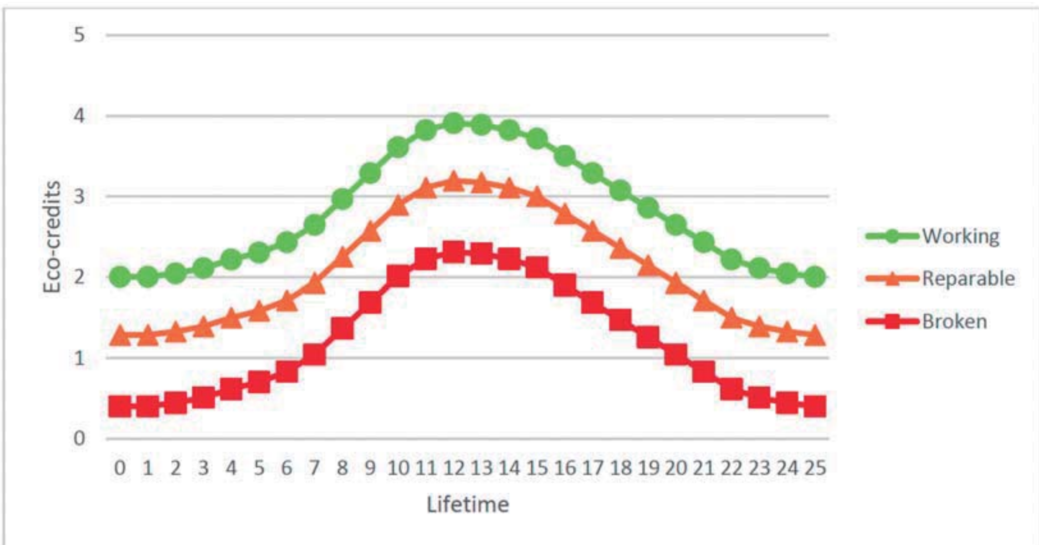
Accordingly, in this example the maximum number of eco-credits that can be obtained is 43 for a working tablet after 5 years of use. This value is reduced when the tablet is sent to the collection point before the average lifespan (penalising the throw-away culture) or after the average lifespan (penalising stock piling). On the other hand, the minimum eco-credits that is possible to earn is 5, corresponding to a broken tablet in the first year of its life or to a tablet after 18 years of its purchase.

4.2 LEDs

The second case study corresponds to a LED bulb, specifically, a 10.5 W LED bulb of 71g has been chosen (Panasonic, 2020). All the metals included in the bulb, which are summarised in Table 2 and Table 3, account for 23g while the rest is composed by polycarbonate, polyester and polyamide. However, when these values are converted into exergy it is possible to see how aluminium represents the highest share, corresponding to almost 50% of the entire bulb.

The total rarity value is 25 MJ for a working or reparable LED bulb and 13 MJ for a broken LED bulb. The same recycling values as before have been used to calculate the material that is possible to recover from each device. For the second term of equation (7), as before, 1 corresponds to a working device, 0.5 if the device is reparable or 0 when the device cannot be used nor repaired. Manufacturers estimate a lifetime for LED of 25 years (with a use of 3h per day). Still, not all bulbs are used this long and the average lifetime is between 12 and 14 years.

Figure 7 Eco-credit evaluation for LEDs (see online version for colours)



Then, these numbers must be multiplied by a normalising factor in order to provide the correct weighting of each parameter in the equation. For that reason, and as was explained through equation (9), A, B and C have been recalculated obtaining the parameters shown in Table 5.

Figure 7 summarises the results obtained. As it can be seen, the maximum eco-credits that are possible to obtain is 3.9, 12 years after buying the bulb and if it is still working. On the other hand, the minimum eco-credits that are possible to obtain is 0.4 for a broken bulb that is disposed of the same year that it was bought or for a broken bulb that is recycled after 25 years of use (the lifetime stated by the manufacturer).

The main difference between tablets and LED bulbs is mainly related to their end of life. A tablet is more likely to be stockpiled due to obsolescence after a new device with more and updated features is bought. Whereas for LED bulbs, they are usually replaced when they stop working or if they break, therefore, the most likely scenario is that the consumer only gets 0.5 ecocredits for a broken LED.

It must be stated that the extension of the lifetime of the tablet or LED bulb (or any other device for that matter) is being encouraged in order to avoid buying a new one when the old one is still working. This approach penalises very early and very late returns, therefore encouraging people to use their devices longer than the expected lifespan and avoiding stockpiling. For that reason, the maximum amount of eco-credits can be obtained not during the average lifespan of each device, but a few years later.

5 Conclusions

This paper has shown how the exergy analysis through an indicator called thermodynamic rarity can help offering relevant information to users regarding the materials contained in the devices that are being thrown away when they get to their EoL. With thermodynamic rarity we can better assess the relevance of each element that is included in the composition of the devices rather than using mass or price as a yardstick.

The need of the recyclability and reusability is becoming more important with each passing year as the sales of electric and electronic devices such as mobile phones, tablets or LED bulbs are growing progressively year after year as well as the amount of electronic waste associated. Minerals, from where the elements that make up those devices come from, are not infinite but their use in society is increasing exponentially. The demand of some elements, especially for some labelled as critical, could be higher than the primary production in the nearby future. Ideally, that difference could be covered with recycling and reusing, but first, the user must be aware that electric and electronic equipment must be properly recycled. For this reason, an index or a numeraire must be developed so that the end-user can easily understand it and make use of it.

This problem has been assessed in this paper with the implementation of an index to calculate the so-called eco-credits. In addition to the thermodynamic rarity, that considers the composition of each device, this index incorporates two other parameters that consider the state of the device (i.e. whether it is reusable, reparable or just recyclable) and its lifetime. Such index could be implemented in a platform or app through a pilot plant especially devoted for the recycling of tablets and LEDs. This way, end users can obtain eco-credits in exchange for properly recycling their devices which in turn could be exchanged for different incentives.

To better understand how the eco-credits are calculated, two examples have been carried out, one for tablets and another one for LED bulbs. CE aims at recovering all the metals whenever is possible to reuse them for new devices or new applications, and this is encouraged in our methodology. Additionally, an extension of the lifetime is also encouraged, avoiding the consumer culture established in our society.

The final goal of this work is to raise awareness in society concerning the huge impacts caused by the spiralling consumption and non-recycling of technological gadgets that contain valuable and scarce raw materials. If such devices are thrown away, stocked ad infinitum at home or end up in landfills, all such materials become lost or unavailable. The result is that more raw materials need to be extracted from the crust, depleting the deposits and polluting the environment.

In addition to this preliminary study, further research must be carried out in order to evaluate the environmental impact of the processes; comparing the environmental impacts associated with the extraction of minerals from mines and with recycling. With those studies and more information analysed and gathered, identifying the problems derived from WEEE would be easier and therefore, better solutions could come up in order to avoid depletion, contamination or stockpiling issues.

Creating eco-credit systems would also help to create awareness in end users, even if it is by using economic incentives or alike that benefit them directly to partially solve this problem. On the other hand, government and councils also have an important and huge job to do towards a more sustainable society. Laws must be created to facilitate the transition and to avoid the vast amount of WEEE that is being created every day. Additionally, an increase of motivation and interest must be shown (i.e. providing real data to help further investigation, more actions against this behaviour, etc.) to determine which is the real problem, how to face it and solve it as soon as possible. The method developed in this paper could be a first step in raising awareness about the problem, which is ahead and must be solved.

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