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Beyond a tonnage perspective for the assessment of mineral reources. Focus on Latin America and the Caribbean

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Tesis Doctoral

BEYOND A TONNAGE PERSPECTIVE FOR THE ASSESSMENT OF MINERAL REOURCES. FOCUS ON LATIN AMERICA AND THE CARIBBEAN

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Beyond a tonnage perspective for the assessment of mineral resources. Focus on Latin America and the Caribbean

José Luis Palacios Encalada

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II. Palacios, J., Abadias, A., Valero, A., Valero, A., & Reuter, M. A. (2019). Producing metals from common rocks : The case of gold. Resources, Conservation & Recycling, 148(February), 23–35. https://doi.org/10.1016/j.resconrec.2019.04.026

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- Palacios, J.-L., Calvo, G., Valero, A., Valero, A., & Ortego, A. (2018). El rol de la minería de América Latina en una sociedad descarbonizada. Papeles, 143, 109–117. Retrieved from http://www.revistapapeles.es/archivo.aspx
- Palacios, J., Calvo, G., Valero, A., & Valero, A. (2019). Valorando los Recursos Minerales de América Latina Appraising the mineral resources in Latin America GEO Latitud. Geolatitud, 2, 56–62.

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con como co-autor en la siguiente publicación:

• Valero, Al. Valero, A. Calvo, G. Ortego. A, Ascaso. S, **Palacios**, J. Global material requirements for the energy transition. An exergy flow analysis. *Energy*. September 2018. https://doi.org/10.1016/j.energy.2018.06.149

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The present doctoral thesis is made up of a compendium of research works, previously published

in scientific journals. Below are the bibliographical references that form the thesis:

I. Palacios, J.-L., Fernandes, I., Abadias, A., Valero, A., Valero, A., & Reuter, M. A. (2019). Avoided energy cost of producing minerals: The case of iron ore. Energy Reports, 5, 364–374. https://doi.org/10.1016/J.EGYR.2019.03.004

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Impact Factor: The international conference ECOS has a great reputation in the field of Thermodynamics and is carried out for more than 30 consecutive years.

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- Palacios, J.-L., Calvo, G., Valero, A., Valero, A., & Ortego, A. (2018). El rol de la minería de América Latina en una sociedad descarbonizada. Papeles, 143, 109–117. Retrieved from http://www.revistapapeles.es/archivo.aspx
- Palacios, J., Calvo, G., Valero, A., & Valero, A. (2019). Valorando los Recursos Minerales de América Latina Appraising the mineral resources in Latin America GEO Latitud. Geolatitud, 2, 56–62.

In addition, throughout the research process conducted during the doctorate, has been contributed as coauthor in the following publication:

• Valero, Al. Valero, A. Calvo, G. Ortego. A, Ascaso. S, **Palacios**, J. Global material requirements for the energy transition. An exergy flow analysis. *Energy*. September 2018. https://doi.org/10.1016/j.energy.2018.06.149

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"Quienes pueden, pueden porque piensan que pueden" Virgilio

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"Those who can, can because they think they can." Virgilio A Sofia Tu vida ha sido una fuente de inspiración durante esta ventura

To Sofia Your life has been a source of inspiration during this journey

Resumen

Los minerales son esenciales para mantener el estilo de vida de la sociedad moderna. En los tiempos actuales se emplean casi todos los elementos de la tabla periódica en la fabricación de dispositivos y aparatos eléctricos y electrónicos.

Mientras el consumo de los minerales va en aumento, también se produce un rápido aumento la pérdida de capital mineral en los países y regiones donde se producen. Al mismo tiempo, los depósitos geológicos con altas leyes de mina han sido ya explotados, y el consumo energético para la producción de metales se ha incrementado.

La preocupación sobre la importancia y el agotamiento de los recursos minerales desde hace mucho tiempo ha llamado la atención de los investigadores. Se han establecido algunas formas para valorar los recursos minerales con sus respectivas ventajas y desventajas. En el presente trabajo, en función de la revisión bibliográfica estos métodos han sido clasificados en tres categorías: por el peso, por el precio comercial y según metodologías fundamentadas en principios energéticos. El método más común de evaluar los recursos minerales ha sido probablemente según el precio. El mismo que no revela el valor de los mismos, además los precios son volátiles debido a que se encuentran sujetos a varios factores como por ejemplo, oferta-demanda, aspectos geopolíticos y especulación, entre otros. Aunque la valoración de los minerales según su peso, ha tenido un amplio desarrollo y han permitido realizar estimaciones importantes, especialmente mediante metodologías de Análisis de Flujo de Materiales (MFA por sus siglas en Inglés) y su variante EW-MFA. Entre las desventajas de estos métodos se encuentran que según esta perspectiva una tonelada de hierro es igual a una tonelada de oro, sin embargo no se toma en cuenta la escasez geológica del oro, ni el mayor requerimiento energético para su procesamiento. Una alternativa para una evaluación más adecuada de los recursos de los minerales se fundamenta en leyes energéticas. Particularmente se destacan las metodologías fundamentadas en la Segunda Ley de la Termodinámica, Exergía, que toman en cuenta no solo la cantidad, sino también la calidad de los recursos. Con base en aquello, la una división de Exergoecología plantea la evaluación de los recursos no solo en cuenta tomando en cuenta la exergía química, sino también la exergía de los recursos minerales respecto a su concentración. En tal sentido se ha establecido el concepto del costo exergético de reposición (ERC por sus siglas en Inglés). El mismo que estima la energía necesaria para concentrar los minerales desde un estado de dispersión, denominado Thanatia. La metodología de cálculo para el ERC para distintos metales, se fundamenta en análisis estadístico de información del consumo de energía para el procesamiento de metales en función de la ley de mina y extrapolaciones. Aunque los valores reportados de ERC han sido importantes para estimar la pérdida de capital mineral, estos fallan, por su método de cálculo en una estimación más precisa de los recursos minerales. En tal sentido, se hace necesario una nueva metodología de cálculo de ERC tomando en cuenta criterios de procesamiento de minerales y sus tecnologías actuales. Por tanto, en la presente tesis doctoral se establece una metodología estimar valores más precisos de los ERC en función del análisis de los procesos minero-metalúrgicos para la concentración de minerales. Esto mediante de modelos computacionales realizados a partir de un reconocido paquete informático HSC.

En función de disponibilidad de información y de los requerimientos de metales para nuevas tecnologías se han escogido tres metales claves producidos en América Latina y El Caribe. Estos metales son el hierro, cobre y oro. Para estos tres metales se determinan los nuevos valores de ERC a partir de HSC y se realiza una comparación con los valores anteriores. Aunque a nivel cualitativo la importancia de los metales es la misma respecto a los valores anteriores y nuevos de ERC, su diferencia es en órdenes de magnitud. También se enfatiza en la búsqueda de mecanismos sostenibles para la producción de metales, así como en el reciclaje. Finalmente, se revela la importancia de continuar con la elaboración de más modelos en HSC para estimar valores más precisos de ERC para el resto de minerales.

Abstract

Minerals are essential to maintain the lifestyle of modern society. Currently, almost all the elements of the periodic table are used in the manufacture of electrical and electronic devices While the consumption of minerals is increasing, there is also a rapid increase in the loss of mineral capital of the countries and regions where they metals are produced. At the same time, geological deposits with higher ore-grades have already been already exhausted, and the energy consumption for metal production has also increased.

The concern about the importance and depletion of non-fuel mineral resources have long attracted the attention of researchers, who have established some methodologies for the assessment of mineral resources. These methodologies have their respective advantages and disadvantages. In the present work, based on the literature review, these methods have been classified into three categories: by weight, by wholesale price and methodologies based on energy principles.

The most common method for valuing non-fuel mineral resources has probably been according to price. This method does not reveal the real value of minerals, in addition prices are volatile because they are subject to several factors such as supply and demand, geopolitical aspects and speculation, among others. Although the assessment of non-fuel minerals according to their weight, has had a comprehensive development and have allowed realizing important estimations, primarily through methodologies of Material Flow Analysis (MFA) and its variant EW-MFA. Among the disadvantages of these methods are that according to this perspective a ton of iron is equal to one ton of gold. However, the geological shortage of gold or the higher energy requirement for processing is not taken into account. An alternative for an adequate evaluation of mineral resources is based on energy laws. Particularly noteworthy are the methodologies based on the Second Law of Thermodynamics, Exergy. The latter takes into account not only the quantity but also the quality of the resources. Based on that, a division of Exergoecology proposes the evaluation of non-fuel minerals not only taking into account the chemical exergy, but also the exergy of mineral resources concerning their concentration. In this regard, the concept of exergy replacement cost (ERC) has been established. ERC estimates the energy needed to concentrate minerals from a state of dispersion, coined as Thanatia. The calculation methodology for the ERC for different metals has been based on a statistical analysis of energy consumption information for metal processing and extrapolations. Although the reported values of ERC have been influential in estimating the loss of mineral wealth, they fail, because of their method of calculation in a more accurate estimation of valuing mineral resources. In this regard, a new methodology for calculating ERC is necessary, which takes into account mineral processing criteria and current technologies. Therefore, in the present doctoral thesis, a method is established

to estimate more precise values of the ERC in the function of the analysis of the miningmetallurgical processes for the concentration of minerals. This has been done through computer models made from a well-known computer software HSC. Based on the availability of information and the requirements of metals for new technologies, three key metals produced in Latin America and the Caribbean have been selected. These metals are iron, copper, and gold. For these three metals, the new ERC values are determined from HSC and a comparison is made with the previous values. Although at a qualitative level the importance of metals is the same concerning the last and new values of ERC, their difference is in orders of magnitude. Emphasis is also placed on the search for sustainable mechanisms for the production of metals, as well as recycling. Finally, it is revealed the importance of continuing with the elaboration of more models in HSC to estimate more precise values of ERC for the rest of the minerals.

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Nomenclature

b_{chi}	standard chemical exergy of the elements $n_{j,i}$ (kJ/kg)					
$\Delta G_{f,i}$	Gibbs free energy (kJ/kg)					
b_{ti}	total exergy of non-fuel minerals (kJ/kg)					
b_{ci}	concentration exergy (kJ/kg)					
R	gas constant (8.314 J/molK)					
To	absolute reference temperature (298.15 K)					
χ_m	concentration in the mines measured (g/g)					
χ_c	concentration in the Earth's crust (g/g)					
χ_r	concentration at the refining stage (g/g)					
Δ bc	exergy to the concentration of minerals from a dispersed state (kJ/kg)					
B^*	exergy replacement costs (GJ/t)					
k	dimensionless constant called unit exergy cost (-)					
$E\left(x_m \to x_r\right)$	real cumulative exergy required to accomplish the process of concentrating the mineral from the ore grade x_m to the commercial grade x_r (GJ/t)					
$\Delta b_c(x_m \to x_r)$	minimum thermodynamic exergy required from x_m to x_r (GJ/t)					
А	coefficient determined for each mineral from the energy as a function of ore-grade (-)					
W	specific energy consumption of the mill (kWh/t)					
W_i	work index "Bond index" (kWh/t)					
P80	80% passing sizes of the product (μm)					
F80	80% passing sizes of the feed (μm)					
EFx	Rowland efficiency factors					
Т	throughput tonnage (t/h)					
Rr	total reduction ratio (-)					
kf	fast kinetics constants (-)					

Abbreviations

AG	Autogenous mill
AP	Acidification potential
ASGM	Artisanal and Small-scale Gold Mining

CEPAL	Economic Commission for Latin America and the Caribbean
CIRCE	Research Centre for Energy Resources and Consumption
CL	Cleaner
COP21	21st Conference of the Parties, 2015 United Nations Climate Change Conference
DE	Domestic Extraction
DMC	Domestic Material Consumption
E	Exports
ECLAC	Economic Commission for Latin America and the Caribbean
EP	Eutrophication potential
ERC	Exergy replacement cost
EU-28	European Union
EW-MFA	Economy Wide Material Flow Accounts
GDP	Gross Domestic Product
GDP	Gross Domestic Product
GWP	Global warming potential
HDI	Human Development Index
HHV	High Heating Value
HIF	Helmholtz Institute Freiberg for Resource Technology
HIG	High-intensity grinding mill
Ι	Imports
IEA	International Energy Agency
LA&C	Latin America and the Caribbean
LA-20	Latin America and the Caribbean
LBP	Lower Boundary Price
LCA	Life Cycle Assessment
LIMS	Low Magnetic Intensity Separators
LME	London Metal Exchange
LME	London Metal Exchange
LMW	Loss of Mineral Wealth
MCI	Mining Contribution Index
MFA	Material Flow Analysis
MFA	Material Flow Analysis
MIPS	Material Input per Unit of Service
OCMAL	Observatoty for Mining Conflicts of Latin America
OLADE	Latin American Organization of Energy

PGM	Platinum group metals
POCP	Photochemical ozone creation potential
RE	Reference environment
REE	Rare earth elements
RG	Rougher
SAG	semi-autogenous mill
Sca	Scavenger
SEEA	System of Environmental-Economic Accounts
SFA	Substance Flow Analysis
SLon	High Intensity and Gradient Magnetic Separators
SNA	System of National Accounts
TEC	Thermo-Ecological Cost
TheRy	Thermodynamic rarity
UBP	Upper Boundary Price
UNEP	United Nations Environmental Programme
USGS	the US Geological Survey
WEC	World Energy Council

Chapter 1. Introduction

1.1. Objectives

The general objective of this Thesis is to improve the exergoecology method for the proper evaluation of mineral resources and apply it to assess the loss of natural stock because of mineral production in Latin America and the Caribbean.

Specifically, the thesis has the following goals:

- To study methods currently used for the evaluation of mineral resources and establish their pros and cons.
- To examine the exergoecology method and the concept of the exergy replacement cost (ERC) as an alternative to estimate the physical quality of minerals.
- To analyze the method of calculation of the ERC and determine its strengths and weaknesses.
- To define a new way for a more accurate procedure to estimate the ERC
- To compare new and previous values of ERC and analyze their differences or similarities
- To apply the methodology for the quantitative assessment of the loss of natural stock in Latin America and the Caribbean

1.2. Thesis Structure

This Thesis is presented as a compendium of six scientific publications. These works have followed a research line on the evaluation of mineral resources based on their physical quality from a Second Law of Thermodynamics perspective.

The Thesis effectively begins in **Chapter 2** by pointing out the importance of minerals for keeping today's lifestyle. Particularly, the urgent need for green technologies to be developed as an alternative for the decarbonization of the atmosphere to mitigate climate change is discussed. The requirements of minerals for the production of these technologies are then described in the chapter. In this sense, the role of Latin America and the Caribbean in a globalized commodity market is highlighted.

Because of the need for minerals, the evaluation of mineral resources has gained importance in the last years. Therefore, in **Chapter 3**, the methods used for this endeavor are presented along with their drawbacks for an accurate assessment. The chapter shows that arguably, the evaluation of minerals is more appropriate when considering their physical quality since aspects of their geochemical scarcity are deeply considered. The concept of the exergy replacement cost (ERC) and, thermodynamic rarity (TheRy), are explained. The ERC was defined as the energy required to concentrate minerals from a state of total mineral dispersion, coined as Thanatia. The TheRy was conceptualized as the energy for producing metals from Thanatia. Both, ERC and TheRy were previously estimated based only on empirical and historical data. Although these values were useful to roughly determine the loss of mineral wealth of nations, they were inaccurate because of their procedure of estimation.

Due to the weak points detected in the methodology for the determination of the ERC an upgrade is required. **Chapter 4** presents a new approach for this task with the use of mineral processing knowledge in conjunction with a specialized and well-proven software HSC. Three representative minerals produced in Latin America and the Caribbean were identified, iron, copper and gold. They were modeled in HSC to show the potentialities of this new approach for upgrading the methodology of ERC. The computational models are described in detail in chapter 5, 6 and 7. For the models,

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Thanatia, was considered as the rock from which minerals will be concentrated. Accordingly, **Chapter 5** deals with the model for the concentration of iron-ore, while the concentration of copper-ore and gold are presented in **Chapter 6** and **Chapter 7**, respectively. The research of **Chapter 5** is derived from **Paper I. Chapter 6** and **7** are based on **Paper II** and **Paper III**.

The structure of the mentioned three papers is similar; they start by introducing the importance of the minerals, and then the computational models developed in HSC are explained, followed by the results and conclusions. **Chapters 5, 6,** and **7**, specifically focus on the new values of ERC obtained as well as the main assumptions they are based on. The new values are compared with the previous ERC.

Having the model set for the concentration of minerals from very low ore grades, it is straightforward to analyze a key aspect in mineral production: energy increase as a function of ore grade decline. Many scholars have carefully studied the issue of ore grade decline, yet its effect over the energy for metal production has been analyzed only through analytical procedures and simulations from an environmental perspective (LCA software). **Chapter 8** fills this gap, and the correlation between ore-grade decline on the specific energy for metal production has been analyzed by considering mineral processing criteria with a model in HSC. For this endeavor, the methodology presented in **Chapter 8** can be found in **Paper VI**.

From the models developed in the previous chapters, the need to value more appropriately the current mineral capital is undoubtedly revealed. Therefore, the evaluation of the loss of mineral stock in countries where minerals are extracted is vital. With this in mind, **Chapter 9** applies the knowledge of the ERC to determine the routes of mineral exports in twenty countries in Latin America and the Caribbean. The analysis in this chapter is due to the research applied in **Paper IV**. Then, in the chapter the methodology used to quantitatively determine the loss of mineral stock in Latin America and the Caribbean (involved in **Paper V**) is shown. Results of this chapter call to action towards the establishment of a fairer scheme of prices for mineral commodities to compensate for the loss of natural stock.

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Finally, **Chapter 10** summarizes the main contributions of the Thesis and presents perspectives for future research. The chapter is also written in Spanish according to the requirements of the University of Zaragoza.

Chapter 2. Demand and supply of metals

2.1. Introduction to the chapter

To provide a valid framework for the current work, this chapter presents the importance of metals to achieve targets for the reduction of carbon emissions into the atmosphere. The significance of Latin America and the Caribbean because of its reserves and production of non-fuel minerals at the global level is also portrayed. The production of metals in accompanied by social and environmental effects in the region.

2.2. Climate change and metal increasing

The 21st United Nations Framework Convention on Climate Change (COP21) took place in Paris at the end of 2015. The so-called Paris Agreements established a global framework against climate change to be adopted in 2020. Particular interest was given to a transition towards a low-carbon economy. One of the main results of Paris Agreements was agreed to hold the increase in the global average temperature to well below 2°C above pre-industrial levels [1].

Institutions such as the International Energy Agency (IEA) [2], the World Energy Council (WEC) [3] and Greenpeace [4] have published studies with different energy scenarios until 2050 and a wide variety of alternatives to achieve the targets of COP21. The common feature among these scenarios is the increase in the share of renewable energy technologies (green technologies) for electricity production, including solar panels, windmills, etc. In the transport sector, it is becoming of high importance the replacement of gasoline and diesel engines with electric vehicles and other sustainable transport systems [5].

It should be stressed however, that in all such scenarios, one aspect that is not carefully taken into consideration is the demand for materials that will be required because of the deployment of such technologies. **Figure 1** depicts some representative metals that are necessary for the manufacture of four green technologies. For example, it is estimated that the Toyota Prius, the most famous for the hybrid vehicles requires 1 kg of neodymium, and the batteries need 10-15 kg of lanthanum [6], both considered as rare metals due to their scarcity. The global production of rare earths, neodymium, and lanthanum included, in 2017 was only 130.000 tons. In contrast, copper ore produced in

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the same year was 19 million tons [7]. From **Figure 1**, it is observed that the vast majority of metals will be needed for electric vehicles in contrast to the other green technologies. In this respect, it is estimated that the demand for lithium, a metal essential for the proper operation in batteries of electric and hybrid vehicles, will increase by 300% in 2020 [8].



Figure 1. Some metals used in the manufacture of green technologies. (Published in [9] and based on [10])

2.3. Critical materials

Minerals are so essential in today's modern society that the United Nations summit on Sustainable Development held in Johannesburg in 2002 claimed this fact [11].

Publications of international research groups have addressed the issue of material supply, mainly from a geopolitical and economic perspective that could put at risk the sustainability of some global economies [12]. Besides, there are also studies carried out by organizations and entities such as the European Commission and different geological services from European countries, and the United States on material criticality. One of the most used on a large scale, and widely used as a reference, is that from the European Commission, which already in 2008 began to request reports on the use of different materials to establish a strategy and actions that member states had to carry out in order to guarantee the supply of raw materials [13] for their economies. Subsequently, in 2010, it published a report in which a total of 14 elements were identified as critical for the European Union. The list was expanded in successive reports in 2014 and more recently in 2017 [14]. In this report, a total of 27 minerals were identified as strategic for the

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development of new technologies in the region. Such minerals are also considered strategic because of identified supply risks: their production is concentrated in a few countries, in some cases politically unstable. In this respect, Mexico and Brazil, two of the largest metal producers in Latin America, were considered as key suppliers of niobium and fluorspar to European industries with a share of 71% and 38%, respectively.

The United States, with the National Defense Stockpile program published a report on Strategic and Critical Materials in 2015 [15]. In the report, aluminum oxide and antimony were identified for a shortfall from Latin American countries with Venezuela and Mexico supplying these materials, respectively.

2.4. Latin America and the Caribbean as key metal producers

Certain metals are essential for the correct operation of green technologies, and those minerals cannot be easily replaced by other substituents [16–18]. Some of these metals categorized as critical are produced in Latin American countries. For example, Bolivia, Chile, and Argentina are the leading producers of easily extractable lithium [19–21].

In 2017, Latin America and the Caribbean¹ (LA-20) produced essential metals, such as, from a total global production standpoint, 43% copper, 50% of silver, 21% of tin, 12% of nickel, and 11% of gold [7]. Furthermore, exports of fuels and mining products generated about 277 billion US dollars in 2014; and the reserves of oil, natural gas and coal accounted for 20%, 4%, and 2%, respectively, of the total world's proven reserves [22].

In a publication about material requirements for the energy transition towards a decarbonized society [23], metals such as aluminum, iron, and copper will be essential. Also, the transport sector will be a higher consumer of lithium, cobalt for the production of batteries [23]. LA-20 is currently one of the leading producers of these metals, **Figure 2**.

¹ For the Thesis, twenty countries of Latin America and the Caribbean were considered: Argentina, Bolivia, Brazil, Chile, Colombia, Costa Rica, Cuba, Dominican Republic, Ecuador, El Salvador, Guatemala, Honduras, Mexico, Nicaragua, Panama, Paraguay, Peru, Uruguay and Venezuela

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Figure 2. The share of global reserves and production of metals of Latin America and the Caribbean (based on: [7]).

According to the report of the Economic Commission for Latin America and the Caribbean (ECLAC) [24], in 2016 the share of the mining activity in the region was about 4.7% of the Gross Domestic Product (GDP). One of the ECLAC's reports pointed out that 500 mining projects were announced between 2003 and 2015 with an investment of 150 billion US dollars [25]. Most of these projects are oriented for the production of gold and silver.

Mineral extraction in LA-20 has produced social, geopolitical, and environmental conflicts. Growing concern about the ecological and social effects as a result of mining activities in the region has been pointed out by scholars such as Gudynas [26,27], Martinez-Alier [28], West and Schandl [29] and others. The studies suggest that because of the need of public spending in South American countries and the booming prices of raw materials, the pressure for the exploitation of natural resources increased along with environmental damage [26,27,30]. A publication by Martinez-Alier describes conflicts caused by mining activities in different countries, including some South American countries. The unfair treatment of lawsuits against mining companies between powerful and non-powerful nations was pointed out by the author [28].

In the web page of the Observatory for Mining Conflicts of Latin America (OCMAL), more than 240 conflicts in the region were reported [31], **Figure 3**.

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Figure 3. Conflicts due to mining activities published by the Observatory of Mining Conflicts in Latin America (OCMAL) [31].

Although many books and publications have sharply criticized the equitable share of revenues coming from mining activities and rejected mining itself [32] openly calling it "the curse of natural resources in Latin America," others have developed indicators to intend to measure the benefits of mining [33]. One indicator, named Mining Contribution Index (MCI) considers a variety of variables, such as mineral and metal exports, its impact on the national GDP along with the Human Development Index (HDI). Using MCI, whose values are between 0 and 1, where 0 identifies no benefits and 1 represents positive impacts of mining revenues, a ranking among 214 countries was generated for 2014. The results are then shown as percentages where these countries are quantitatively classified. Based on these data, most of the LA-20 countries had an MCI index above 0.6 and less than 0.8 [33].

Another serious issue in the region is illegal mining. Illegal gold production was estimated at 158 tons that accounted for 6.9 billion US dollars in 2013. Countries with the highest percentages of unlawful gold production were Venezuela, Colombia, and Ecuador with 91%, 80%, and 77%, respectively [34]. Another critical problem, not only in LA-20 but also at a global level, is artisanal mining, which usually does not appear on official mining statistics. Just in 2011, it was estimated that 15 million people around the world were working in the so-called Artisanal and Small-scale Gold Mining (ASGM) [35]. Apart from environmental problems that artisanal mining can produce because of

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the lack of adequate procedures and materials, a severe health hazard is produced by mercury, which is added during the purification of gold in most artisanal mining operations in LA-20 [36]. Although many efforts have been made to promote formalization of miners [37,38] and reports about health hazards of mercury have been published [36–39], the problem persists. Additionally, most of the products extracted from artisanal mining are not reported to official authorities but always end up in the global economy.

Authors, such as Gudynas [26,27], Martinez-Alier [28], West and Schandl [29] and OCMAL have pointed out the conflicts and effects of mining activities in LA-20. Nevertheless, it is required to establish a framework in which mineral resources can be quantitatively estimated, as well as the loss of natural capital.

2.5. Concluding remarks

The study of the current status of the consumption and production of metals and the implications of mining activities in LA-20 has been presented in this chapter. The next remarks aid as supportive arguments to develop this thesis:

- Metals are essential for keeping today's society, and some of them are considered critical for the widespread of green technologies towards a decarbonized society.
- Latin America and the Caribbean (LA-20) play an essential role because of their mineral reserves and production in a globalized context.
- Although the exploitation of mineral resources constitutes an essential source of income in LA-20, the complexity of mining activities in terms of social, geopolitical and environmental aspects has raised a series of conflicts.
- Organizations and research institutions have published reports concerning critical materials, mainly the European Commission and the United States However, from the standpoint of metal-producer countries little in this regard has been done. That is why to promote a deep discussion, the current work focuses on LA-20.
- There is a need on the establishment of schemes with scientific rigor for the appropriate evaluation of mineral resources, with particular attention on producer's countries, such as LA-20 to get a better appraisal of their resources.

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That is why the next chapter focuses on methods for the assessment of mineral resources.

Chapter 3. Assessment of mineral resources

3.1. Introduction to the chapter

As it was raised in the previous chapter, metals are becoming more and more critical for the manufacturing of green technologies. Due to the need for appropriately valuing minerals, this chapter is devoted to describing methods for their assessment. The information presented in this chapter is a summary of the information published by Valero and Valero [40] and Rankin [6]. Accordingly, these methods have been grouped into three categories based on mass, market prices, and energy approaches. The first sections describe two common approaches commonly used: through tonnage (weight), and through market prices, and energy-based approaches. A novel method for this evaluation, along with its advantages in comparison to the previous techniques, is presented.

3.2. Mass-based approach

A common way to evaluate mineral resources has been through their mass (weight). The law of conservation of matter establishes that matter is neither created nor destroyed. This provides the fundamentals for Mass balances and Material Flow Analysis (MFA) [41]. Both methodologies are used to understand the flow of a substance or a product with their accompanying wastes in a limited framework. The latter can be an industry, a country, or region or the whole world [42]. The total inputs are equal to the total outputs plus the bet accumulation, with the appropriate information this is easily done, that is why MFA are widely applied. In **Figure 4** a simplified general balance for a MFA for a country is presented.



Figure 4. Simplified diagram of MFA system for a nation. (adapted from: [41])

Beyond a tonnage perspective for the assessment of mineral resources. Focus on Latin America and the Caribbean As mentioned in [41], MFA has some limitations, such as the no inclusion of the environmental services provided by Nature, for instance, dilution of pollutants, cooling, water cycling, etc. These are provided for free by Nature and are essential at the national level. In this respect, Schmidt-Bleek [43] proposed an indicator named as the Material Input per Unit of Service (MIPS). MIPS measures in kilograms or tons of material input moved to produce a good or service from the cradle to the grave.

The European Commission, through its official database Eurostat in 2007, released the first compilation guidelines for the Economy-Wide Material Flow Accounts (EW-MFA) [44]. The purpose of EW-MFA, as stated by Femia and Paolantoni [45], is "to provide an aggregate overview, in tons, of the material inputs and outputs of an economy, including inputs from the environment, outputs to the environment, and the physical amounts of imports and exports."

A macroeconomic tool that has been agreed internationally is the System of National Accounts (SNA). It considers the distribution of production among different consumers, and businesses, within a national government and other countries. It is similar to a year balance of a private company, and its most well-known outcome is the GDP [46]. To integrate environmental and economic statistics into the national accounts, the United Nations (UN) proposed a similar methodological accounting method as the SNA, named as the System of Environmental-Economic Accounts (SEEA). This holistic decision-making tool integrates the next categories for its accounting: Agriculture, Forestry and Fisheries; Air Emission Accounts; Energy; Environmental Activity Accounts, Ecosystem Accounts, Land Accounts, Material Flow Accounts, and Water [47]. The SEEA provides a common framework, concepts, terms, and definitions. An important contribution of SEEA is the establishment of a universal language in which the categories are expressed, for instance, the standard unit for energy flows is joules, for the accounting of solid waste, wastewater, emissions to water, soil and air, SI units are recommended [40,47].

From the conservation of mass, which is the basis for SEEA and EW-MFA, Nature is seen as a source of natural resources and sink of residues. This fact simplifies the role of Nature and the interactions that occur on it. Notwithstanding, SEEA and EW-MFA

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have their advantages in terms of accountability of nations. SEEA intends to bring Nature into the stage by considering environmental effects. However, from a massperspective point of view, a ton of iron is equal to a ton of gold. But the geochemical scarcity is not even taken into account in this perspective.

In the same way, a small amount of a toxic substance may a have massive impact on the environment, a fact that is not usually considered when the evaluation is carried out in mass terms. Therefore a mass-based approach alone is not appropriate for the assessment of non-fuel mineral resources, in particular, for precious metals like gold, silver, etc. One way to solve these drawbacks has been to link MFA with other physical accounting methodologies [41,48] for instance, energy-based approaches, that will be described in section 3.4.

3.3. Market-price based approach

One alternative to value mineral resources is by the conversion of mass into money through the market price. As pointed out by Stanek et al. [49] probably the market-price is the most widely used for valuing mineral resources.

The SNA and SEEA recommend the Net Present Value (NPV), which brings the net cash inflow-outflow over a period of time. However, there are other methods like the Net Price Method [50,51] and the User Cost Method [52]. In the former method Repetto [50,51] proposed to treat the depletion of non-renewable resources as capital depreciation. It would mean that depletion of Nature will be compensated by revenues for selling minerals. The Net Price Method considers non-renewable resources as the market price, minus the costs of discovery, extraction, and marketing; then it multiplies this quantity by the net yearly extraction. In this method, there is a clear interaction between "the extractor and the market," hence all the intricacies between supply and demand regulated by the market through the price. In order to overcome these scenarios, El-Serafy [52] established the User Cost Method. The author defined the "user cost" as the difference between revenues (R) and income (X). He made a distinction between revenue and income, saying that not all revenues derived from the extraction in any year (R) should be considered as "true income" (X). Accordingly, El-Serafy conceptualized the "true income" as the "sole amount of income that could be sustained indeterminately

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for consumption". In this method, the resource depletion and environmental remediation should be considered into the national accounts by the "user cost".

According to the so-called "Hartwick Rule" the rent for selling non-renewable resources should be invested by nations in infrastructures, knowledge, etc [53] so that this investment is higher than the depletion. When this happens, it is said as a saving. According to Pearce and Atkinson [54], they called it "genuine savings". This conceptualization has been used by the World Bank and has been used extensively by many countries to support economic sustainability [55].

Under these approaches, Nature is not really compensated by the depletion of non-renewable resources. Only human beings understand the concept of money, but not Nature. Besides, as stated by many authors, mineral commodity prices are very volatile [56–58], and factors that influence this volatility can be attributed to stock variations, supply-demand interactions, geopolitics, market speculation, etc. [17,56,59]. To further decipher the volatility in mineral prices from 1960 to 2015, Figure 5 has been split into four groups of minerals. At the upper left (a), the change in the price of gold can be seen. In 2010 its price was 39.5 million US\$/t, and the last reported value was 37.4 million US\$/t in 2015. The most recent peak price for gold occurred in 2012 when its price reached 53.8 million US\$/t. At the upper right corner (b), the historical trend of silver price is shown, its price was 1.13 million US\$/t in 2011, and the last reported price was 0.5 million US\$/t in 2015. Nickel, at the lower left (c), oscillated between 37.2 thousand US\$/t in 2007 and 11.8 thousand US\$/t in 2015. Other minerals produced principally in Latin America can be found in the lower right corner (d). Iron ore-price decreased from 99 US\$/t in 2010 to 81 US\$/t in 2015, with a peak in 2012 of 116 US\$/t. For copper, prices varied from 7.7 thousand US\$/t to 5.7 thousand US\$/t, in 2010 and 2015 respectively, with a peak 2011 of 8.9 thousand US\$/t. Lithium price increased from 3.8 thousand US\$/t in 2011 to 4.5 thousand US\$/t in 2015.

A fairer price of commodities has been claimed as a necessity to tackle the longlasting environmental and societal issues caused by the exploitation of natural resources, not only in Latin America but also in other regions [60–63]. The Fairtrade certification of gold in Latin America and sub-Saharan Africa could have been a better alternative, at

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least to overcome some issues faced by small-scale miners. However, some authors did a more in-depth analysis of this initiative [60–62] and found that more actions were required, beyond a logo of Fairtrade, for better outcomes for miners.

One way to face up to economic and environmental difficulties is through the direct intervention of governments. For instance, China, a world leader in the production of rare earths, nationalized, and closed some rare earth mines for strategic reasons in 2011 [64–66]. The Venezuelan Government in 2013 ignored intermediate negotiators and guidelines of the London Metal Exchange (LME) and imposed "fairer prices" for iron, steel, and aluminum [67]. Nevertheless, both of those mentioned above, direct governmental measures brought severe economic and geopolitical implications at national and international levels.



Figure 5. Mineral price variation of different non-fuel mineral commodities mainly produced in Latin America since 1960 presented in four graphs. a) gold and platinum, b) silver only, c) and d) mineral commodities whose higher price was 70 and 35 thousand US\$/t, respectively (Published in [68]based on information of [69]).

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3.4. Energy-based approaches

As it pointed earlier, a drawback of conventional MFA, which are based on a massapproach, is that neither environmental damages nor the loss of natural stock caused by mining activities are reflected in such analyses. The mass-based approach leaves out the physical quality of commodities [70–72]. Market prices suffer changes over time because of the interaction of different factors as pointed out in the previous section (section 3.3). Therefore, both approaches do not adequately depict the real physical value of mineral resources [40,49,73].

To overcome some simplifications of MFA, this methodology has been linked to other approaches based on approaches, such as the ecological footprint. Wackernagel and Rees [74] proposed it and estimated the aggregate amount of land necessary for a given population to live sustainably[75]. The ecological footprint follows the use of six categories of productive surface areas: cropland, grazing, land, fishing grounds, builtup land, forest area, and carbon demand on land. Then, they are compared to the biocapacity of a city, state or nation which represents the productivity of its ecological assets. This comparison is carried through a standardized measure of average world productivity named as global hectares [76]. While the ecological footprint reveals an accurate measurement on the re-generation of biotics systems, it does not show a real measure of abiotic resources, such as non-fuel minerals [40]. Even though the ecological footprint is not a purely energy-based approach, because of its message in terms of regeneration, it has been considered in this category.

Concerning energy indicators, Hannon [77] proposed the concept of the Embodied energy as the energy required to manufacture a product or service during its entire life-cycle. This methodology is taken into account in most of the Life Cycle Assessment (LCA) commercial software [78]. In words of Valero and Valero in [40], the embodied energy fails while doing the allocation of energy in co-products and by-products and there is no international agreement because of its lack of thermodynamic basis.

Odum [79] suggested the use of Emergy to estimate the amount of direct and indirect solar energy required to produce any product or service. Emergy is measured

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by the solar emergy joule (seJ) or emjoules. To determine the solar emergy of a commodity, it is necessary to go backwards in the production chain into its resources and energy required, then they need to be translated into the equivalent amount of solar energy. The solar transformity (seJ/J) is the solar emergy per unit product or output flow.

The solar transformity has to be calculated for each commodity. Hence they are dependent on the period of time and place. Emergy is useful in the analyses where the sun has played a central role, for instance, in renewable resources. However, the use of Emergy in mineral resources, where the sun has not played any role in their creation, its usage is questionable.

One way to overcome the issue of proper evaluation of mineral resources is through the Second Law of Thermodynamics. Exergy has been traditionally used to measure any energy source and is defined as the minimum amount of work that may be theoretically performed by bringing a system into equilibrium with its surroundings. It is a property of a system-environment combination [80] and helps to recognize and evaluate environmental impacts and consumption of non-renewable resources [81–83], especially in the case of fuel minerals [84–86].

In this regard, the cumulative exergy accounting by Szargut and Morris [87], alike the exergy cost proposed by Valero et al. [88], considers the sum of all resources required to build a product from its parts, expressed in exergy units [40]. The Thermo-Ecological Cost analysis (TEC) by Szargut, Stanek, and colleagues [89–91] takes the cumulative exergy accounting principles and adds the additional exergy consumption required for the compensation of environmental losses produced by residues into the environment. Others authors, such as Ayres et al. [92,93] have used the concept of exergy for assessment of materials in the United States, Sciubba [94] stretched Szargut's approach to include capital, labor, and environmental impacts into the stage for calculations. Connelly and Koshland [95] have proposed exergy-based definitions and methods for resource depletion, and Cornelissenn and Hirs [96] have applied exergy principles to LCA and established the exergetic life assessment.

Dewulf and colleagues [97] proposed the Cumulative Exergy Extraction from the Natural Environment (CEENE) to add the exergy embedded in the extracted resources,

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for instance copper. This is as the exergy difference between a resource as it is found in nature and the defined reference state in the natural environment. The reference state is defined by using the description of Szargut and colleagues [89], and it is represented by a reference compound considered to be the most probable product of the interaction of the element with other common compounds in the natural environment and that typically one that shows high chemical stability, for example, SiO₂ for Si [98]. For metals, this method calculates the exergy value of the mineral species, for instance, chalcopyrite (CuFeS₂) containing the target metal, in this example copper. Therefore, this calculation is not dependent of the ore-grade.

Exergoecology, proposed by Valero [99] has been established for the evaluation of natural resources, and one division of this discipline is Physical Geonomics, which investigates how the exergy concept can be applied to the assessment of non-fuel minerals [40,99].

The exergy content of fuel minerals is associated with their chemical composition and can be approximated with no significant error to their High Heating Value (HHV), which can be obtained from [100]. Non-fuel minerals cannot be evaluated using this same approach as they are not combustible. This is why non-fuel resources have been traditionally assessed through their chemical exergy content. The latter in turn can be obtained from the Gibbs free energy of the given substance $\Delta G_{f,i}$ and the chemical exergy of the elements that form the substance as expressed in Equation (1).

$$b_{chi} = \Delta G_{f,i} + \sum_{j} n_{j,i} \cdot b_{ch,j}$$
(1)

where b_{chj} is the standard chemical exergy of the elements $n_{j,i}$ that compose substance *i*. Gibbs free energy indicates the thermodynamic potential available for usage until a system reaches chemical equilibrium at constant pressure and temperature [101,102]. Commonly, the chemical exergy of the elements is usually taken from the values obtained by Szargut [103], and the Gibbs free energy can be obtained from chemical databases or estimated with different calculation procedures [104,105].

This way of assessing the exergy of substances, including mineral resources, has been used by different authors including Szargut et al. [72,90,106], Ayres [92] or Dewulf et al.

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[107]. As demonstrated by Domínguez et al. [108], assessing minerals solely with chemical exergy disregards essential aspects that make minerals valuable. As an example, the chemical exergy of precious metal gold is 60 kJ/mol, whereas that of aluminum is 796 kJ/mol. With this, it is appreciated that the chemical exergy alone does not reflect the real value of minerals. To overcome this issue, an additional factor needs to be taken into consideration as will be explained in the next subsection.

3.4.1.1 The exergy replacement cost

In addition to the chemical exergy, minerals have a significant physical feature that makes them valuable, mainly their relative concentration in the crust. Accordingly, the total exergy of non-fuel minerals (b_{ti}) is determined by adding chemical exergy (b_{chi}), as depicted in Equation (1), and concentration exergy (b_{ci}), Equation (2).

$$b_{ti} = b_{chi} + b_{ci} \tag{2}$$

The fact of having minerals concentrated in mines and not dispersed throughout the crust represents a "free bonus" provided by Nature which allows reducing the costs associated with mining significantly. When mines become depleted, this free bonus is reduced, meaning that more energy is required to extract the same amount of metal.

Such a bonus can be assimilated to a hidden or avoided the cost that can be quantified through the so-called exergy replacement costs (ERC). These are defined as the exergy costs that would be needed to extract and concentrate a mineral from a completely dispersed state to the conditions of concentration and composition found in the mine using prevailing technology. ERC values are, thus, related to the scarcity degree of a given mineral, which can be reflected through the concentration exergy (b_{ci}) calculated with Equation (3).

$$b_{ci} = -RT^{0} \left[lnx_{i} + \frac{(1-x_{i})}{x_{i}} \right] ln(1-x_{i})$$
(3)

where b_{ci} represents the minimum theoretical work, exergy, required to concentrate a substance *i* from an ideal mixture of two components; x_i can be either the average concentration in the mines measured in $g/g(x_m)$ or the concentration in the Earth's crust

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(*x_c*); *R* is the gas constant (8.314 J/molK), and T_0 is the absolute reference temperature (298.15 K).

The exergy (Δ_{bc}) associated to the concentration of minerals from a dispersed state in the crust to that in a given mineral deposit is determined by the concentration exergy when $x_i = x_c$ and when $x_i = x_m$, thus Equation (4).

$$\Delta b_c(x_c \to x_m) = b_c(x = x_c) - b_c(x = x_m) \tag{4}$$

Since exergy only reports minimum values and human-made technology is very far removed from reversibility, we need to resort to exergy costs. Accordingly, the so-called exergy replacement costs (B^*) are computed with Equation (5).

$$B^* = k(x_c)\Delta b(x_c \to x_m) \tag{5}$$

where variable *k* is a dimensionless constant called unit exergy cost. It is the ratio between a) the real cumulative exergy required to accomplish the process of concentrating the mineral from the ore grade x_m to the commercial grade x_r (and b) the minimum thermodynamic exergy necessary to achieve the same process $\Delta b_c(x_m \rightarrow x_r)$ [109], Equation (6). An implicit assumption in the methodology is, thus, that the same technology applies for concentrating a mineral from x_m to x_r as from x_c to x_m .

$$k = \frac{E(x_m \to x_r)}{\Delta b_c(x_m \to x_r)} \tag{6}$$

The $E(x_m \rightarrow x_r)$ was determined by looking at the behavior of ore decline and energy consumption required for the concentration of cobalt, copper, gold, nickel, and uranium. From the analysis of this data, it was observed that while ore grade decreases, the energy for concentration increases exponentially [109]. In this research, Valero et al. proposed a general equation to estimate the energy consumption because of the ore grade, Equation (7).

$$E_{(X_m)} = A \cdot X_m^{-0.5} \tag{7}$$

where $E_{(X_m)}$ is the energy for the concentration and extraction of minerals at the ore grade (x_m), and the coefficient A is determined for each mineral.

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The methodology as mentioned earlier is used to calculate the exergy replacement costs of the primary mineral commodities currently used by the industry on a global basis. It should be noted that for obtaining the global ERC of minerals, it is assumed that each product (i.e. copper) is obtained from a single type of ore (i.e., chalcopyrite). For each mineral, the average global ore grades were considered (x_m), mainly derived from Cox and Singer [110], as well as the average energy values of state-of-the-art technologies in mining and beneficiation. The depleted ore grade (x_c) was obtained through a model of dispersed Earth, called Thanatia [40]. Thanatia comes from the Greek Thánatos that means death. In this perspective, Thanatia is a baseline for the exergy assessment of mineral resources and represents an idealization of the planet when all fossil fuels have been burned, and all minerals have been entirely dispersed into the continental crust [40,111].

At this point, it is required to distinguish between Thanatia and the reference environment (RE). As it was mentioned earlier in section 2, exergy is a thermodynamic property of the system-environment, since the environment from which the exergy is to be determined is fundamental for this endeavor. A common RE established to measure the chemical exergy of substances is the one proposed by Szargut [89]. Thanatia is the baseline from which the exergy resource of non-fuel minerals is going to be estimated. Thanatia itself has chemical exergy with respect to a RE, in fact, the total exergy of nonfuel minerals b_{ti} is the sum of the chemical exergy, from Szargut's reference, plus the concentration exergy, as represented in Equation (2). A key difference between Thanatia and the RE is the number of substances considered. As pointed earlier in this section Thanatia has a chemical composition and concentration which approximates to the average Earth's crust and the number of substances in Thanatia is around 300, i.e. the most abundant minerals found in the crust. On the contrary, a typical RE only has 85 reference substances with only one chemical substance allocated per element, for instance, only one reference substance is related to aluminum in Szargut [103]: the aluminum oxide (Al₂O₃) [40]. The fact that the RE only provides the chemical composition and not the concentration of the reference substances in the environment clearly differentiates it from Thanatia. In the latter, the concentration is a key issue for

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estimating the loss of mineral wealth. While the ore grade of a mineral deposits increases, its exergy increases exponentially with respect to a state of mineral dispersion. More arguments about the differences between Thanatia and the RE have been deeply discussed in [40].

As previously mentioned, Thanatia's crust is composed of the 300 most abundant minerals at average crustal concentrations [40]. Once exergy replacement costs of minerals are obtained (i.e., for chalcopyrite), those of the element (i.e. for Cu) are calculated through their corresponding molecular weights.

One key aspect that differentiates exergy replacement costs (ERC) from other thermodynamic properties is that ERC considers the scarcity degree of the commodities in the crust and the energy required to extract them. When a mineral is scarcer, and its extraction and beneficiation processes are more difficult, its ERC value becomes higher. This is why, contrarily to what happens when only chemical exergy is used for the assessment, precious metals such as gold and silver, exhibit higher values of ERC than more abundant ones, such as iron or limestone. Higher values of ERC thus represent a higher quality of minerals and would also mean a higher loss of the natural stock in a region if these become depleted.

To highlight the importance of considering the physical quality of non-fuel minerals, the next comparison between ERC values is provided. Gold and silver have ERC values of 553250 and 7371 GJ/ton, respectively, while limestone and phosphate rock have values of 3 and 0.4 GJ/ton, respectively, **Table 1**. Higher values of ERC indicate a higher quality of minerals and imply a higher loss of mineral wealth when they are extracted. It can be seen that ERC values for minerals that are abundant and easily extracted are lower than those whose concentration in the mines is much lower, implying higher energy consumption during the extraction process.

3.4.1.1.1 Example of the determination of the ERC of copper

As an example of how the ERC for different metals were calculated, the calculation of the ERC for copper has been summarized in the next lines from the work by Valero et al. [112]. The first step is to obtain through a literature review the real energy consumption in the mining and concentration process (from x_m to x_r) as a function of the

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ore grade (x_m). Second, the exergy of the same process as the difference in concentration energy as described in Equation (4). The unit exergy cost, Equation (6), at the crepuscular grade x_c was estimated as follows. Copper in mineral deposits is frequently found as chalcopyrite (CuFeS₂) which has a crustal concentration of $x_c = 6.64 \times 10^{-5}$ g/g. By the information published in [110], it was assumed an average ore grade of $x_m = 1.67 \times 10^{-2}$ g/g. Then, with Equation (3), the value of $\Delta b_c(x_c \rightarrow x_m)$ was determined at 5.28 ×10² GJ/t mineral or 0.21 GJ/t-Cu. By the report of the Kennecott Utah Copper in [113], it was found the average ore grade after beneficiation $x_r = 0.81$ g/g. Accordingly, with Equation (3) $\Delta b_c(x_c \rightarrow x_r) = 0.13$ GJ/t mineral. In order to determine the unit exergy cost in Equation (6), the study of Mudd [114], in which the energy required for the concentration of copper as function of the ore grade was assumed to $23.81x_m^{-0.35}$ GJ/t-Cu, **Figure 6**. By extrapolating this curve, the energy for concentration when $x_m = x_c$ would be 5.28 ×10² GJ/t-Cu or 183 GJ/t, then $k_c = E(x_c \rightarrow x_r)/\Delta b_c(x_c \rightarrow x_r) = 183/0.13 = 1387$. Finally, the ERC of copper is $B^* = k(, x_c)\Delta b(x_c \rightarrow x_m) = 1387 * 0.21 = 292$ GJ/t - Cu.



Figure 6. Energy needed for the production of copper from sulfides ores as a function of the ore grade. (Adapted: [114])

3.4.1.2 Thermodynamic rarity

The exergy required to obtain specific commodity from Thanatia with current technology is known as thermodynamic rarity (TheRy) [40,73]. TheRy is the sum of the

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exergy involved in the process of beneficiation, smelting, and refining (embodied exergy) and the ERC. It means that TheRy considers a physical cost represented by the exergy used to transform a mineral into a commodity (embodied exergy) and a hidden cost denoted by the free bonus provided by Nature to have minerals with high concentrations in mines (ERC) [12]. **Table 1** presents the values of ERC and TheRy of different commodities in GJ per ton of element, as presented in [12].

Element	Mineral ore	ERC (GJ/t)	TheRy (GJ/t)
Aluminum	Gibbsite	627	681.7
Antimony	Stibnite	474	487.4
Arsenic	Arsenopyrite	400	427.0
	Barite	38	38.9
Beryllium	Beryl	253	710.2
Bismuth	Bismuthinite	489	545.4
Cadmium	Greenockite	5898	6440.4
Chromium	Chromite	4.5	40.9
Cobalt	Linnaeite	10872	11010.2
Copper	Chalcopyrite	292	348.7
	Fluorite	183	184.5
Gallium	in Bauxite	144828	754828.0
Germanium	in Zinc	23750	24248.0
Gold	Native gold	553250	663307.6
	Graphite	20.39	21.5
	Gypsum	15	15.2
Indium	in Zinc	360598	363917.7
Iron ore	Hematite	18	32.1
Lead	Galena	37	41.2
	Lime	2.6	8.8
Lithium	Spodumene	12.5	978.5
	Magnesite	26	35.5
Manganese	Pyrolusite	16	73.6
Mercury	Cinnabar	157.0	28707.0
Molybdenum	Molybdenite	908	1056.0
Nickel Pentlandite	Sulphides	761	876.5
Nickel Gamierite	Laterites	168	581.7

Table 1. Exergy replacement cost (ERC) and thermodynamic rarity (TheRy) of different commodities in GJ per ton of element (summarized from [12]).

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Element	Mineral ore	ERC (GJ/t)	TheRy (GJ/t)
Niobium	Ferrocolumbite	4422	4554.0
Palladium		8983377	9566710.3
Phosphate rock	Apatite	0.4	5.3
Platinum		4491.69	4783356.7
Potassium	Sylvite	665	666.7
REE	Bastnaesite	348	361.9
Rhenium		102931	103087.0
Silver	Argentite	7371	8937.6
Sodium	Halite	44.07	86.9
Tantalum	Tantalite	482828	485918.9
Tellurium	Tetradymite	2235699	2825104.3
Tin	Cassiterite	426	452.6
Titanium	Ilmenite	4.5	139.8
Titanium	Rutile	8.8	266.4
Tungsten	Scheelite	7430	8024.0
Uranium	Uraninite	901	1089.8
Vanadium		1055	1572.0
Yttrium- Monazite		159	1357.3
Zinc	Sphalerite	155	196.9
Zirconium	Zircon	654.43	2025.5

3.5. Concluding remarks

This chapter has gone through different methods to value non-fuel minerals based on a literature review. For this thesis, they have been classified as mass, market-price, and energy approaches. Main contributions and authors for each approach have been emphasized, as well as their advantages and weak points. The next points can be highlighted to support the purpose of the Thesis:

 Traditionally non-fuel minerals have been assessed because of their weight and commercial price. As pointed out in the previous section, mass and market pricebased approaches have some weaknesses to estimate the loss of mineral patrimony accurately. Basically, from a mass-based approach, a ton of iron is equal to a ton of gold. However this perspective disregards the geological scarcity of gold. Market-prices varies because of many reasons; the balances

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between market forces, speculations, etc. They do not portray the real value of mineral resources, only reflects the effort made for their extraction. Both approaches do not show the role of Nature, and only recognize it from a manmade perspective for the compensation of depletion of resources through a manmade creation, money.

- Approaches based on energy principles have been proposed to value minerals. Some of them are established based on the Second Law of Thermodynamics to estimate minerals not only because of their quantity, but also because of their physical quality.
- Exergoecology, based on the Second Law of Thermodynamics –Exergy, has been
 postulated to assess non-fuel minerals accurately. In this regard, the concepts of
 the exergy replacement costs (ERC) and thermodynamic rarity (TheRy) had been
 conceived to value the effort of Nature to have minerals concentrated in mines
 and not dispersed through the Earth's crust.
- The main benefit of the thermodynamic-based approach is that the evaluation is supported by physical principles and show essential aspects of non-fuel mineral such as scarcity and metal processing. They do not vary because of economic, political, or other reasons alien to the physical reality of the material.
- Although the concepts of ERC and TheRy portrait the hidden cost (energy saved) freely provided by Nature, the way of their calculation is arguable. In the next chapter, several weaknesses are identified.

Chapter 4. Upgrading exergoecology calculations

4.1. Introduction to the chapter

This chapter analyses several shortcomings identified in the method of calculation of the ERC and shows a new way for their estimation. In that sense, in the first section, the weak points on the ERC's method are described. Subsequently, the need for a new scheme for mineral processing is highlighted. The chapter then proposes to use a robust and well-proven software HSC Chemistry 9 for such an endeavor. An overview of the software and basics on mineral processing are finally explained.

4.2. Identified shortcomings on the ERC determination

Although the ERC and TheRy are concepts strongly supported by the Second Law of Thermodynamics and their meanings are oriented towards a quantitative estimation of the "free bonus" provided by Nature, some aspects in their calculation could be improved to firm up the theory. Accordingly:

- 1. As it was pointed out in subsection 1 the determination of the ERC was derived from the analysis of data available in that time mainly compiled by Cox and Singer in the '90s regarding the average global ore grades (x_m). Hence, the data for the calculation of the ERC was not updated and changes in time may influence the ERC.
- 2. Through Equation (5), the ERC is directly influenced by a dimensionless constant called unit exergy cost variable (k). The latter is the ratio between the real and minimum thermodynamic exergy to concentrate mineral from the ore grade (x_m) to the commercial grade (x_r). The manner that this real exergy was estimated can be significantly improved. It was determined by the observation of the behavior over time of the specific energy versus the ore grade decline of a few metals (cobalt, copper, gold, nickel, and uranium) for which data was available. For the others, it was assumed that similar behavior would be expected and a general mathematical expression was proposed, Equation (7).
- Geological principles prevailed over metallurgical consideration on ERC values. They were calculated without considering the effect on different routes of metal processing.

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4.3. The need for a new approach

The reasons explained in the section above are drivers to search for some alternatives to strengthen the determination of ERC.

The target is to analyze how much energy would be required to concentrate minerals from Thanatia by using current mining and metallurgical technology to estimate more realistic values of ERC. That is why it is necessary to establish a more rigorous procedure for the ERC. To set the foundation of this new methodology, three key metals have been chosen, based on 1) the availability of data, 2) standing to LA-20 in a global context, and 3) importance for the development of new technology. Accordingly, iron, copper, and gold were selected. Based on the calculation of the previous ERC values, as described in the previous subsection 3.4.1.1, the stages to be analyzed with a new methodology are depicted in **Figure 7**.



Figure 7. Stages of mineral processing to be analyzed with the new methodology.

To perform the stages of concentration and refining, a deeper understanding of metal processing and its effect on their estimation was required. That is why a closed collaboration between Prof. Dr. Markus Reuter and his group at the Helmholtz Institute Freiberg for Resource Technology (HIF) and the Research Centre for Energy Resources and Consumption (CIRCE Institute) was initiated to look for a new approach to determine more accurate values of ERC. For this endeavor, a specialized and well-proven software HSC Chemistry [115] was used. An explanation of these stages in **Figure 7** is presented in the next lines.

4.4. Thanatia

As it was explained in sub-section 3.4.1.1, Thanatia is an idealization of a complete state of mineral dispersion into the Earth's crust. Thanatia is made up of the 300 most abundant minerals at average crustal concentrations [40]. By classifying these minerals from the list reported in [40] according to their chemical composition, they can be

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assembled into 9 groups. This classification, as well as the most representatives with their composition in Thanatia is presented in **Table 2**.

Group	Number of minerals in Thanatia	Most representatives	Composition (wt-%) in Thanatia
	50	Barite	7.65x10-2
		Celestine	6.38x10-2
		Pyrite	3.02x10-2
		Anhydrite	2.16x10-2
0 1 1 1		Pyrrhotite	1.43x10-2
Sulphides		Gypsum	1.15x10-2
		Sphalerite	9.49x10-3
		Chalcopyrite	6.33x10-3
		Pentlandite	5.47x10-3
		Galena	6.35x10-4
		Quartz	21.79
		Opal	1.18
0.11.	50	Magnetite	0.76
Oxides		Ilmenite	0.45
		Ulvöspinel	0.11
		Hematite	0.09
	129	Albite	12.87
		Oligoclase	11.34
		Orthoclase	11.20
Silicator		Andesine	5.20
Silicates		Paragonite	3.77
		Biotite	3.63
		Illite	2.89
		Augite	2.86
	7	Halite	5.61x10-2
Halides		Fluorite	1.07x10 ⁻³
		Sylvanite	1.95x10-4
	16	Calcite	7.68x10-1
Carbonatos		Ankerite	2.58x10-1
Carbonales		Dolomite	1.35x10-1
		Siderite	2.31x10-2
Phosphates	11	Phosphate Rock	2.31x10 ⁻²

Table 2. Classification of Thanatia's minerals by their ion and the composition (source: [40]).

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Group	Number of minerals in Thanatia	Most representatives	Composition (wt-%) in Thanatia
		Apatite	3.84x10-2
		Monazite	9.81x10 ⁻³
		Francolite	4.15x10-3
Wolframates	4	Scheelite	2.54x10-4
		Wolframite	3.05x10-5
Hydroxides	6	Diaspore	1.68x10-1
		Gibbsite	1.32x10-1
		Goethite	9.92x10 ⁻²
		Boehmite	5.51x10 ⁻²
Native elements	51	Gold	1.21x10-7
		Lead	6.02x10-6
		Silver	1.98x10-6

Chapter 4. Upgrading exergoecology calculations

By analyzing **Table 2**, the dominant element because of their weight-percentage are the oxides and silicates with quartz and albite like the most representatives.

4.5. Ore-handling

This stage involves the transportation of the ore from the mine to the facility where further processing for the concentration and refinement will take place. The transport of the ore is typically done with haul trucks or belt conveyors [116,117].

In our particular case, since Thanatia will be taken as the deposit for the concentration of minerals, it will be assumed as an open pit mine. Hence surface mining will be considered. As previously explained in section 4.4, Thanatia is a mix of different diluted minerals. Hence, for mineral processing purposes it will be dealt as a complex ore, and it will be more favorable to assume the transportation by haul trucks with a minimum distance between the mine to the concentration plant so that the fuel consumption per ton of ore prevails over the distance of transportation. Data published by Rankin [6] will be considered as a reference for handling from Thanatia to the concentration facility.

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4.6. Comminution

Beneficiation or mineral processing consists of mainly two stages, comminution, and concentration where the useful metal (concentrate) is separated from unwanted material (gangue) into discardable waste (tailings) [6,118].

The comminution is the reduction of the size of the particles so that the desired metal can be liberated by crushing and grinding [116,118]. Comminution is the stage with the highest energy consumption of beneficiation [116]. The final particle size is a decisive factor for such requirement of energy [6,119]. During the comminution process, a fundamental equation to compute the specific energy required for the mill is Bond's equation [117,120], Equation (8).

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

where W is the specific energy consumption of the mill (kWh/t), Wi is the work index measured in a laboratory mill, commonly refer to "Bond Index" (kWh/t), P80 and F80 are the 80% passing sizes of the product and the feed (µm) into the crushers or mill, respectively. Finally, EFx is the product of the Rowland efficiency factors which depend upon mill, size, and type of media, kind of grinding circuit, etc. [117,120–123]. Then, theoretical power draw by the mill (kW) is calculated by W x T, where T is the throughput tonnage (t/h) [117].

Crushing is the first mechanical stage in which the principal target is the liberation of the valuable minerals from the gangue. This stage is typically a dry operation and is performed in two- or three stages, for example, primary, secondary, and tertiary crushing. During the primary crushing, jaw or cone crushers are commonly used to reduce the size of the run-of-mine from 1.5 m to 10-20 cm [116,117,124].

During grinding particles are reduced in size by a combination of impact and abrasion, either dry or commonly done in the suspension of water. The final size in grinding is in the order of microns. Crushing and grinding is usually done in several stages named as comminution circuits. Crushers and mills are configured so that particles in the desired size range are removed while they areproduced and the oversized are returned to the circuit. The requirement for effective liberation determines

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the final particle size during comminution according to each ore. Typical figures for metallic ore are in the range of $50 - 500 \mu m$ [6]. These sizes are for mines with average ore grades. Autogenous (AG) and Semi-autogenous (SAG) mills are typically used for grinding, the latter uses balls in addition to the natural grinding media [117].

Due to the low concentration of minerals in Thanatia, as it is seen in **Table 2**, the particle size to reach a desired concentration is unknown. However, values of particles sizes as the previous ones will be considered in a first attempt for the models in HSC. Then, the issue of which size is the more appropriate will be considered for each mineral.

4.7. Concentration

After comminution, the next step is to separate the desired minerals from the gangue to produce a concentrate. This separation can be based on any physical or chemical properties. For effective separation, the most common properties are size and shape, density, magnetic susceptibility, electrical conductivity and surface chemistry. The next lines briefly describe this concentration techniques [117,125–127].

The most widely used method for separation is froth flotation (hereafter flotation). This process takes advantage of natural or induced surface properties of mineral ores. As mentioned before, sulfide ores are typically concentrated by this process. In flotation, hydrophobic (water-fearing) particles are separated from the hydrophilic (readily wetted by water) particles. The valuable metal is then collected from the froth in direct flotation and the contrary is done in reverse flotation [117,125–127]. This separation occurs in tank cells, the thanks where the highest percentage of the mineral containing the desired metal are called roughers. After them, tanks named as scavengers are connected in closed circuit to concentrate as much as possible. The number of tank-cells and the arrangements of cleaners and recleaners is determined by the type of ore and the desired concentration.

In the computational models to be developed, direct flotation will be employed for the concentration of chalcopyrite and reverse flotation for iron minerals. Due to the low concentration of these minerals in Thanatia the number of tank-cells and the

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arrangements of cleaners and re-cleaners will be strategically done so that the desired concentration will be achieved with resonable residence times.

Because of the difference in settling velocities particles are separated. Classifiers are the devices based on gravity, gas cyclones, and hydrocyclones rely on centrifugal force. Gravity separators, jigs, work due to the difference in particle density. Magnetic separators rely on the differential movement of materials in a magnetic field. The differences in electrical properties of materials are used to separate the desired metals with high voltage up to 50 kV [6].

Gravity separators will be key for the concentration of native gold in the model to be developed with HSC. Due to the high magnetic susceptibility of iron minerals, magnetic separators will be employed to separate them from the gangue in the HSC model for the concertation of iron minerals. The circuits and numbers of magnetic separators, as well as gravity separators, will be determined according to the concentration of iron-minerals and gold, respectively, in the models.

4.8. Refining

Once the metal in the ore has been concentrated, then it is purified by adding heat (pyrometallurgy) or chemical substances (hydrometallurgy) [6,117]. During this stage, the chemical composition of the metal remains as originally found in the ore.

Particularly, only the refining of gold will be modeled in HSC in this Thesis as an example to assess not only, the new ERC, but also the Thermodynamic rarity. Due to the characteristics of gold in native form and enclosed in tellurides in Thanatia, some stages of hydrometallurgy will be modeled. For each stream, native and tellurides, a different treatment will be applied. As commonly done in current refinement facilities, cyanidation will be applied as a hydrometallurgy technique for purifying gold for both streams and in the case of the tellurides, roasting before the cyanidation is required to liberate gold from the tellurides. In the latter heat is applied in a controlled atmosphere so that tellurides are separated by the difference in heating temperature from gold. In that sense, roasting and smelting should be differentiated. The purpose of roasting is to convert base metals into their oxides. The usual range for roasting is between 600 to

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700°C. In our case, as for the presence of tellurides, through roasting, calaverite (AuTe₂) is converted (oxidized) into tellurium dioxide (TeO2). On the other hand, the target of the smelting is to get rid of the base metals or impurities, for that high temperature is required on the range of 1000-1200°C [128,129].

The stages described in the previous sections will be carefully explained according to each model to be developed for iron, copper, and gold in Chapters 5, 6, and 7, respectively.

4.9. HSC Chemistry software

Specialized software for metal processing HSC Chemistry 9 [115] was used to model routes of metal concentration. The software has twenty-four modules to conduct thermodynamic and mineral processing calculations. HSC is a versatile software in which new processes are modeled and simulated to improve existing ones and test innovative solutions before to be proven in laboratories or pilot plants.

In particular, the HSC SIM-Simulation Module enables the development of a considerable variety of chemical, metallurgical, mineralogical, and economic processes. From an engineering approach, models by dragging and dropping units in graphical flowsheets different methods can be modeled, and Sankey diagrams show results. The HSC software has been developed and tested with a real process by Outotec. For detailed information on the capabilities of the software, refer to official information in [130].

Figure 8 depicts a screen of the HSC-Sim module of a model for the comminution process to concentrate iron-ore from Thanatia. It can be seen that the process flow streams are identified with different thicknesses according to the mass flow rate.



Figure 8. Screen capture of the crushing and grinding in a model for the concentration of iron-bearing minerals.

4.10. Concluding remarks

As pointed out in subsection 4.2, the current ERC calculation method fails on the fact that most of the criteria for its calculation were based on the analysis of the statistical trend of a few metals. Also, only the geological perspective was considered disregarding the importance of metal processes. It is required a mineral processing perspective to improve the calculation of ERC and strengthen the theory of the assessment of non-fuel minerals. For this endeavor, partner-work with a research group at the HIF started.

Within the scope of the thesis, the models for iron, copper, and gold, which are representative metals produced in LA-20 and valuable for the construction of new technologies, were modeled and simulated with HSC Chemistry 9. Their results will be compared to the ERC previously published in [12]. In chapters 5, 6 and 7 the models of these three metals and their respective analyses are carried out.
Chapter 5. The concentration of minerals from Thanatia: iron ore

5.1. Introduction to the chapter

In this chapter, the first model for the concentration of iron-ore from a dilute state, Thanatia, is developed with a computational model in HSC software. Before to begin with the description of the methodology for modeling and simulation, the chapter portraits some statistics about which countries are the most extensive worldwide producers of iron. Then, the stages for the concentration of the mineral from Thanatia are explained. Finally, a description of the model is performed along with the validation of results with a literature review. The information presented in this chapter corresponds to a summary of **Paper I**.

5.2. World iron-ore production

Even though iron is one of the most abundant minerals in Earth's crust [131], the rich deposits have already been exploited owing to the massive consumption of metals by humans. Thus, new deposits must be found in remote locations, and the energy expenditure for not only handling the ore but also processing metals has increased [132]. Steel—a carbon–iron alloy—is fundamental in the modern world. Although iron has one of the highest recycling rates among metals [133], in 2015, iron ore production was 2.2 billion tons, 233% higher than in 1990 [7,134]. According to historical global statistics from the U.S. Geological Survey (USGS) [7,134], the leading iron-ore producers from 1900 to 2015 were China (38%), Australia (19%), and Brazil (17%), **Figure 9**. This high production of iron ore implies a loss of natural minerals in these countries [40,71,72].

Additionally, a decarbonized society implies the use of renewable energy technologies [2,135,136]. These technologies require a considerable amount of metals, and steel is extensively needed; however, iron production is only economically feasible when ores with high concentrations of iron are available.

In this study, we estimate the specific energy needed to concentrate minerals from Thanatia via a more rigorous approach than the one used previously. The methodology developed for this endeavor relies on a computational model using the HSC Chemistry software [115], which is a specialized software for mining and metallurgical processes that are commonly used in industry. The aim is to provide

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accurate values regarding the amount of energy needed if no more concentrated ironore deposits exist. This exercise, which has not been previously performed with such detail, reveals the tremendous amount of energy savings due to having minerals concentrated in mines and not dispersed throughout the crust.



Figure 9. World iron ore production by country (based on: [7,134])

5.3. Concentration of iron ore from Thanatia

In this model for the concentration of high-iron content minerals, Thanatia will be used as a common rock. Because Thanatia has many minerals, only those with an iron content of >15% (by weight) are shown in **Figure 10.** Iron-bearing minerals in Thanatia. The left axis (in black) indicates the content of the mineral in Thanatia. The right axis (in grey) indicates the content of iron of the mineral.

A complete list of the substances in Thanatia considered in the present study, along with their chemical formulas and percentages by weight, can be found in [40]. Owing to the high iron content of magnetite in Thanatia and because hematic deposits are highly valued for iron production, e.g., Carajás in Brazil. Hematite and magnetite are considered for concentration in our computational model.

For the interest of this chapter, **Figure 10** shows the ERC value of 73% hematite (Fe₂O₃) required to go from Thanatia (x_c) to the average concentration in mines (x_m).

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Figure 10. Iron-bearing minerals in Thanatia. The left axis (in black) indicates the content of the mineral in Thanatia. The right axis (in grey) indicates the content of iron of the mineral.

Table 3. ERC for iron ore in GJ per ton of element. (adapted from [12])

Mineral	Mineral ore	x_c (g/g)	x_m (g/g)	ERC (GJ/t)
Iron ore	Hematite	9.66E-04	7.30E-01	18

5.4. Development of the model and results

5.4.1. Explanation of the model

Iron is produced from deposits where its extraction is technically feasible and economically viable [137]. Ore with higher iron-bearing minerals is preferable because the production of iron only entails low-energy stages in mineral processing and concentration. Pilbara, a region in Western Australia, and Minas Gerais, a state of Brazil, are some examples where many deposits and iron ore mines are located [138]. Ores with high iron content, such as hematite (Fe₂O₃), magnetite (Fe₂O₄) are being searched for iron extraction. An example of hematite ore is Carajás, an open pit mine that has been in operation since 1985 [139,140]. Its reserves are estimated at 18 billion tons with an average content of at least 65% iron [141]. Searching for high iron-content sites, in 2016

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started the operation of the S11D complex located in the municipality of Cajarás. The iron content in this complex reaches 66.7% Fe [139,141]. The process for the extraction of the valuable metal depends upon the type of ore. Physical properties of iron-bearing minerals, such as high specific gravity (SG), magnetic susceptibility (**Table 4**) are used for separation because they imply lower energy consumption processes [116,125,137].

Mineral	SG	Mineral	Magnetic susceptibility (1x10 ⁻⁶ m ³ /kg)
Ulvöspinel	2.8	Magnetite	625-1156
Ankerite	3.05	Hematite	0.6-2.16
Siderite	3.96	Specularite	3.7
Goethite	4.28	Limonite	0.31-1.0
Ilmenite	4.7	Siderite	0.7-1.5
Hematite	5.1	Ilmenite	0.34-5
Magnetite	5.15	Quartz	0.0025-0.126

Table 4. Physical properties of common iron-bearing minerals (source: [125,137])

Because of the high specific gravity of iron-bearing minerals and high magnetic susceptibility, the concentration is done by magnetic separation and reverse flotation. With the usage of substances, sometimes a combination of depressants and collectors, the ore is concentrated [142–145]. Iron concentration in the ore can be around 30% and the concentrate can have 60% of iron content [137,138,146]. Then, according to the particle size, the concentrate can be classified from coarser to finer in lump (32 to 6 mm), sinter feed (6 to 0.15 mm), and pellet feed (0.15 to 0 mm) [147].

The concentration of minerals involves stages of transportation of the rocks from the mine to the concentration plant and different processes of mineral concentration [6]. Thus, the total specific energy to concentrate iron ore in average ore grade (-50% Fe) from Thanatia (3.63% Fe) was considered as the sum of the energy in the ore handling process plus the energy for concentration, **Figure 11**. In this model, the minerals for concentration are obtained from Earth's crust and surface mining is assumed. As reported by Chapman and Roberts [148], ore transportation plays an essential role in the total energy requirement of the ore-handling process. This is why the energy requirement for drilling and blasting is considered to be negligible in our model, in comparison with the energy for ore-handling and concentration. The ore-handling

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process involves the transportation of the ore from an open pit to the concentration plant, generally using haul trucks. At the facility, comminution and concentration are performed.



Figure 11. Conceptualization of the total energy needed to concentrate iron ore from Thanatia as the sum of energies for the handling and concentration processes.

For the ore handling, a minimum distance between the mine and the facility was assumed, so that the fuel consumption per ton of ore prevailed over distance. Then, taking into account the iron concentration in the feed stream of 3.63 Fe%, the specific energy per ton of iron ore was calculated.

The purpose of this study is to develop a model for concentrating iron-bearing minerals, mainly magnetite and hematite, from Thanatia until a concentration in equivalent-iron content similar to the one published in the ERC for hematite (Fe₂O₃). This indicates a starting concentration of 3.6% iron in Thanatia (x_c) and an ending concentration of approximately 50% iron in the mine (x_m). The latter comes from the stoichiometric conversion of the iron content in 70% hematite reported for the ERC of hematite, as shown in **Table 3**.

Because Thanatia is an ideal ore, the stages of comminution and concentration at the facility were designed according to an extensive literature review and analyses of different flowsheets of iron concentration plants. The fundamentals of iron-ore processing and the layouts of processing plants were adapted from Lu [137] and Sousa [149]. Technical reports of iron-ore projects were also studied [140,147,150,151]. Publications by Houot [152] and Filippov [142] regarding the beneficiation of iron were reviewed, as well as papers regarding the flotation of iron ores by Frommer [153] and

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Araujo et al. [154]. The use of collectors and reagents for iron ores was examined according to the results of Schulz and Cooke [155], and a lifecycle assessment (LCA) of iron ore mining performed by Ferreira et al. [156] was considered.

The experience of the research group concerning mineral processing was significant for the final design of the model using the software HSC Chemistry version 9.5.1 [115]. In the model, many variables were considered, but only the most important ones are described herein. For the simulation, an Intel core i7-6600 2.60 GHz central processing unit with 32 GB of random-access memory was used.

On the basis of the analysis of technical reports of iron projects [140,147,150,151], the study of the layouts in [137], and previous works on models by Abadías et al. [157], the ore feed for the model was assumed as 2,500 tons per hour with a top size of 600 mm. To illustrate the model, **Figure 15** depicts the main stages for the concentration of iron from Thanatia.

Three circuits in the comminution were considered for the model: crushing, grinding, and two regrinding stages for liberating the maximum amount of metal from Thanatia. The 80% passing through the primary crusher (F80) 264 mm is fed into the comminution circuit. Crushing is performed by a gyratory crusher and a cone crusher, with the particle-size output (P80) set as 200 and 60 mm, respectively. A screen with a cut size of 32 mm is placed in a closed circuit with the cone crusher. The screen reports to the grinding circuit, which consists of two ball mills. The sizes of the passing particles (P80) for these mills are 4000 and 75 μ m, respectively. Equation (2) was used to determine the theoretical power draw during the comminution stages. Both, the feed (F80) and the product (P80) passing sizes were obtained from the HSC model. **Figure 12** shows the comminution circuit for the concentration of iron ore.

The work index (*W_i*) for unidentified iron ore can vary from 4 to 31 kWh/t [125]. For the first calculation of the specific energy consumption (*W*), a representative value of 14 kWh/t was considered. A similar value for this conversion (61.22 kJ/kg) was employed by Valero and Valero [158] to calculate the exergy of comminution and concentration for different minerals.

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Figure 12. Comminution circuit for the concentration of iron-ore from HSC software.

To reduce the complexity of using the Rowland efficiency factors (EF_x) in Equation (2), the procedure proposed by Will and Finch [117] was followed for the selection of mills. Accordingly, a value of 1 for EF_x was assumed, and the specific energy consumption (W) for every mill was computed. According to the W values for the mills and information from catalogs provided by the manufacturers, models of mills were selected. Then, the number of mills was estimated. Data published in [124,159] for primary gyratory and cone crushers were considered. For the grinding and re-grinding ball mills, we considered a survey of data regarding the specific energy (7.82 kWh/t) for these tumbling mills reported by Latchireddi and Faria [160]. For classification, the power of spirals and low and high magnetic separators were taken from [116]. The power required for the flotation process of the main iron-bearing minerals was obtained directly from the HSC model [115]. The specific energy per ton of iron was determined according to the feed flow rate (2500 t/h) and the iron concentration in Thanatia (3.63% iron).

After the start of the classifying process in comminution, high-iron-content minerals are separated from the unwanted minerals because of their higher specific gravity (SG) and magnetic susceptibility. Thus, the comminution process reports to two spiral concentrators, where low-SG minerals, such as quartz and silicates, are partially separated. To ensure the separation of unwanted minerals, a combination of three

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Figure 13. The arrangement of classifiers, cyclones, low and high-intensity magnetic separators for the classifying stage in the concentration of iron-ore from Thanatia.

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Figure 14. Regrinding and reverse flotation for the concentration of iron-ore from Thanatia.



Figure 15. Flowsheet of concentration and tailings from Thanatia to iron ore.

5.4.2. Results and validation

As it was explained in sub-section 4.6 in Equation (8), the specific energy consumption of the mill W necessary to calculate the Power Demand is based upon the work index (Wi). In a first attempt, to determine the specific energy, it was considered a value of 14 kWh/t. With these considerations and others pointed out for the model setup previously explained in the methodology, the power demand for the flotation plant was estimated, **Table 5**.

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Stage	Power Demand (MW)	Power Demand (%)
Crushing	2	1.9
Grinding	71	87.1
Re-grinding	9	10.6
Classifying	0.06	0.1
Reverse Flotation	0.52	0.4
TOTAL	81	

Table 5. Power draw for comminution and concentration processes.

As it is shown in **Table 5**, most of the power demand was due to the comminution process (more than 99%), and grinding was the highest consumer. Then, the specific energy for the concentration of high-iron content minerals from Thanatia was calculated, **Table 6**.

Table 6. Specific energy for the concentration of iron minerals from Thanatia inkWh per ton of ore.

	Iron concentration	Flow rate	Specific Energy
	(wt-%)	(t/h)	(kWh/t)
Feed Ore	3.63	2500	33

To estimate the specific energy required for ore handling, consumption of 2.2 kg/t as reported by Norgate and Haque [162] in their work on based on Life Cycle Assessment (LCA) for iron ore and other minerals was considered. The ore handling, which is the movement of ore from the mine to the concentration plant, and all the stages for concentration, crushing, grinding, re-grinding and reverse flotation for a Wi of 14 kWh/t are shown in **Table 7**.

Table 7. Specific energy for the concentration of copper from Thanatia in GJ per ton of element.

	Specific Energy (GJ/t)
Ore handling	2.3
Concentration	3.2
TOTAL	5.6

Because Thanatia represents a complex ore, where its Bond's index Wi cannot be accurately determined for the more significant number of minerals, it is appropriate to estimate the specific energy through a sensitivity analysis. This analysis is based on the variation of Wi from 4 to 31 kWh/t, a possible range for iron ores. The values considered

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for the sensitivity analysis were: 4, 9, 14, 21 and 31 kWh/t. According to the model developed in HSC and the methodology described in this work, the specific energy required to concentrate iron minerals from Thanatia would be more accurately represented by the variation of parameters of the comminution process, the highest energy consumption stage, and hardness of the rock. These parameters have been represented by the total reduction ratio (Rr) and Bond's work index (Wi). **Table 8** shows the range of total reduction ratios considered for the sensitivity analysis.

Scenario	Total reduction		
	ratio (Rr)		
1st	436		
2nd	491		
3rd	574		
4th	657		
5th	739		
6th	844		
7th	958		
8th	1145		
9th	1433		
10th	1943		

Table 8. Values of the total reduction ratio of the mills for the sensitivity analysis.

Similarly, as reported in **Table 8**, **Figure 16** shows the specific energy for the concentration of minerals with the high content of iron from Thanatia. In the analysis, the total reduction ratio (Rr) was changed, as shown in **Table 5**, to represent the different particles sizes required to extract iron from bearing minerals in Thanatia.

As shown in **Figure 16**, the specific energy increases as the total reduction ratio (Rr) increases. There is a proportional relationship between the specific energy and the Bond work index, as indicated by Equation (8).

The result based on the HSC model is compared with the ERC value converted into iron content (through molecular weights) and the embodied energy (mining and concentration) of iron reported by Calvo et al. [12]. The energy spent on loading and crushing reported in [162] is used to draw a comparison. In the model, the values of the specific energy can vary according to Rr and *Wi*. For the lowest Rr (436) and softest rock

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(W_i = 4 kWh/t), the energy required was 3.3 GJ/t-Fe. For the highest Rr (1943) and hardest rock (W_i = 4–31 kWh/t), the energy required was 14.1 GJ/t-Fe.



Figure 16. Specific energy for the concentration of high-iron minerals from Thanatia with respect to the total reduction ratio (Rr) and Bond work index (Wi).

By doing a comparison of the values in **Table 8**, it can be seen that there is a difference of one and two orders of magnitude if the energy required to concentrate high-iron content minerals (free bonus given by Nature) and the current expenditure of energy for processing iron ores. In comparison to the ERC, this number is in the same order of magnitude as the one obtained in the current work by a combination of the finest particle size (Rr = 1943) and the hardest iron ore (Wi = 31 kWh/t).

The range of results of the specific energy in **Figure 16**, were obtained under the assumptions previously explained in this section. The sensitivity analysis done by changing the total reduction ratio (Rr) and Bond's index (Wi) should be taken as the uncertainty of the required final particle size needed to liberate the iron metal from unwanted minerals and different hardness that Thanatia would have for processing.

The previous ERC has the same order of magnitude of the specific energy as the present work with a combination of the finest particles (Rr = 1943) and the hardest iron ore (Wi = 31 kWh/t). Importantly, in our model, minerals with a high iron content were

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concentrated. The mathematical calculation of the ERC for iron by Valero and Valero [40] corresponds to only hematite, as shown in **Table 3**.

Table 9. Comparison of the specific energy of the current work with other reported values in GJ per ton of element.

	Specific Energy (GJ/t-iron)	Source
ERC based on HSC	3.3 to 14.1	current work
Previous ERC	18	[12]

As shown in **Figure 16**, the specific energy for the concentration of iron minerals depends on the hardness of the rock (W_i) and the final particle size (represented by Rr). As shown in **Table 7**, for W_i = 14 kWh/t, which was also considered by Valero and Valero [158] as a common value for different minerals, and a common final size of P80 = 40 µm (Rr = 436) for iron ore, the specific energy for the concentration is 5.6 GJ/t-Fe. This value can be considered as a "New ERC for iron from HSC," assuming that Thanatia exhibits behavior similar to that previously described (W_i = 14 kWh/t and Rr = 436).

In summary, the previous and new ERCs for iron differ considerably in the method of estimation. While the previous one was determined only according to mathematical and analytical analysis, the new one has strong support from a metallurgical viewpoint. For the previous ERC for iron, it was roughly assumed that only hematite could be concentrated from Thanatia. On the other hand, from a more realistic perspective, minerals with high iron content in Thanatia, such as magnetite and hematite, are easily concentrated, and their separation is difficult. Additionally, in the case of the previous ERC, the processing of iron to obtain pellets or lumps for producing pig iron implies an additional expenditure of energy. This is because, in the calculation of the previous ERC, the separation process (crushing and grinding) was not even considered. In contrast, further treatment for the iron ore of the new ERC allows energy saving because the ore is already ground to P80 = $40 \mu m$.

5.5. Concluding remarks

The computational model developed in this chapter was the result of the analysis of different layouts of current iron concentration iron plants. Based on a comparison of

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parameters obtained from the model and those respective ones published in the literature, results from the HSC model were logical and reliable. The following conclusions can be drawn:

- With the methodology described a sensitivity analysis by changing two key parameters for the concentration of iron minerals were performed. The first parameter characterizes the uncertainty of the final particle size before the reverse flotation processes. The size is required to liberate iron metal presented in a very-low concentration stage in Thanatia; this becomes represented by the variation of particle size in the comminution process (Rr). The second parameter in the sensitivity analysis denotes the change of hardness in Thanatia by the Bond's index.
- Results of the sensitivity analysis vary in a range of values that show a difference of one order and two orders of magnitude in comparison to current processes. A comparison with the ERC for iron, reveals that this value is in the same order of magnitude as the one corresponding to the current works with the finest particle size (largest Rr) and hardest ore.
- From the model, a new ERC value for iron can be taken as 5.6 GJ/t-Fe by assuming that Thanatia would exhibit similar behavior as previously described (Wi=14 kWh/t and Rr=436). This value is three times lower than the previous one (18 GJ/t), yet they are still in the same order of magnitude. Both values differ on the method of calculation. While the previous value was estimated by mathematical and analytical analysis, the new one has strong support from an engineering point of view with specialized software.
- Results of this model leave an important message on the need to value more the current high-iron content deposits, particularly in countries where iron ore is vastly extracted.
- The loss of natural patrimony in those nations where minerals are extracted should be also taken into account. The role that these nations have in a globalized economy should also be reconsidered.

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Chapter 6. The concentration of minerals from Thanatia: copper ore

6.1. Introduction to the chapter

The chapter is devoted to the development of a model in HSC software of copper ore from Thanatia. An overview of the worldwide production of copper ore is analyzed. It is also shown how the concentration of copper in deposits have been declining over time because of the high consumption of this metal. Then, the methodology for the computational model, followed by a sensitivity analysis is described. Results of this model leave essential messages concerning the importance of giving more value to the current copper deposits. The information presented in this chapter is a summary of **Paper III.**

6.2. World copper-ore production

The extraordinary properties of copper, such as high electrical conductivity, heat conduction, antibacterial behavior, etc. have made copper a preferred mineral for a variety of applications from a plain penny, domestic uses, like in doorknobs until high-tech usage as a semiconductor in silicon chips for energy-efficient microprocessors [163,164]. That is why the consumption of copper has increased significantly in the last years. The growing demand has led to the rapid extraction of copper. Meinert et al. [165] gave an astonishing value that one-quarter of the total copper mined in human history was produced in just ten years (from 2005 to 2015).

The high consumption of copper has caused that rich deposits have been already exhausted. Many authors have undertaken the issue of the decline of ore grades in copper deposits. In some publications [132,166–170], the effect of ore decreasing in the last years has been pointed out. This fact has been supported by publications based on analyses of historical data by Mudd [114,166,171–173], Craig et al. [174] and Norgate [170]. Findings of a study by Calvo et al. [132], had established that the problem of ore decreasing is not a theoretical issue anymore, instead it is a reality. In that research, the decline of ore grades in 25 mines in Chile, Australia, and Peru was investigated. The production of these mines accounted for 32% of the total copper production. During ten years, from 2003 to 2013, it was observed a 25% reduction on average of the ore grade. The decline in copper ore grade was accompanied by an increase in 46% energy

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consumption on average. Another key finding in that publication was related to the close relationship between the decrease of ore-grade and the increment of specific energy. It was observed for copper and zinc the exponential growth of the energy required for metal extraction when the concentration of metal decreased in the mine and approximated to the concentration in the Earth's crust [132].

From a production site, according to statistics and reports of the US Geological Survey (USGS) [175–178], the primary producers of copper mine were: Chile, the United States, and Peru with an average of 4.0, 1.5 and 0.8 million tons per year, respectively as indicated in **Figure 17** from 1900 to 2014.



Figure 17. World copper mine production by country. Other means the total production of countries whose average individual production was lower than 430 million tons per year. (Source: [175–178])

The Andes Mountains in South America is a region with essential copper deposits. Findings of a study on the assessment of mineral resources of copper, molybdenum, silver, and gold published by Cunningham et al. in 2008 estimated that "may be almost 1.3 times as much copper to be found in porphyry copper deposits of the Andes as has already been found" [179]. This shows the potential of the region for copper production. Although copper is the most recycled metal, 90% recyclability according to a study of the United Nations Environment Programme (UNEP) [180], its consumption has increased rapidly, as previously noted. This also means that deposits

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with higher content of copper have been already exploited. This situation has produced the increment on the energy demand because of the production from lower-ore grade deposits. In the limit, minerals would be concentrated from common rocks. In the next section the concentration of copper from a low concentration ideal deposit is studied.

6.3. The concentration of copper ore from Thanatia

In this case, Thanatia would represent a mixture of ore-bearing minerals with chalcopyrite, at low concentration in the Earth's crust (x_c). The concept of ERC accounts for the energy required to have copper concentrate at an average ore-grade (x_m) from Thanatia (x_c). In order to calculate the ERC, Valero et al. [40] made assumptions, some of the main ones were: concentration of copper in the Earth's crust x_c = 6.64×10^{-5} g/g [111], average ore grade x_m = 1.67×10^{-2} g/g [110]. Also, the authors considered that 60% of the total energy was utilized for the mining and concentration processes [109], **Table 10**.

Table 10. The exergy replacement cost (ERC) for copper in GJ per ton of element. (adapted from [12])

Mineral	Mineral ore	x_c (g/g)	x_m (g/g)	ERC (GJ/t)
Copper	Chalcopyrite	6.64E-05	1.67E-02	292

Typical copper ore-grade in open-pit mines are 0.5%, and 1% or 2% in underground mines [181]. To extract the valuable metal, the processing route depends upon the type of ore. Two main ore types can be found, sulfides and oxides. For both ores, the comminution process is required. During this stage, particles are reduced in size through crushing and grinding until the metal can be liberated [117,125].

The main route for sulfide ores includes the concentration through a flotation process [43]. Afterward, a pyrometallurgical process which includes smelting and refining is performed. Schlesinger et al. [181] report that a vast majority (80%) of copper is obtained from sulfide ores and only a small amount (20%) via a hydrometallurgical process. The most common sulfide ore is chalcopyrite (CuFeS2) [182].

The purpose of this chapter is to upgrade the previous value of ERC for copper. Therefore the same conceptual scheme will be applied. It means that the target is to concentrate copper from its ore, chalcopyrite, available at Thanatia's composition ($x_c =$

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0.006%) to the average copper content in mines ($x_m = 0.5\%$), expressed as a percentage by weight.

6.4. Development of the model and results

6.4.1.Explanation of the model

Figure 18 shows the stages of comminution and concentration for the computational model.



Figure 18. Stages of modeling and simulation. The comminution process consists of crushing and grinding. The concentration is based on froth flotation.

The total specific energy to concentrate copper to an average ore grade (0.5% Cu) from Thanatia (0.003% Cu) was calculated: as the sum of the energies in the ore handling process and the energy required for its concentration, **Figure 19**.

The ore handling process included transportation of the ore with Thanatia composition to the concentration plant. In the concentration facility processes of comminution and flotation were supposed to be performed. A complete list of the substances in Thanatia, chemical formula, and the percentage by weight considered for this model can be found in [183]. The ore-handling phase was considered to involve the transportation of ore from an open pit mine (surface mining) to the concentration plant. For this, it was assumed a minimum distance between the mine and the concentration plant, so that the fuel consumption per ton of ore prevailed over the distance of transportation. Then, taking into account the copper concentration in the feed stream of 0.003%, the specific energy per ton of copper was calculated.

The comminution was assembled into three circuits: crushing, grinding, and regrinding. During crushing, the reduction of particles, size was carried out in primary and secondary crushers. The grinding stage was achieved by semi-autogenous (SAG) and ball mills. As Thanatia represents a complex ore mine (a mixture of different low-content minerals), a regrinding stage was also considered before flotation.

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Figure 19. Conceptualization of the total energy required to concentrate copper ore from Thanatia as the sum of energies for handling and concentration processes.

In order to determine the theoretical power draw during comminution, Equation (8) was used. Both, feed (F80) and product (P80) passing sizes were obtained from the HSC Sim 9 [115] model. The work index (Wi) for copper ore may vary from 4 to 30 kWh/t [125]. An average value of 14 kWh/t was considered for the calculation of the specific energy consumption (W). This value was also taken by Valero and Valero [158] to compute the exergy of comminution and concentration of different minerals. To reduce the complexity of using Rowland Efficiency factors (EFx) in Equation (8), the procedure explained by Will and Finch in [117] for the selection of mills through manufacturer's data was followed. In this procedure, EFx with a value of 1 was assumed, then the specific energy consumption (W) for every mill was computed. With the W value of every mill and information by manufactures, models were selected, then the number of mills was estimated. Accordingly, for primary and secondary crushers, information published in [124,159] for gyratory and cone crushers was considered. For grinding, we regarded data of specific energy for SAG and ball mill reported by Latchireddi and Faria [160]of 10.26 kWh/t and 7.59 kWh/t, respectively. Technical data for the HIG mill published in [117] was utilized. Then, with the nominal power available for every mill, the power draw in comminution was calculated. The power required on the flotation process of copper was obtained directly for the model in HSC Sim 9 [115] model. Then, with the feed flow rate (4500 t/h) and its copper concentration (0.003% Cu) the specific energy per ton of copper was determined.

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The starting point for the design of a concentration plant is the analysis of the ore type in the laboratory. From these analyses and best practice of other similar facilities, the appropriate flowsheet for the plant was designed. In our case, due to the lack of experimental data of Thanatia, the computational model was done based on an extensive literature review of copper-concentration plants and experience of the research group.

For the development of the model with HSC Chemistry-version 9.4.1 software [115], different references were studied to analyze both flowsheets and state-of-the-art technologies for copper concentration [116,117,125,169,170,181,184–187]. Also, the work on Abadias et al. [157] about modelling of copper processes from a circular-economy perspective was considered. For the model, many variables were considered for the comminution and flotation process. Due to the high number of variables for the model, only some are described.

Figure 20 shows the circuits in the comminution and flotation processes modeled with HSC Sim 9 software [115]. Computational requirements for this model were the same as for the model of iron-ore. An explanation of the stages is developed below.

Based on an analysis of operating data for copper flotation mills published in [125], and information of a low-ore grade mine available in [186], a flow rate of 4500 tons per hour was assumed as the input for the concentration plant. A top size in the ore feed of 600x105 μ m was considered. Three circuits in the comminution were assumed for the model: crushing, grinding and regrinding. The raw material with 260x105 μ m (F80) size was the feed in the crushing circuit. Crushing was carried out by a gyratory and cone crushers as primary and secondary crushers. Controls for particle size output (P80) were set-up for the crushers, 175000 μ m, and 45000 μ m, respectively. Between the primary and secondary crushers to the grinding circuit. The latter was made up of SAG and ball mills with controls for particle size output (P80) of 5000 and 145 μ m, respectively. After the SAG mill was placed a classifier with a cut size of 2300 μ m. The conjunction of classifiers, mixer, and hydrocyclone in the crushing and grinding circuit allowed to achieve a particle size in the comminution process about 100 μ m, **Figure 21**.

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Flotation

Figure 20. Flowsheet of concentration and tailings from Thanatia to copper ore.

The hydrocyclone overflow reported to the flotation circuit. The first stage consisted of conjunction of rougher and scavenger cells. Taking into account, Thanatia represents a complex ore mine, and a regrinding stage was also considered. A high-intensity grinding mill (HIG) was selected for this task with a control for the output particle size of $34 \,\mu\text{m}$. Concentrates from the rougher and scavenger cells were assumed as the feed into the HIG mill. The output of the HIG mill reported to the second arrangement of cleaner and scavenger cells. Tailings from the scavenger of the first and second concentration stages were conducted to the final tailings thickener, **Figure 22**. To achieve the required concentration of copper, the overflow of the latter stage was the input in a pack of flotation tanks, re-cleaner 2.

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Figure 21.Comminution process for the concentration of copper ore from HSC Sim 9 software.

For the flotation process, fast kinetics constants (kf) were set up for chalcopyrite, the main copper carrier, in the range of 1 to 2.5. These values were under those reported by Dua et al. [188] and Fuerstenau et a. [189]. The volume and number of cells for the flotation tanks were established upon typical values of cells per bank on manufactures data published by Weiss [125], and Wills and Finch [117]. With these considerations, the model was set up for the comminution and flotation processes.

6.4.2. Results and validation

From the model, direct results were: particle size for feed and output of the crushers and mills in the comminution process as summarized in **Table 11**. The reduction ratio (Rr) is determined by dividing F80 to P80 for every mill, and the total reduction ratio is the product of every mill, as indicated in [116]. In this case, the total reduction ratio is 480. For the flotation process, direct results were retention time and power consumption, **Table 12**.

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The result of the flotation process was a product with a mass flow rate of 19.81 t/h with a concentration copper of 0.5%. During the concentration process of copper from Thanatia, its recovery was 87%. Along with copper other elements were recovered, their recovery rates are shown in **Figure 23**.



Figure 23. Recovery of elements from the concentration of copper from Thanatia.

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Stage Equipment		F80 8 (µm)	P80 (μm)	Reduction ratio (Rr)
Crushing	Crushing Primary crusher		175000	2
	Secondary crusher	219797	45000	5
Grinding	SAG mill	16145	5000	3
	Ball mill	1204	145	8
Re-grinding	HIG mill	84	34	2

 Table 11. Feed and product size and reduction ratio for the comminution process.

Table	<i>12</i> .	Retention	time	and	power	draw	for	the	flotatio	on	process.
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Stage	Retention time (min)	Power (kW)
Rougher	7	960
Scavenger	5	660
Cleaner	29	1540
Scavenger	37	1540
Re-cleaner 1	13	450
Scavenger	15	450
Re-cleaner 2	16	264

The validation of the model consisted of the comparison of the results obtained from the model for the comminution and concentration processes. For the comminution, a parameter to consider was the particle size. As previously mentioned, a typical particle size is below 100 μ m. From the simulation, a value from comminution (crushing and grinding) was 145 μ m (**Table 11**). Although there was a difference of 45 μ m between both values, it did not mean that the model was wrong for the comminution. It was expected since the model was handling a complex ore with a low concentration of metals with different size distribution. To reduce further the particle size, in the model, a regrinding stage was included, identified by HIG mill in Figure 7. The particle size after regrinding was 34 μ m (**Table 11**).

Another parameter for validation was the retention time in flotation, **Table 12**. In [125] retention time for the roughing circuit was in the range of 13 to 16 minutes. In comparison with those of the model, for Rougher 1 and 2 were in this range. However, the retention time of Rougher and Cleaner were shorter and larger, respectively. It is expected to have a lower concentration of copper in the first rougher, considering that Thanatia was a complex ore. That is why a shorter time was obtained in Rougher. In the case of the Cleaner, recirculation produced an increment in retention time. Recirculation circuits were necessary to achieve the final concentrate with 0.5% Cu.

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A key parameter for the validation of the model was final recovery. Haque et al. [190] modeled pyro and hydrometallurgical low-grade copper deposits. In this publication, the recovery of copper was assumed to have a yield between 86% to 89%. The recovery obtained from the simulation campaign in that paper was 87%, which was in the range of the expected recoveries.

Even though Thanatia is a mixture of primary minerals in the Earth's crust with low concentration, the results from the model developed in HSC Sim 9 software [115] under the assumptions described for the model set-up, were logical and reliable as shown above.

With the considerations for the model set-up previously explained in sub-section 6.4.1, the power demand for the flotation plant was estimated, **Table 13**.

Stage	Power Demand (MW)	Power Demand (%)
Crushing	3.8	2.0
Grinding	174.9	92.7
Re-grinding	4.1	2.2
Concentration	5.9	3.1
TOTAL	188.6	

 Table 13. Power draw for comminution and concentration processes.

From **Table 13** most of the power demand in the concentration process was due to the comminution process (c.a. 97%). Within this process, the grinding circuit was the biggest consumer. By following the methodology previously explained, the specific energy for the concentration process was calculated, **Table 14**.

Table 14. Specific energy to concentrate copper from Thanatia based on the power demand of 188.6 MW.

	Cu-concentration	Flow rate	Specific Energy
	(wt-%)	(t/h)	(kWh/t)
Feed ore	0.003	4500	42

The energy required for the concentration of copper from Thanatia can be represented by a ton of ore or concentrated metal accordingly to the feed or output flow rate. The specific energy was equivalent to 151 MJ/t. This figure was more than twice the average value of electricity consumption at a concentration copper plant in Chile for 2015

Beyond a tonnage perspective for the assessment of mineral resources. Focus on Latin America and the Caribbean (80.8 MJ/t) as reported in [191]. If the specific energy is expressed by a ton of concentrated metal, this value was 34278 MJ/t. This represents one order of magnitude higher than the specific energy required in current copper-concentration processes reported by Norgate and Haque [190].

Considering the flow rate of 4500 t/h and its copper concentration of 0.003%, and the methodology described, the specific energy for the concentration of copper from Thanatia was computed. For the ore-handling stage, a value of 1.2 liters of diesel per ton of rock was considered for the specific fuel consumption. This was a figure reported by Calvo at al. [132] as an average value for the energy consumption in the Chuquicamata open-pit mine. The specific energy for the concentration of copper from Thanatia is shown in **Table 15**.

Table 15. Specific energy for the concentration of copper from Thanatia in GJ perton of element.

	Specific Energy (GJ/t)
Ore handling	1546
Concentration	5030
TOTAL	6576

For the current work, the ore-handling phase accounted for 24% of the total specific energy in the concentration process of copper. This agrees with figures reported by Norgate and Haque [162].

The second stage for the re-cleaner in the layout should be thought for the requirement to concentrate copper from very-low copper ore (Thanatia). The regrinding circuit in the layout should be interpreted as the need to reduce the particle size to get metal from the complex ore (Thanatia). This agrees with the study by Norgate and Haque [162] that illustrated that the most energy-intensive stage when decreasing ore-grades in copper was mineral processing.

Due to the complexity of Thanatia to determine which particle size will be optimum to recover as much as chalcopyrite, a sensitivity analysis was to be performed. In the study, two parameters were considered as independent variables to estimate the specific energy. The first parameter represented the possible hardness of Thanatia during the comminution process. For this, it was assumed that the values of Wi were: 4, 9, 20 and

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30 kWh/t. The other parameter that is key in the estimation of the specific energy is the total reduction ratio (Rr). Values of reduction ratios for the sensitivity analysis for this model are shown in **Table 16**.

Scenario	Total reduction	
	ratio (Rr)	
1st	480	
2nd	626	
3rd	766	
4th	953	
5th	1260	
6th	1758	
7th	2667	
8th	4081	
9th	6247	
10th	11673	

Table 16. The total reduction ratio of the mills for the sensitivity analysis.

By considering the variation in reduction ratios (Rr) and Bond work index (Wi), **Figure 24** shows the specific energy for the concentration of copper from Thanatia. In order to have a scheme of comparison the information was converted into GJ per ton of copper. Then with this and the exergy replacement cost (ERC) for copper reported in [12] a comparison with the specific energy of the current work was done in **Table 17**.

Table 17. Comparison of the specific energy of the current work with other reported values in GJ per ton of element.

	Specific Energy (GJ/t-Cu)	Source
ERC based on HSC	3100 - 30890	current work
Previous ERC	292	[12]

The differences of values of the specific energy to concentrate copper from Thanatia from the model in HSC vary in orders of magnitude. The lowest value of the specific energy from the simulation was one order of magnitude higher than the ERC for copper.



Figure 24. Specific energy for the concentration of chalcopyrite from Thanatia with respect to the total reduction ratio (Rr) and Bond's work index (Wi).

From **Figure 24**, the specific energy for the concentration of chalcopyrite depends on the hardness of the rock (Wi) and the final particle size (represented by the Rr). To estimate a value for a "New ERC's copper" according to the model in HSC, it would be taken a value of Wi=15 kWh/t as previously explained in sub-section 6.4.1. This value agrees with the major element in Thanatia, where more than 22 wt-% in Thanatia's composition is due to quartz [40]. The latter exhibits a Bond index of 14.4 kWh/t according to characterization and testing of samples published in [192]. Also, it would be assumed that for the concentration in Thanatia (*x*_c) as shown in **Table 10** the final size of P80=34 μ m (Rr=480) for chalcopyrite would be enough to extract as much as the metal from Thanatia. With these two assumptions, then specific energy for the concentration would be 6576 GJ/t-Cu. Note this value is obtained as an example of a model in HSC in **Table 15**.

In summary, the previous ERC and the new ERC for copper differ considerably in the method of estimation. While the previous one was determined only based on mathematical and analytical analysis, the new one has strong support from a metallurgical point of view. If considering the previous ERC further processing of copper to obtain copper in cathodes, additional stages of crushing will be required, which will imply an extra expenditure of energy. The latter is because, in the calculation

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of the previous ERC, the separation process (crushing and grinding) was not even considered. On the contrary, further treatment from the new ERC for copper would mean an energy saving because the ore is already ground to P80=34 μ m.

6.5. Concluding remarks

The layout was established upon an extensive literature review of different copper concentration facilities and experience of the research group. By the results of this model, the next concluding remarks can be drawn:

- The comparison of results of the model was in the same range of parameters published by other authors; hence, the results of the model were logical and reliable.
- From the model, a new ERC value for copper can be taken as 6576 GJ/t-Cu by assuming that Thanatia would exhibit similar behavior as previously described (Wi=15 kWh/t and Rr=480). This value is twenty-three times higher than the previous ERC. Both differ considerably on the method of calculation. While the previous value was estimated by mathematical and analytical analysis, the new one has strong support from an engineering point of view with specialized software.
- Results also reveal that when dealing with low-ore grade copper deposits, a closer look should be paid to regrinding and recirculation circuits in the flotation process.
- It points out the importance of the mineral heritage of nations, especially in South American countries, where these deposits are located, they should reconsider the significance they already have in a global commodity market.

Chapter 7. The production of metals from Thanatia: gold

7.1. Introduction to the chapter

This chapter deals with a model in HSC software for the production of gold considering the mineral composition of Thanatia. First of all, a model to get a rich-gold mine is being performed, and its result is compared to the previous ERC. Secondly, based on the experience of the model for gold-ore, some modifications will be done to obtain gold in cathodes. In addition to calculating, as in the other cases, the new ERC of gold, in this case, one step further has been done, and it was obtained the thermodynamic rarity, which is the sum of the ERC plus the embodied exergy, or the useful energy needed to obtain gold from Thanatia. The information **Paper II** has been considered in the present chapter.

7.2. World mine production

Because of its excellent properties, such as electrical conductivity, stability at environmental conditions, and meaning of nobleness in ornaments, gold has been exploited for centuries. In 2015, leading gold producers were: China 20%, Australia 12%, Russia 11 % and Canada 7%. Peru, South Africa, and Mexico had 6% of world mine production. In **Figure 25**, the production of gold from 1998 to 2015 by country is shown based on statistics and reports of the US Geological Survey (USGS) [7,175].



Figure 25. World mine production of gold by country.

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Statistics of the World Gold Council [193] shows that in 2017 the primary uses of gold were mostly demanded by the manufacture of jewelry (53%), 39% was used for financial purposes for investment and central banks, and 6% in electronics. The historical trend of the consumption of gold by sector is shown in **Figure 26**.



Figure 26. Historic demand for gold by sector. (Source: [193])

7.3. Production of gold from Thanatia

The purpose of this chapter is to obtain gold from Thanatia in order to upgrade the previous value of TheRy reported by Calvo and colleagues [12]. It means that the first step is to estimate the ERC to concentrate gold from Thanatia's composition (x_c) to the average gold content in mines (x_m) and then with additional processing to obtain gold. In **Figure 27** minerals with a high gold concentration in Thanatia are shown. A complete list of the substances in Thanatia can be found in [40].

For the interest of this chapter, **Table 18** shows the ERC and TheRy of gold. As previously explained in sub-section 3.4.1.2, TheRy is computed as the sum of ERC and the energy required for the production of metals obtained from mines (energy for mining, concentration, and smelting and refining). **Figure 28** indicates the idea to estimate the energy needed to get gold from Thanatia.

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Table 18. The exergy replacement cost (ERC) and thermodynamic rarity (TheRy) for gold in GJ per ton of element. (adapted from [12])

Figure 27. Gold-bearing minerals in Thanatia in wt-%. The arrows above each column show the concentration of gold in wt-% of each mineral.



Figure 28. Conceptualization of the total energy required to obtain gold from Thanatia. Thermodynamic rarity (TheRy) as the sum of exergy replacement cost (ERC) and additional processing.

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7.4. Development of the model and results

7.4.1.Explanation of the model

Due to the Nature of Thanatia, the design of different processes to obtain gold has been done based on a literature review and an in-depth analysis of flowsheets. Basics about gold processing were studied from publications by Marsden and House [128], Yannopoulos [194], and mineral processing by Wills and Finch [117]. Technical reports for gold processing plants were also studied, such as Éléonore Project in Canada [195], Fruta del Norte in Ecuador [196], Peñasquito in Mexico [197], and Pueblo Viejo in Argentina [198]. Investigations about the gravimetric concentration of gold were also analyzed, such as works by Carrasco [199], and Valdivieso et al. [200]. The metallurgical recovery of gold was examined based on investigations by Sen [201], Muir et al. [202], Beyuo and Abaka-Wood [203], Brandon et al. [204] and Adams [205]. Publications by Elis and Deschênes [206], Zhang and colleagues [129], as well as the layout of Emperor mines in Fiji published in [128], were studied for processing of tellurides ores. The energy consumption in gold mines was derived from the research by Ballantyne and Powell [185], and modeling and simulation of processing plants for recycling of gold from that of Reuter and van Schaik [207].

For the model, many variables were considered, yet due to its high number, only the important ones are written in the next lines. Computational requirements for the model and simulation were the same as for the model for iron-ore concentration. The feed for the model was assumed to 6000 tons per hour with a top size of 600 mm. This comes from and the analysis of technical reports about open-pit gold mines [197,198,208] and information about telluride mines [128,209],. **Figure 29** shows the main stages for the concentration of gold from Thanatia.

During ore handling, it was assumed consumption of 0.6 l/ton of rock as fuel consumption as reported in [132] for open pit mines. For this, it was supposed that the facility was located in the nearby of the mine so that the distance did not influence fuel consumption. For the concentration, three circuits in the comminution were set up: crushing, grinding and regrinding. The 80% of particle size passing through the primary crusher (F80) 200 000 um is fed in the comminution circuit. Crushing is carried out by a

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cone crusher, control for particle size output (P80) is set-up for the crushers to 60 000 um. A screen (Screen 1) with a cut size of 100 mm is placed in a closed circuit with the cone crusher. Then, Screen 1 reports to the grinding circuit made up with a Semi-Autogenous Grinding mill (SAG) and two ball mills. Screen 2, which has a cut size of 20 mm, is connected in closed circuit with the SAG mill. The control for the particle size output (P80) for the SAG mill is 6000 um. Screen 2 feeds the circuit of the two ball mills (Ball Mill 1 and 2). Control of the passing particle size (P80) for these mills were 500 μ m and 75 μ m, respectively. Cyclone 1 is located between both ball mills with a cut particle size of 150 μ m. Cyclone 2, placed after Ball Mill 2 separates due to the high density of native gold from tellurides. The cut size in this cyclone was 19 μ m.

In order to determine the theoretical power draw during comminution, Equation (8) was used. The feed (F80), as well as the product (P80) passing sizes were obtained from the HSC model. The work index (Wi) for a gold ore may vary from 3 to 42 kWh/t [192]. In a first trial to estimate the specific energy consumption (W) a representative value of 15 kWh/t was considered. A slightly lower value with this corresponding conversion (16.3 kWh/t) was assumed by Valero and Valero [158] to calculate the exergy of comminution and concentration of different minerals. The arrangement of mills for comminution is shown in **Figure 30**.

As it was done for iron and copper, to simplify the complexity of using Rowland Efficiency factors (EFx) in Equation (8), the procedure explained by Will and Finch in [117] for the selection of mills was followed. Hence, a value of 1 for EFx was assumed, then the specific energy consumption (W) for every mill was computed. With W for every mill and together with the information in catalogs by the manufactures, models of mills were selected. The power required for the flotation process was obtained directly from the HSC model [115]. The specific energy per ton of gold was determined with the feed flow rate (6000 t/h) and its concentration in Thanatia (x_c = 1.28E-3 g/t).

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Figure 29. Flowsheet for the processing of gold from Thanatia.

After Cyclone 2, two streams are split because of the difference in density: one with native gold (high density) and the other containing gold-bearing tellurides (low density). Each stream will have different treatments, **Figure 30**. Due to the high density of gold, only gravity concentration is necessary for the native gold stream. Schematics of gravity concentrators is shown in **Figure 31**. Information regarding continuous gravity concentrators from [210] was used to determine the energy spent on this stage. With the

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processing of the native gold stream, the concentration in mines (x_m) named in **Figure 27** as "gold ore" was reached. Hence the ERC was computed by adding the energy of the processes involved in its production, such as ore-handling, comminution, grinding and gravity concentration.

To produce gold, it is necessary to continue with further processing (coined as "additional processing" in **Figure 27**) of the native gold stream through a metallurgical process. Since cyanidation is widely used for the production of gold [6,128,205], leaching was considered to recover gold from this stream.



Figure 30. Comminution circuits for the production of gold from Thanatia.

On the other hand, after Cyclone 2 the stream with tellurides requires a different treatment to extract as much gold as possible. For tellurides, a re-grinding stage up to 12 μ m is the first process. Subsequently, flotation is required to separate sulfides and other unwanted minerals, **Figure 32**. The flotation process consists of two stages of arrangements of rougher, scavenger, and cleaner. The combination of stages of reverse flotation, recirculation, and cleaners guarantees the appropriate concentration of gold before the pyrometallurgical process of roasting. The volume and number of cells for the flotation tanks were established upon common values of cells per bank on manufactures

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data published by Weiss [125], and Wills and Finch [117]. Through roasting, most of the gold contained by the tellurides are liberated. For the model, data from [128] about roasters was considered. The consumption of natural gas was assumed for the roaster to be 0.35 GJ/t Au as reported by Norgate et al. [211] on a publication about the assessment of environmental impacts of gold production. Then, leaching through cyanidation is required for the processing of this stream of gold. Electricity consumption during leaching was taken as reported in [211] and equal to 1.4kWh/t ore.



Figure 31. Grouping of gravity concentrators for the production of gold.

Finally, electrowinning for the refining of both streams, native and goldtellurides is needed to produce high-purity gold. The specific energy for these stages ("additional processing") is calculated from the concentration of gold ore (x_m). For the electricity consumption in electrowinning, a value of 3100 kWh/t Au was taken as reported by Norgate et al. [211]. It is important to note that, for the production of gold from common rocks understood from "gold ore," additional grinding is not required because the particles are already in the accurate size for concentration. This means an energy saving factor to estimate the total specific energy for the production of gold from Thanatia. This is a considerable difference with the previous ERC for gold. Representative components of the metallurgical processes for the production of gold, roasting, leaching, and electrowinning can be seen in **Figure 33**.

Beyond a tonnage perspective for the assessment of mineral resources. Focus on Latin America and the Caribbean The thermodynamic rarity (TheRy) entails the energy required to produce gold from Thanatia. Hence it adds the specific energy to concentrate gold ore (from Thanatia to gold ore) and the energy required for additional processing to produce pure gold.



Figure 32. The arrangement of flotation cells prior to the metallurgical treatment for the production of gold.



Figure 33. Schematics for roasting and leaching for the production of gold.

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7.4.2. Results and validation

In agreement with **Figure 28**, results are presented in two parts, the first one the energy required to concentrate gold-ore from Thanatia and the other for gold-ore to pure gold. **Figure 28**. Conceptualization of the total energy required to obtain gold from Thanatia. Thermodynamic rarity (TheRy) as the sum of exergy replacement cost (ERC) and additional processing.

7.4.2.1 Specific energy from Thanatia to Gold-ore

Direct results of the computational model in HSC for the concentration of gold-ore from Thanatia entails the processes of comminution, grinding, and gravity concentration. The particle size for feed (F80) and output (P80) for comminution are shown in **Table 19**. Feed (F80) and product size (P80) for the comminution process during concentration of gold-ore from Thanatia. For gravity and concentration, four continuous concentrators were assumed, and their power draw is shown in **Table 20**. Power consumption for the gravity concentration during concentration of gold-ore from Thanatia.

Table 19. Feed (F80) and product size (P80) for the comminution process during concentration of gold-ore from Thanatia.

Stage	Equipment	F80 (µm)	P80 (µm)
Crushing	Primary crusher	245,631	200,000
	Cone crusher	249,916	60,000
Grinding	SAG mill	39,439	6,000
	Ball mill 1	2,253	500
	Ball mill 2	127	75

Table 20. Power consumption for t	the gravity	concentration	during co	oncentration of
gold-ore from Thanatia.				

Equipment	Power (kW)
Rougher	3,000
Cleaner	750
Re-cleaner 1	150
Re-cleaner 2	30

The specific energy depends upon the work index (Wi), and final size (P80) as written in Equation (8), the validation of the model was done for a representative work index of 15 kWh/t and final size of (P80) 75µm. With the methodology described above and other assumptions for the model set-up previously explained, the power demand

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and specific energy, based on the feed of 6000 t/h and concentration of 1.28E-3 g/t, are shown in **Table 22**. From this table, comminution represents more than 90% of the power demand. Therefore, a key parameter for the validation of the model is a comparison of the specific energy for comminution. This value was in agreement with figures for energy requirements for beneficiation reported by Chapman and Roberts [148]. Then, taking into account the ore handling and the previous values for comminution and gravity concentration, hereafter concentration, the total specific energy per ton of element is calculated **Table 22**.

Table 21. Specific energy for the concentration of gold from Thanatia in GJ per ton of element.

	Specific Energy (GJ/t)
Ore handling	1.62E+07
Concentration	4.54E+07
TOTAL	6.17E+07

Table 22. Power demand and a specific energy for comminution and concentration processes from Thanatia to gold-ore.

Stage	Power Demand (MW)	Specific Energy (kWh/t)
Comminution	102	17.03
Gravity concentration	4	3.67
TOTAL	106	20.7

Because of the complexity of Thanatia, where its work index Wi cannot be accurately predicted because of the large number of minerals, it is necessary to estimate the specific energy using a sensitivity analysis. In this analysis, Wi is varied from 3 to 42 kWh/ as reported in [192]. For the sensitivity analysis, five working indexes were considered, such as 5, 7, 15, 21, and 42 kWh/t. The specific energy required to concentrate gold until an average representative concentration in mines from Thanatia would be more precisely denoted by the variation of a parameter of the comminution process, and hardness of the rock. These parameters have been represented by the final particle size (P80) at the end of the comminution and work index (Wi). **Figure 34** shows in logarithmic scale the total specific energy to concentrate gold from Thanatia as a function of the final particle size (P80) with five working indexes. As can be observed in this figure for the five working indexes, the specific energy for comminution increases as the final size

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decreases. Also, when the ore is harder (higher work index), more energy is required for its processing. For visual comparison purposes, the value of ERC for gold from Valero and Valero as reported in [12] (assuming that it had been calculated with 75 μ m) is also shown in **Figure 34**, the difference in orders of magnitude is highlighted in this figure. Values of specific energy can vary from 3.3E+07 GJ/t-Au to 3.8E+08 GJ/t-Au for 80% final size (P80) from 75 μ m to 10 μ m and Wi = 5 and 42 kWh/t, respectively.

By making a comparison of the specific energy necessary to concentrate gold ore from Thanatia with the HSC model as shown in **Table 23** with the exergy replacement cost (ERC) of gold reported in [12], it can be seen that they differ in two orders of magnitude. This discrepancy is due to the difference in procedures to calculate both values, while the current work is based on a mineral processing model developed in HSC, the one published by Calvo et al. [12] is based on assumptions of Valero and colleagues about the analysis of ore-grade decline and increase of energy for processing expressed by Equation (7).



Figure 34. Total specific energy to concentrate (in the log. scale) gold from Thanatia as a function of the final particle size (P80) and different working indexes. For comparison purposes the value of ERC for gold of 5.5E+05GJ/t Au (reported in [12])

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Specific Energy (GJ/t-Au)	Source
3.3E+07 to 3.8E+08	current work
5.5E+05	[12]
	Specific Energy (GJ/t-Au) 3.3E+07 to 3.8E+08 5.5E+05

Table 23. Comparison of the specific energy to concentrate gold from Thanatia with other reported values in GJ per ton of element.

As can be seen in **Figure 34**, the specific energy for the concentration of iron minerals depends upon the hardness of the rock (Wi) and the final particle size. To estimate a value for the new ERC for gold according to the model in HSC, it would be taken a Wi from **Table 21**. As also considered by Valero and Valero [158] as a typical value for different minerals of Wi=14 kWh/t. This value agrees with the significant element in Thanatia where more than 22 wt-% in Thanatia's composition is due to quartz [40]. The latter exhibits a Bond index of 14.4 kWh/t according to characterization and testing of samples published in [192]. Besides, it would be assumed that for the concentration in Thanatia (*x_c*) as shown in **Table 18** the final size of P80=75 μ m for gold ore would be enough to extract as much as the metal from Thantatia. With these two assumptions, then the ERC calculated in **Table 21** agrees with these two assumptions. Hence the new ERC for gold would be 6.17E+07 GJ/t-Au. This value differs in two orders of magnitude with the previous ERC.

From a mineral processing point of view, in a benchmark for energy consumption in comminution for the processing of copper and gold ores in Australia, Ballantyne et al. [185] reported an average value of 0.353 MWh/oz-Au. If this is converted into the same units of the specific energy herein stated, most of the energy is due to comminution; a comparison is valid. This comparison shows a difference of three orders of magnitude. It means that the concentration of gold-ore from common rocks, Thanatia, would imply consumption of three orders of magnitude higher than the current expenditure of energy for comminution.

By taking 75 μ m as the final particle size for comminution, the different stages for the concentration of gold can be represented in a graph for different work indexes, **Figure 35**.

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Figure 35. Specific energy for the concentration of gold from Thanatia for P80=75 μ m for different work indexes (Wi).

By analyzing **Figure 35**, it is appreciated that the highest energy consuming stage during the concentration of gold from Thanatia is the crushing and grinding processes. Ore handling and gravity concentration remain stable because the same amount of ore would be moved and concentrated regardless of its work index. Also, it is seen how the specific energy increases as the ore become harder (higher Wi). An exponential trend in energy consumption is shown when the ore becomes harder. This effect is again evidence of the entropic Nature of mining processes.

7.4.2.2 Specific energy from the ore to gold

For the production of gold, no additional grinding is needed, only two other concentrators, flotation, and metallurgy must be added. The results from the model are shown in the next tables as follows: gravity concentration in **Table 24** and flotation in

Table 25.

Table 24. Additional gravity concentration to produce gold from Thanatia.

Equipment	Power (kW)
Conc. 1	7.5
Conc. 2	7.5

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Stage	Retention time (min)	Power (kW)
Rougher (RG)	5	528
Scavenger (Sca)	10	1000
Scavenger 1 (Sca 1)	5	320
Cleaner (CL)	6	320

Table 25. Retention time and power draw for the flotation process.

The retention time from the model in HSC,

Table 25, was in the range of values reported by [125,137,189], this fact constitutes a first step on the validation of results. Although Thanatia is a complex ore as an idealization of mineral dispersion and despite the singularity of the flowsheet for this research, the results from the model in HSC were logical and reliable.

As explained in the sub-section 7.4.1, and depicted in **Figure 28** by doing additional processing, gold can be obtained from Thanatia. The specific energy to produce pure gold from Thanatia based on the model in HSC would be equivalent to the thermodynamic rarity (TheRy) of gold reported in [12] postulated by Valero and Valero [40]. Accordingly, the energy required for additional processing to produce gold from the ore with Wi of 15 kWh/t and 80% passing through of 75 µm is shown in **Table 26**.

As it was expected most of the energy to produce gold from Thanatia corresponds to the ERC. As seen in **Table 26**, the difference in orders of magnitude between the ERC and additional processing is considerable (three orders of magnitude). Within the additional processes, the highest energy consumer was the leaching process, because no additional grinding is needed in this stage as explained in the methodology section. In comparison to the thermodynamic rarity for gold published in [12] (6.6E+05 GJ/t), there is a difference of two orders of magnitude because the difference of the new ERC for gold previously obtained.

	Specific Energy (GJ/t)
ERC	6.17E+07
Additional processing	
Concentration	4.80E+02

3.50E-01

7.70E+03

Roasting

Leaching

Table 26. Specific energy to produce gold from Thanatia.

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Cyanidation	1.90E+03
Electrowinning	9.6E+00
TOTAL	6.17E+07

7.5. Concluding remarks

From the analysis of results of the models to concentrate gold-ore and to produce gold in cathodes the next remarks can be done:

- The new ERC for gold would be 6.17E+07 GJ/t-Au by assuming hardness of the rock Wi=15 kWh/t and a final particle size of P80=75 µm. This value is two orders of magnitude higher than the previous ERC. Both values differ on the method of calculation. While the previous value was estimated by mathematical and analytical analysis, the new one has strong support from an engineering point of view with specialized software.
- Drawing a comparison with the TheRy, the result of our model shows a difference of two orders of magnitude with the one of Valero's. It means that the fact of having minerals concentrated in deposits is a representative factor of energy saving in the production of metals. The "free bonus" provided by Nature for having gold concentrated in deposits saves a tremendous amount of energy in the gold production process.
- In the limit, when ore grades decline until crustal concentrations, these ultimate costs will be required to mine and refine minerals, thereby making them unaffordable.

The issue of the decline in ore-grade on the specific energy for metal processing is studied in the next chapter.

Chapter 8. The ore-grade decline and its effect on the energy for metal processing

8.1. Introduction to the chapter

In the previous chapters it has been seen, at the limit of the Earth's crust, energy cost would increase enormously. The question now is, what would be the trend of energy consumption for metal processing when the ore grade decline. This question is solved through the case of gold using the metallurgical procedure with a model in HSC. This model confirms the exponential trend of the behavior of the specific energy when the ore grade decline. Some environmental impacts are evaluated with GaBi software. The information presented in this chapter is a summary of **Paper VI**.

8.2. Overview

The evolution of the decline of high-grade deposits has been investigated by different authors, such as Mudd [114,166,171–173], Craig et al. [174], Norgate [170] or Calvo et al. [132]. In this respect, and although the recycling of gold accounted for approximately one-third of the total supply from 1995 to 2014 [212], Mudd [166] observed a clear decline tendency of the ore grades Mudd [166] of gold-producer countries, such as Brazil, Australia, South Africa, Canada, and the United States,. For instance, in Australia in 1859 ore grades in gold deposits were 37 g/t and nowadays the concentration is found at 2 g/t. Cox and Singer reported in 1992, the average gold content of 0.22 g/t for different gold deposits [110]. While the ore grade decreases over time, the energy for metal processing increases. In 1991, the average energy consumption of two gold mines was 172 GJ/kg of gold, while in 2006, for twenty-two mines investigated was 187 GJ/kg of gold [166].

The need for renewable energy technologies for a decarbonized society will imply the use of more metals [2,135,136]. In a recent publication by Valero et al. [10] on material restriction for the manufacture of renewable energy technologies, it was pointed out that moving towards a low carbon economy would cause a deeper reliance on non-fuel minerals.

Norgate and Haque [211] and Rankin [6] have portrayed the exponential growth of the specific energy for metal processing while the ore-grade decline. Their research has been done from theoretical analyses of equations, assumptions or environmental software. The model in this section tries to more accurately study the effect of the ore-

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grade decline on the specific energy to produce gold from a metal processing point of view.

8.3. A model for the ore-grade decline

In this section, based on the model developed to produced gold from Thanatia, previously explained in section 7.4, some modifications were done to study the behavior of the specific energy required to produce gold by varying the ore-grade. For this endeavor, it was considered that the ore grade would decline from an average representative ore-grade to a concentration of gold found in common rocks. For simplicity with previous models with Thanatia, in this work, Thanatia's composition was modified by gradually decreasing its ore-grade from 2.72 g/t-Au to 1.44 1.44E-03 g/t-Au. The former ore-grade represents the current average concentration, and the latter is a concentration of total mineral dispersion (gold concentration in Thanatia). **Figure 36** depicts the conceptualization for the current model. A simplified flow chart of the comminution, concentration, and refining processes for the set-up of the model is shown in **Figure 37**.



Figure 36. Scheme for the study the effect of the decline of ore on the specific energy.

Also, by assuming that the ore will be located in different countries, some environmental impacts with GaBi software were estimated. For this task, version 8.7.0.18, and database 8007 [213] of GaBi were employed. The purpose of this work is to add more information to look for more sustainable mechanisms for the production of

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metals. Furthermore, we would like to encourage more in-depth analysis of the production processes of metals for a proper evaluation of the environmental impacts.





For ore-handling, the consumption of fuel for transporting the open pit mine to the facility plant was assumed 0.6 L/ton of rock as suggested in [132], where the tonnage prevails over the distance. Due to the dispersed state of minerals in Thanatia, it was treated as a complex ore. Therefore, the input ore in the model was assumed 6000 tons per hour. The concentration process consists of comminution (crushing, grinding, and re-grinding), gravity concentration and flotation. The specific energy during comminution was calculated with Equation (8). The 80% passing size of the feed (F80), and the product (P80) for every crusher and mill were obtained directly from the HSC model. Since Thanatia is a complex-ideal ore, a single value for its hardness cannot be readily determined. Similarly as described in section 7.4.2, it was considered a range of values for the work index (Wi) from 3 to 42 kWh/t [192]. The fact that of not taking into

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account a single value for Wi constitutes a difference with Valeros ' approach [12,40] to estimate the specific energy.

Because of the high density of gold, only gravity concentration is necessary for the native gold stream [117,199,200]. Manufacture's data about gravity concentrators were reviewed [210] about the consumption of energy. In case of the gold associated with the tellurides, a re-grinding is required to liberate much as gold as possible from tellurides. Then, flotation consists of circuits of roughers, scavengers and a cleaner which assure that gold is concentrated enough before roasting. The latter is a pyrometallurgical process in which gold contained by tellurides is liberated. In a publication about the estimation of some environmental impacts of gold production, Norgate and Haque [211] reported some figures for the specific consumption of energy. From this paper [211], it was assumed that consumption of natural gas was 0.35 GJ/t Au for roasting, 1.4kWh/t ore during leaching and 3100 kWh/t Au for electrowinning. The specific energy per ton of gold was estimated through the flow rate in the model and the respective ore grade.

8.3.1.Results and comments

As an example of the different procedures followed during the simulation campaign, **Table 27** shows the results to obtain the specific energy to produce gold with a representative work index (Wi) of 15 kWh/t and assuming 75 μ m (P80) size. As seen in this table, 57% of the total energy to produce gold from Thanatia corresponds to the concentration process (comminution, gravity conc., and flotation). To examine the energy consumption of these processes, the power draw and specific energy are shown in **Table 28**. In this table (**Table 28**) more than 90% of the energy is consumed by the comminution process (crushing and grinding).

Therefore as a way to validate the result from the model in HSC, the specific energy during this process is compared with values reported in the literature. Chapman and Roberts [148] and Ballantyne et al. [185] in their researches published some representative figures for the specific energy in the comminution process in general and processing of gold, respectively. By doing the appropriate conversion of 17.0 kWh/t into the same units as reported by Chapman and Roberts [148] (61 MJ/t) and Ballantyne et al. [185] (194 kWh/oz-Au), it is in the same range of magnitude with the figures reported by

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the authors. Therefore, we take the results of our model are logical and valid. These will be presented and analyzed in the next sections.

Process	Specific Energy (GJ/t-Au)
Ore-handling	8.53E-03
Concentration	2.39E+04
Roasting	3.50E-01
Leaching	7.68E+03
Cyanidation	1.85E+03
Electrowinning	9.57E+03
TOTAL	4.20E+04

Table 27. Results for Wi=15 kWh/t and P80 final size of 75 μm for an ore grade of 2.72 g/t-Au.

Table 28. Power draw and a specific energy for comminution, gravity concentration and flotation for Wi=15 kWh/t and P80 final size of 75 μ m for an ore grade of 2.72 g/t-Au.

Stage	Power Demand (MW)	Specific Energy (kWh/t-ore)
Comminution	102	17.0
Gravity concentration	4	0.7
Flotation	2	0.4
TOTAL	108	18.0

In the table above (**Table 28**) more than 90% of the energy is consumed by the comminution process (crushing and grinding).

Figure 38 shows the specific energy for the production of gold from Thanatia as a complex ore. The next processes were considered: ore-handling, concentration (comminution and gravity conc.), roasting, leaching, cyanidation, and electrowinning. **Figure 38** has been plotted by changing the ore grade (from 1.44-03 g/t Au to 2.72 g/t Au) and by a range of the work indexes and different final particle size (P80).

As it was expected, the higher values of the specific energy are higher when the work index (Wi) and the final size (P80) increase. An exponential growth exists, the specific energy consumption increases when the ore-grade of the deposit decreases. Also, when the particle size decreases, the specific energy for processing increases. That is why the band of specific energy is wider for P80 of 10 μ m rather than 75 μ m, and the former overlaps the latter.

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Figure 38. Specific energy for the production of gold with Thanatia's composition by changing the ore grade, work index (Wi) and final size in comminution (P80).

The model in HSC allows the use of a complex composition of minerals in low concentration, as they exist in Thanatia and it was possible to incorporate changes in ore grade. That is why our model in HSC is a more robust way to determine what was previously done by mathematical procedure done by Rankin [6] and with SimaPro by Norgate and Haque [211].

8.3.2. Some environmental impacts

The life cycle assessment (LCA) is a methodology to evaluate the effects on the environment of a product by measuring the impacts of the corresponding fabrication process [214]. LCA's principles have been applied to assess the environmental effects of the production of gold for a general location by Norgate and Haque [211] and China by Chen et al. [215]. None of these studies have gone deeper in the variables that intervene directly on the production process, for instance, the effect of the final size in comminution. In this work, through the direct export-import link between HSC and GaBi, we will evaluate the environmental impacts of the production of gold from ore with Thanatia composition.

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The assessment of impacts is mainly associated with electricity during comminution because it accounts for the highest energy consumption during the production processes. The LCA tool in HSC software allows doing the life cycle inventory (LCI), which is a stage before the LCA, easily by the production process under study. The tool enables to export an Ecospold file that is ready to be imported in GaBi. We followed this procedure, and we assumed that the ore deposit with Thanatia composition would be placed in one representative country in five continents and we interlinked the electricity mix of every country with the process imported from HSC. As an example, **Figure 39** shows the connection of the introduced production process from HSC with electricity mix to evaluate some environmental impacts with GaBi.



Figure 39. Screen capture of GaBi to assess some environmental impacts of the production process imported from HSC.

GaBi software, version 8.7.0.18 and database 8007 [213] were used for the environmental impact categories investigated were air pollution trough global warming potential (GWP), acidification potential (AP) and photochemical ozone creation potential (POCP) and for water pollution eutrophication potential (EP). **Figure 40** shows the previous impact categories for an ore grade of 2.72 g/t Au, work index (Wi) of 15 kWh/t and assuming an 80% passing (P80) size at the end of comminution of 75 μ m.

The largest GWP occurs in South Africa followed by China. Then, one order of magnitude lower is the GWP for the United States and, the European Union and finally Brazil. These differences depend mainly on the composition of the electricity mix.

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According to statistics of the International Energy Agency (IEA) in 2016, 90% and 68% of the primary electricity production came from coal in South Africa and China, respectively. On the other hand, approximately 33% and 31% of the electricity was produced by burning natural gas and coal in the United States. For the European Union, 23% of the electricity was generated by coal firing power plants. Hydroelectricity meant approximately 76% of the total electricity produced in Brazil [216]. As we can see, comminution represents the most extensive energy consumer process in the production of gold from Thanatia. Thus the composition of the electricity mix will have a direct influence on the number of pollutants released to the environment.



Figure 40. Main environmental impact categories in different locations for 2.72 g/t Au, work index 15 kWh/t and P80 at the end of comminution of 75 μ m.

8.4. Concluding remarks

The high consumption of metals in the last years has caused that rich metal deposits have been already exploited. In the limit, when no more attractive deposits would exit, metals would be produced from common rocks.

• With the HSC model, a gradual decrease in the concentration of free-gold and other gold-bearing minerals, trends of the specific energy were studied. The ore grades varied from an average representative value of 2.72 g/t Au to the concentration that gold would have in common rocks. Thanatia, an ideal state of mineral dispersion, was taken as the common rock from which gold will be

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produced. The concentration of gold in Thanatia is three orders of magnitude lower than the current values, 1.44-03 g/t Au.

- The results of the model show that comminution is the highest energy consuming process. The specific energy was compared to the respective ones reported in the literature, and they are in the same range of values; hence the results of the model are rational and reliable. Our model confirmed the trend of exponential growth on the specific energy consumption because of the decline of the grade studied by mathematical equations and LCA analyses until now. The advantage of having a model in HSC will allow the assessment of ores with different mineral compositions and ore grades in gold mines. In contrast to LCA analyses, which consider the metal production process like a "black box."
- With the model in HSC, the effect of a variable on the overall production process and its impact on the environment can be better estimated. The model can be used to forecast the impact of the ore grade decline in mines. Also, pathways to reduce energy consumption towards sustainable production of metals can also be studied with the interlinked connection between HSC and GaBi software.
- While the consumption of metals is expected to increase in the coming years, tools like HSC along with other existing ones can be used in the search for more sustainable routes for metal production.

Results from Chapters 6 to 9 lead to reconsider the adequacy of the value currently granted to mineral deposits, especially in those countries were metals are highly extracted. With the apparent booming of renewable energy technologies for the decarbonization of the society, the increasing need for purer metals, and particularly gold, will be imminent.

With the exhaustion of ore-rich deposits, recycling and more sustainable production processes are urgently required for keeping today's standard of living and the expectations of a better future of the coming generations.

While a globalized economy is eager for the consumption of more and more metals, the natural patrimony of nations with rich mineral deposits will be drastically diminished.

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This is why fair global accountability of the mineral capital and its degradation velocity is required.

From the models, it was also seen the need for valuing better current deposits, especially those in countries where minerals are highly extracted. One way to value these non-fuel mineral resources is through quantitative evaluation of the loss of mineral patrimony of nations due to the extraction of their minerals.

From the detailed analysis in Chapter 3, mass and market-price approaches fail to assess non-fuel minerals accurately. Therefore, exergoecology principles will be applied for a more precise evaluation. Due to the high number of minerals produced in a country, published values of Valero et al. reported in [12] are still valid for evaluation of non-fuel minerals. Therefore, from a very conservative perspective, as seen by the comparison in **Table 36**, a quantitative assessment of mineral exports and the loss of mineral heritage are going to be done for LA-20. This analysis is in the next chapter 9.

Chapter 9. Exports, production, and loss of mineral wealth in LA-20

9.1. Introduction to the chapter

In previous chapters, it was seen the necessity to grant a fairer value to the current mineral deposits, particularly in countries were minerals are vastly extracted. Due to the lack of proper evaluation of non-fuel mineral resources through other methodologies, as previously explained in Chapter 3, other approaches have emerged. Exegoecology is one of these approaches and considers the physical quality of non-fuel minerals and reveals other characteristics which are disregarded in other methodologies. By following exegoecology guidelines, in this chapter, the evaluation of the loss of natural stock, mineral heritage or loss of mineral wealth (hereafter LMW) is done for twenty countries in Latin America and the Caribbean. This evaluation is done with the previous values of ERC, and then a qualitative comparison is performed with the three "new ERC from HSC." The information in this chapter corresponds to a compilation of **Paper IV** and **V**.

9.2. Exergoecology for the proper evaluation of non-fuel minerals

In Chapter 3, in particular, in section 3.2, a mass-based approach is the most common method used to value non-fuel minerals. In this section, a deeper explanation about the disadvantages of using mass-based approaches will be described in depth, in particular MFA, because a number of considerable studies have been conducted for countries in Latin Amreica. Conventional MFA use tonnage (weight) as the unit of measure. Indeed, MFA offers a complete and systematic description of a specified system to support policymakers [218]. It provides data regarding extraction and trade of materials, hence offering useful information for the establishment of sustainable schemes [219–223].

Moreover, this approach has been used to show the dependence of a region on mineral imports. To that end, Schaffartzik et al. [221] analyzed patterns and trends of materials extraction, trade, and consumption of 177 countries in the world, grouped in six regions, from 1950 to 2010. They stated the importance of Latin America and the Caribbean as metal producers, especially for copper, silver, tin, and iron, supplying 12% of the world's metal demand. Other prominent studies have analyzed material flows, focusing only on Latin America. For instance, country-specific MFA were undertaken by Vexler et al. for Chile [224], by Perez-Rincon for Colombia [225], by Vallejo for Ecuador [226], Tanimoto et al. for Brazil [227], and Walter et al. for Argentina [228].

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On a multi-country perspective, in 2007 a report published by the United Nations Environmental Programme (UNEP) on material flows and resource productivity, analyzed ten countries of South America and the Caribbean: Argentina, Plurinational State of Bolivia, Brazil, Chile, Colombia, Ecuador, Guatemala, Mexico, Peru, and the Bolivarian Republic of Venezuela [229]. The main conclusion of this study was that growth in demand for resources of other regions could have effects on Latin America's material flows. Thus, MFA for Latin America is crucial in a globalized economy.

In another study, Russi et al. [230] analyzed the consequences of neoliberal economic reforms on natural resources of Chile, Ecuador, Mexico, and Peru through MFA from 1980 to 2000. This study demonstrated that domestic material extraction had increased in these four countries as a consequence of economic reforms. Similarly, West and Schandl [29] analyzed material use and efficiency in 22 countries in Latin America and the Caribbean. Material flows from 1970 to 2008 were studied, and a remarkable conclusion was that these countries were less efficient in gaining economic profit using selling their natural resources.

A similar conclusion was made in the study by Giljum and Eisenmenger [231], which observed "an unequal environmental distribution" at the global level between the distribution of environmental goods and environmental burdens between the North and the South. The North, such as the European Union [232], which is mostly resources dependent on southern countries, sells high-value products to the South while leaving the negative environmental impacts associated to raw material extraction in the South [231].

Thus, to have an order of magnitude for the loss of natural stock in Latin America due to mineral extraction, and to identify where such valuable minerals ended up, this chapter undertakes a material flow analysis (MFA) based on the Second Law of Thermodynamics. A total of 20 countries in Latin America and the Caribbean (LA-20). For this purpose, the mineral balance for LA-20 was examined, using indicators that can help evaluate the self-sufficiency or dependency of the region and evaluating exports by destination.

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With the mineral balance, both in mass and ERC terms, mineral production from 1995 to 2013 was assessed, and differences between both approaches were explored. Mineral exports by destination were examined for a particular year to see which countries benefit from the natural stock loss of LA-20. To that end, we have followed the exergoecology method proposed by Valero et al. [233] and guidelines of investigations published by Calvo et al. [72,234,235] and Carmona et al. [71]. In these studies, the ERC concept was used to develop MFA for European countries (EU-28) and Colombia in 2011. Alongside these studies, we seek to demonstrate that considering the thermodynamic quality of minerals through ERC would further improve the potential of MFA, especially when dealing with non-fuel minerals. The final aim is to contribute to a deeper discussion on the search for sustainable paths on mineral production in Latin America.

9.3. Mineral balance

In order to elaborate a mineral balance of LA-20, first of all, it was necessary to collect data about the production, imports, and exports of fuel and non –fuel minerals. Collection of production data of fuel and non-fuel minerals. For this study, three main fossil fuels (oil, natural gas, coal) and 37 non-fuel mineral commodities were studied: aluminum, antimony, barite, beryllium, bismuth, cadmium, chromium, cobalt, copper, fluorite, gold, graphite, gypsum, iron, lead, limestone, lithium, magnesite, manganese, mercury, molybdenum, nickel, niobium, platinum group metals (PGM), phosphate rock, potash, rare earth elements (REE), salt, selenium, silver, tantalum, tin, titanium, vanadium, wolfram, zinc and zirconium. Data regarding fossil fuel production (oil, coal, and natural gas) were provided by the Latin American Organization of Energy (OLADE) [22].

Fuel and non-fuel mineral production, in ERC terms, were taken from a publication by Palacios and colleagues [68]. A summary of the sources of information can be found in **Table 29**.

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Country	Source of information	Country	Source of information		
Bolivia		Argentina			
	[236]	Costa Rica			
Brazil	[220]	Cuba			
	[239]	Dominican Republic			
Chile	[240]	El Salvador			
		Guatemala			
Colombia	[241]	Honduras	[237,238]		
		Nicaragua			
Ecuador	[242]	Panama			
		Paraguay			
Mexico	[243]	Peru			
		Uruguay			
		Venezuela			

Table 29. Sources of information for mineral production.

To fill gaps in the information and for cross-checking purposes, information of British Geological Survey [238], U.S. Geological Survey (USGS) [237], the Economic Commission for Latin America and the Caribbean [244] and UN International Trade Statistics Database [245] was used.

The disaggregation level corresponding to mineral exports and imports was five digits (UN Comtrade license). To avoid double counting, this database allows treating a selected region, in our case LA-20, as a single unit, therefore not taking into account exports and imports between each LA-20 country. Due to the lack of information for Haiti in 2013, it was not possible to include it in the assessment of exports by destination and material flow indicators.

ERC is expressed in GJ per ton of element, hence all mineral information expressed in metal content was taken from these data sources. This information was then converted into exergy terms using the ERC, and different indicators have been calculated. As for the fuel-minerals, their conversion into GJ was by using HHV reported in [100].

Figure 41 shows non-fuel mineral production of LA-20 disaggregated by minerals, data was compiled from USGS statistics (USGS, 2016) and then compared to the

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information provided by national agencies as shown in **Table 29** to ensure maximum coherence and completeness.



Figure 41. Non-fuel mineral production in LA-20 from 1995 to 2013 in mass terms expressed in million tons (left) and in exergy terms expressed in Mtoe (right). Only the minerals that can be seen in the figures are shown in the legend (Source: [70])

Overall, in mass terms, the most extracted minerals in LA-20 from 1995 to 2013, were iron, aluminum, salt, limestone and gypsum (average of 197, 28, 18, 12 and 9 million tons per year, respectively). When these data are translated into the loss of natural stock in the region, through the ERC concept, the highest loss corresponded to aluminum (average value of 413 Mtoe), followed by iron (84 Mtoe). In the period of analysis, iron production represented 72% as an average of the total production in tons, while in Mtoe it represented only 13%. On the opposite side, aluminum, which only represented 10% of the total production in tons, represented 66% in ERC. Hence, the loss of natural stock in LA-20 was mainly caused by aluminum rather than iron. The importance of taking into consideration quality and not only the quantity of non-fuel minerals is revealed with this comparison.

The complete mineral balance disaggregated by mineral for LA-20 in 2013 in mass and ERC terms can be seen in **Appendix A.5**. Analyzing these data in detail, it can be observed that the most extracted fuel minerals in that year were crude oil and natural gas, with a share of 63% and 23% of the total fossil fuels, respectively. Regarding non-fuel minerals, iron, aluminum, and salt were the most produced in mass terms (69%, 9%, and 6%, respectively). When looking at consumption data, crude oil and natural gas were largely consumed within LA-20, and regarding non-fuel minerals, iron, aluminum, limestone, and salt were mostly consumed internally. The cases of limestone and salt can

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be easily explained as usually industrial minerals, which have lower prices than other metallic or non-metallic minerals, are consumed internally rather than exported to other countries.

As stated before, mineral trade can be represented using Sankey diagrams, with arrows showing the production, imports, exports, and domestic consumption proportional to flow quantities. As it was previously mentioned, domestic consumption referred to as apparent and not final consumption. Therefore, and as opposed to conventional EW-MFA, semi-manufactured products (either entering or leaving the analyzed system) were not taken into account. In conventional EW-MFA, the composition of most traded goods is assessed using the main material component or the main raw materials used in the production. On the contrary, in our analysis, if for example, iron was used internally to produce steel, and this, in turn, was exported, the corresponding iron was considered as a commodity consumed internally. This is why, according to the EW-MFA definitions, our results are only partial when analyzing imports and exports as we only consider bulk commodities.

Three countries have been selected for such purposes, Brazil, Chile, and Mexico (**Figure 42**). These countries have been chosen as an example as they approximately represent 65% of the total mineral trade in LA-20. All mineral commodities (38) along with natural gas, oil and coal are described in the diagram, but the legend only shows those that can be easily seen in the figure.

In some countries, when calculating the domestic material consumption, negative values can be obtained for certain commodities such as gold, silver, lead or zinc, as exports are higher than production and imports combined. Illegal and artisanal mining are severe problem in the region, especially in the case of precious metals, such as gold [34,37,39,247]. In 2013, it was estimated that 158 tons of gold were produced illegally, accounting for USD 6.9 billion. Countries with higher illegal gold production rates in that year were: Venezuela, Colombia, and Ecuador [34]. Negative values of domestic consumption can also be explained by the lack of reported data by official authorities and variation in stocks that are not shown on mineral statistics. The difference between input and output flows was represented in the diagram as

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"imbalance." Still, this imbalance on average is quite low when compared to the remaining flows.

Figure 42. Sankey diagrams for Brazil, Chile, and Mexico for 2013 expressed in million tons (upper row) and in Mtoe (lower row) for selected substances (Source: [70])

In Brazil in 2013, in mass terms, the most produced and exported commodity was iron, with a share of 57% of the total domestic production and 85% of the total exports, respectively. When analyzing that same information applying the ERC concept, the main commodity contributing to the loss of natural stock was aluminum, with a share of 66%. In a mere tonnage perspective, there is almost no difference between total exports and total domestic consumption. On the other hand, in terms of quality, consumption of higher-quality minerals, such as aluminum, potash and crude oil, was three times higher than exports.

As for Chile, the country imported large amounts of fossil fuels and principally produced copper, iron, and salt. Chile is a world leader in copper production, and in 2013 copper extracted represented one-third of the global copper production [248]. When transforming this information using ERC, it can be seen that copper plays a major role in exports as more emphasis is placed on its physical quality: it represents more than 90% of the total exports. Total exports in tons represent a fifth of the total outputs

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(exports plus domestic consumption), but when expressed in ERC they only account half.

As for Mexico, the most notable difference with the other two countries is that it mainly produces fossil fuels, along with small amounts of iron. It is also noteworthy that there was no major dependency on the external supply for internal consumption of minerals, as only small amounts of gas and coal were imported. In mass terms, Mexico's consumption was mainly dominated by natural gas and crude oil and was one order of magnitude higher than exports. In ERC terms, consumption was approximately two times higher than exports. A possible explanation for this value is the high fossil-fuel consumption in Mexico as, for instance, in 2014 more than 59% of the total final energy consumption came from fossil fuels [249].

One of the indicators that was used in the study is domestic material consumption (DMC), defined as the amount of physical minerals that are consumed inside one region. Hence, DMC is calculated as the sum of minerals that are produced in the region (domestic extraction = DE) plus imports (I) minus exports (E). The term consumption in this chapter refers to apparent consumption and not final consumption (i.e. goods are excluded for the analysis). Goods are not considered in this analysis for two reasons: first, because of important information gaps regarding semi-manufactured products exported and imported in the analyzed countries; and second, because this same approach was used in Calvo et al. [235] for EU-28 and so the results can be compared. These indicators were calculated both in mass and ERC. Subsequently, using this information, different ratios of domestic extraction (DE/DMC), imports (I/DMC) and exports (E/DMC) were obtained. The usefulness of these ratios is that they can provide information about the dependency and self-sufficiency of a region [235].

Different ratios were calculated: DE/DMC, I/DMC, and E/DMC, each considering domestic extraction, imports, and exports, respectively, compared to DMC. These ratios only include material trade of the fossil fuels and non-fuel minerals listed in previous sections.

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All the ratios were calculated both in tons and in Mtoe for LA-20 for 2013 (**Table 30**). Absolute results are not comparable between both units of measure. Yet that is not the case when we assess ratios such as DE/DMC, I/DMC or E/DMC.

When looking at DE/DMC ratios of non-fuel minerals, it is clear that LA-20 in 2013 produced more minerals than those it consumed internally. Imports were significantly lower than domestic consumption and exports were also significant, which is consistent with the image that LA-20 has of being a net exporter territory. In the case of DE/DMC ratio, the value in mass is higher than in ERC. The explanation relays on the weight of iron, a very abundant element which has a low ERC value (18 GJ/t). When expressed in tons of iron accounts for 68% of the total LA-20 mineral production but in ERC this value is only for 13%. On the contrary, for the I/DMC ratio, the value in ERC is higher than in mass, meaning that the minerals imported have higher ERC values and are therefore more scarce, such is the case of potassium (665 GJ/t), which accounts for 79% of the total imports in ERC but only 19% in mass.

The region produced more fossil fuels than those it consumed internally; analyzing the DE/DMC and E/DMC; it can be seen that a large amount of the fossil fuels produced in the region were exported. No high variation between ratios of DE/DMC, I/DMC, and E/DMC of fossil fuels can be appreciated when comparing the results in mass and ERC. This is related to the high importance of oil and gas in domestic extraction as, as seen before, both represented approximately 85% of the total fossil fuels extracted in LA-20 in 2013. A higher variation would be perceived if coal would play a more important role. This is because coal has a comparatively lower HHV than oil or natural gas.

Calvo et al. [235] applied MFA with an exergoecology approach for twenty-eight European countries (EU-28) using 2011 as the reference year. Although the latter and current study differ by two years, a comparison among the indicators obtained in this study will give us an indication of mineral sufficiency and dependency for both regions. In general, this comparison clearly shows a marked difference between both regions, while DE/DMC is higher than 1 for LA-20 (i.e., exports are more significant than imports), stating the relevance of domestic extraction and exports, for the EU-28 this value is considerably lower. This is understandable as EU-28 relies on minerals imports

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rather than on domestic extraction, therefore shifting the environmental burden of mineral extraction to other territories.

	LA-20 (2013 data)			EU-2	EU-28 (2011 data)		
	DE/DMC	I/DMC	E/DMC	DE/DMC	I/DMC	E/DMC	
Non-fuel minerals							
Mass	1.88	0.11	1.00	0.79	0.30	0.09	
ERC	1.50	0.16	0.66	0.45	0.94	0.40	
Fossil fuels							
Mass	1.36	0.24	0.59	0.52	0.62	0.13	
ERC	1.35	0.22	0.57	0.41	0.76	0.17	

Table 30. Comparison between LA-20 and EU-28.

As expected, non-fuel mineral values of the ratio I/DMC for LA-20 were considerably lower than those for EU-28. This reveals that EU-28 had to rely on importing materials to meet its internal needs while, in LA-20, domestic extraction was sufficient to cover internal demand. In addition, the E/DMC ratio was higher for LA-20 than for EU-28, reflecting the importance of LA-20 as an exporter region.

Contrary to what happens in EU-28, which in 2011 was extremely dependent on fossil fuels, in LA-20 the import to DMC ratio was considerably lower, and for the case of the exports ratio, it reflected the fossil fuel trade that takes place in the region.

Ratios of DE/DMC, I/DMC, and E/DMC, calculated in ERC terms only, for every country, except for Haiti due to a lack of data, are shown in **Table 31**. It is noteworthy that DMC values for Costa Rica and El Salvador are the only ones with negative figures. This is because, as it can be seen in the annexes, export values for these countries are higher than production and imports. The lack of mineral production official data, which can be incomplete or present gaps, can lead to lower values that do not reflect the reality of the country. This is even more notorious in ERC than in mass terms because scarcer minerals have a higher weight.

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Country	DMC (Mtoe)	DE/DMC	I/DMC	E/ DMC
Argentina	73.90	1.07	0.16	0.23
Bolivia	15.22	2.29	0.00	1.29
Brazil	669.62	1.16	0.21	0.37
Chile	63.37	1.38	0.33	0.71
Colombia	37.52	3.27	0.05	2.32
Costa Rica	-6.64	0.00	-0.22	-1.22
Cuba	10.66	0.50	0.50	0.00
Dominican Republic	16.67	0.91	0.17	0.08
Ecuador	10.71	2.91	0.00	1.91
El Salvador	-1.97	-0.46	-0.15	-1.61
Guatemala	0.11	1.00	0.00	0.00
Honduras	1.13	0.94	0.06	0.00
Mexico	148.05	1.59	0.18	0.78
Nicaragua	0.71	0.18	1.00	0.18
Panama	0.02	2.16	0.15	1.31
Paraguay	0.07	0.43	0.57	0.00
Peru	28.87	2.92	0.18	2.09
Uruguay	2.22	0.06	0.96	0.02
Venezuela	113.66	1.94	0.02	0.95
Average LA-20	62.31	1.43	0.19	0.62

Table 31. Ratios of DE/DMC, I/DMC and E/DMC for each country in ERC terms for fossil fuels and non-fuel minerals in 2013.

Countries with a ratio DE/DMC higher than 1 in 2013 were: Colombia, Peru, Ecuador, Bolivia, Panama, Venezuela, Mexico, Chile, Brazil, and Argentina. Colombia, Ecuador, and Peru in 2013 produced three times more fuel and non-fuel minerals than their national consumption.

This classification also shows the importance of performing the analysis using ERC, since, until now, in a mass basis analysis, only a few countries, such as Brazil, Venezuela, Mexico, and Chile, were considered because of their mining and oil tradition as the most significant producers in the region.

9.4. Exports by destination

In this section the destinations of the non-fuel minerals from Latin America were studied, not analyzing only quantities, as other studies previously did [29,221,229–

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231,250], but considering which minerals are more valuable from a quality point of view with the ERC approach.

Although all 38 non-fuel minerals previously mentioned before were considered in the analysis, in the graphs, only those that can be seen appear on the legend. These graphs were based on data from UN Comtrade [245]. As explained before, this database allows avoiding double accounting, being able to eliminate flows between LA-20 countries, and only analyzing trade between LA-20 and the rest of the world.

The main exported minerals were aluminum, iron, zinc, copper, silver, and gold (139, 134, 117, 58, 32, and 23 Mtoe, respectively). As can be seen in **Figure 43**, approximately one-quarter of all the minerals produced in LA-20 ended in North America, mainly going to the United States, while the rest went to other territories. This share can be understood because proximity is a crucial factor in mineral trade and also because some companies that own mines in LA-20 have processing plants in other parts of the world.

High-quality minerals, such as aluminum or gold, were exported mostly to North America (59 and 77%, respectively). The majority of copper produced in LA-20 was exported to China (38%), as well as silver (48%), while most of the zinc exports went to Russia (41%). Additionally, a not negligible 21% of gold went to Europe. More results disaggregated by mineral can be seen in **Appendix A.4**.

It can be observed that even using an ERC approach; iron still accounts for the vast majority of the exports as even if the ERC of iron is quite low when compared to other commodities, the extraction figures are so high that it masks other scarcer minerals. For this reason, some elements were removed from **Figure 43** so other mineral flows can be seen (**Figure 44**).

If those results were analyzed only in tons, it would seem that LA-20 only exports iron, aluminum, and salt, as these three elements alone represent 95% of the total exports to other countries. Still, between only Chile and Peru, they produced more than onethird of the total copper production in the world, Chile alone has 6 of the 10 largest copper mines in the world, while two others are located in Peru and Mexico. Moreover,

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around 12% of gold is produced in LA-20, with some of the largest gold mines being located in the Dominican Republic, Mexico, and Peru.



Figure 43. Non-fuel minerals exported by destination in ERC terms (Mtoe) for 2013. Due to the scale, some minerals are not included in the legend.





9.5. Assessment of the loss of mineral wealth

In a study [70], the authors evaluated mineral exports by the destination of twenty countries in Latin America in 2013 with the use of the ERC concept. Carmona et al. [251], and Calvo et al. [235] carried out investigations using ERC to analyze material flow in

Colombia and Europe, respectively. In this section, we apply the same methodology from a broader perspective, carrying a quantitative assessment of the impact of trading. Therefore, the main goal of this section is to evaluate if in 2013 whether or not the revenues from the sale of minerals compensate the loss of LA-20's mineral wealth.

The mineral endowment was first defined by Harris and Agterberg [252] as the number of metals in a given region. In this respect, mineral deposits can be seen as a free bonus provided by Nature. This is because it avoids a lot of mining exergy which would be otherwise spent if minerals were dispersed throughout the crust instead of concentrated in mines. When mineral deposits become depleted, the corresponding free bonus reduces, meaning that in the future, much more energy will have to be put into place in order to obtain the same amount of resources. In the limit, the bonus completely disappears, and mining would take place at crustal concentrations. In contrast to fossil fuels, which once burned the resource disappears, non-energy minerals do not disappear, they just become dispersed if not adequately managed. The problem of mineral resources is thus not one of scarcity, but rather of an insufficient provision of cheap energy to extract increasingly diluted commodities [40].

Hence, this accumulation of minerals, traded later as commodities, means richness for a country or region. Because of the growing need for minerals, they are extensively extracted, resulting in what can be defined as the loss of mineral wealth of the producing regions [72,251,253]. Exergoecology principles proposed by Valero [254] were used in this study to have a more robust and complete picture of the loss of mineral wealth in LA-20.

The methodology to estimate the LMW in this chapter consists of five stages: 1) data mining collection for non-fuel and fuel minerals, 2) conversion into ERC terms, 3) elaboration of mineral balance in ERC terms, 4) analysis of primary energy sources and 5) economic analysis. For a better understanding of the methodology, all the stages are represented in **Figure 45**.

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The first stage consisted of the collection of production data of fuel and non-fuel minerals, and sources of information from **Table 29** were used.

The second and third stage consisted of converting production data into exergy terms both for fossil fuel and non-fuel minerals. As stated before, the exergy of fossil fuels is comparable to their high heating values [100]. Concerning non-fuel minerals, their exergy is calculated using ERC (expressed in GJ/t). Therefore, once this conversion was done, a mineral analysis in energy terms (Mtoe) was performed.

The next step consists of assessing what would be the economic costs of the "free mineral bonus" lost through extraction, or in other words, to calculate what would be the cost of recovering the extracted minerals once dispersed, back into their initial concentrations in the deposits were they were found. In order to estimate the replacement costs of minerals in monetary units (USD), market prices of primary energy sources in each country were considered (electricity, oil, and coal). In order to have a

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range of comparison, two prices of primary sources were considered. The lowest price was taken to calculate the lower boundary price (LBP) and the highest, to calculate the upper boundary price (UBP), fourth stage. Prices of primary energy sources were compiled from the database of OLADE [255]. The recovery was calculated with Equation (9).

$$Recovery = B^* x UBP \text{ or } LBP$$
(9)

Finally, in the fifth stage, an economic analysis was performed. For comparative purposes, GDP values that correspond to the extractive sector and energy prices of each selected country were compiled [256]. Then, the ratio between LBP and UBP to the total GDP was obtained for every country to assess the loss of mineral wealth in LA-20 in 2013 and to analyze if the revenues of selling the minerals under the 2013 market conditions did or did not compensate this loss.

Note that when converting energy into monetary units, arbitrariness and volatility is introduced in the analysis. Energy prices often fluctuate because of political and socioeconomic factors. The physical analysis, which is robust and universal is therefore valuable in itself. Yet it is worth showing the results in monetary units to bring out in an easier way the order of magnitude of the mineral wealth lost through extraction.

Complete information regarding LA-20 mineral production, exports, and imports in 2013, in mass terms and in ERC terms can be found in the study by Palacios et al. [70]. Based on their information, **Table 32** shows the key minerals produced by country.

Even if only 37 non-fuel minerals are considered in this study, LA-20 produced other mineral commodities, such as bentonite, diatomite, dolomite or kaolin. As the vast majorities are consumed domestically, they did not have a considerable impact on mineral trade or on the extractive GDP. Therefore, these minerals did not influence the subsequent economic analysis.

Table 32. Key non-fuel minerals produced by country in 2013 (Source: [68]).

Country Key elements produced		Country	Key elements produced
Argentina	Iron, salt, gypsum	Guatemala	Gypsum, salt, magnesite
Bolivia	Zinc, Lead, Tin	Honduras	Salt, zinc, lead

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Brazil	Iron, aluminum, salt	Mexico	Iron, salt, gypsum
Chile	Iron, salt, copper	Nicaragua	Gypsum, silver, gold
Colombia	Limestone, iron, salt	Panama	Salt, gold
Costa Rica	Limestone, gold	Paraguay	Iron, gypsum
Cuba	Salt, gypsum, nickel	Peru	Iron, zinc, copper, gold
Dominican Republic	Gypsum, salt, copper	Uruguay	Limestone, iron, gold
Ecuador	Limestone, copper, gold	Venezuela	Iron, aluminum, limestone
El Salvador	Salt		

It can be seen that the weight in mass and in ERC terms changed drastically when mineral production is expressed in ERC terms (**Table 33**) and compared to the mass basis mineral analysis. For instance, the LA-20 production of fossil fuels accounted in mass terms for 57% of the total mineral production (considering both fossil and non-fossil fuels minerals), but when this percentage is expressed in exergy terms, it is reduced to 43%.

The non-fuel mineral with the highest weight in the national production in exergy terms was aluminum, with a total production of 559 Mtoe. Iron, which was the first extracted commodity in mass terms, was the second in exergy terms, with a total production of 122 Mtoe. This is because the ERC value of aluminum is more than thirty times higher than the ERC of iron [40]. This observation reveals that ERC unambiguously highlights its importance because it considers mine concentration and scarcity, along with other factors.

In most countries, the lowest energy price in 2013 corresponded to electricity with an average electricity price of 1,690 USD/Mtoe for the industrial sector. The highest energy price corresponded to oil, with an average value of 685 million of USD/Mtoe. Regarding electricity prices, it is worth mentioning that they are subsidized depending on the reference country. As such, in some countries, electricity prices are lower than in others and also lower than compared to global market prices. Many studies are published on the issue of subsidies with the pros and cons of subsidies and comparison to international fuel prices [257,258]. However, in some countries, the real amount invested in energy subsidies and its impact on national economies is still unclear. In

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another study, Di Bella et al. [259] analyzed the impact of subsidies on fossil fuel and electricity, concluding that it corresponded to an average of 1.8% of the total GDP during 2011-2013 in Latin America and the Caribbean. In our study, the issue of subsidies has not been taken into account and reported prices were directly used. The subsidies on energy are thus an additional reason for giving preference to the physical analysis over the monetary one.

Country	0:1	Natural	Coal	Non-fuel
Country	Oli	gas	Coal	minerals
Argentina	31.21	33.51	0.05	14.39
Bolivia	3.26	14.82	-	16.75
Brazil	111.64	19.57	5.18	642.08
Chile	0.37	0.67	1.51	84.97
Colombia	53.65	13.09	53.30	2.82
Costa Rica	-	-	-	0.01
Cuba	3.22	0.74	-	1.39
Dominican				15 17
Republic	-	-	-	15.16
Ecuador	28.01	1.14	-	1.99
El Salvador	0.55	-	-	0.35
Guatemala	-	-	-	0.11
Honduras	-	-	-	1.06
Mexico	139.21	46.64	5.93	44.09
Nicaragua	-	-	-	0.13
Panama	-	-	-	0.04
Paraguay	-	-	-	0.03
Peru	3.46	13.12	0.19	67.42
Uruguay	-	0.00	-	0.14
Venezuela	159.57	19.58	0.75	40.03

Table 33. LA-20 production in ERC terms for 2013 in Mtoe (Source: [68]).

As it was mentioned in the methodology section, the monetary costs associated with reversing the extractive processes with the usage of local energy sources was also calculated. Market prices of primary energy sources in 2013 for each country in LA-20 were retrieved from the OLADE data base [22] and are shown in **Table 34**. As can be seen from this table, the differences in energy prices are quite remarkable.

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		Ι	LBP		UBP
N⁰	Country	source	(USD/Mtoe)	source	(USD/Mtoe)
1	Argentina	electricity	3.49 x 102	oil	6.96 x 108
2	Bolivia	electricity	5.81 x 102	oil	5.18 x 108
3	Brazil	electricity	1.86 x 103	oil	6.79 x 108
4	Chile	coal	1.02 x 108	oil	6.91 x 108
5	Colombia	electricity	2.33 x 103	oil	6.79 x 108
6	Costa Rica	electricity	1.86 x 103	oil	7.11 x 108
7	Cuba	electricity	1.16 x 103	oil	$7.05 \ge 108$
8	Dominican Republic	electricity	2.56 x 103	oil	1.02 x 108
9	Ecuador	electricity	6.98 x 102	oil	6.96 x 108
10	El Salvador	electricity	3.14 x 103	oil	$7.05 \ge 108$
11	Guatemala	electricity	3.61 x 103	oil	7.11 x 108
12	Honduras	electricity	2.33 x 103	coal	$1.02 \ge 108$
13	Mexico	electricity	1.41 x 103	oil	6.96 x 108
14	Nicaragua	electricity	3.72 x 103	oil	6.96 x 108
15	Panama ⁽¹⁾	electricity	1.51 x 103	-	-
16	Paraguay ⁽¹⁾	electricity	5.81 x 102	-	-
17	Peru	electricity	9.30 x 102	oil	6.96 x 108
18	Uruguay	electricity	1.86 x 103	oil	6.96 x 108
19	Venezuela	electricity	2.32 x 102	oil	6.80 x 108
	LA-20	electricity	1.69 x 103	oil	6.85 x 108

Table 34. Local market prices of primary energy sources.

⁽¹⁾only one primary energy source is available

The most commonly used and straightforward indicator to measure the revenues of the mining sector is the extractive gross domestic product (GDP). According to statistics reported by the Economic Commission for Latin America and the Caribbean (CEPAL), the extractive GDP, which considers the revenue of the extraction of both fuel and non-fuel minerals, varied between 0.12% and 24.8% in 2016 [244].

Accordingly, using GDP as a comparative element, the loss of mineral wealth for LA-20 in 2013 is shown in **Table 35**. The production of fuel and non-fuel minerals (in %) was calculated based on the total production in mass terms. The ratios of the extractive GDP, LBP, and UBP to the total GDP were calculated as previously explained with Equation (9).

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		Production	Production	CDPextractive /	I BP/	LIBP/
Nº Country	Fuel	Non-Fuel	CDPtotal	CDPtotal	CDPtotal	
	Minerals	Minerals	GDI total	GDI total	GDI total	
		(%)	(%)	(%)	(%)	(%)
1	Argentina	88.87	11.13	3.20	6.14	8.32
2	Bolivia	97.27	2.73	14.28	22.42	73.30
3	Brazil	30.43	69.57	2.55	3.33	21.42
4	Chile	11.66	88.34	14.34	2.10	13.02
5	Colombia	91.04	8.96	9.18	14.03	14.60
6	Costa Rica	0.00	100.00	0.29	2.72x10-10	0.01
7	Cuba	90.72	20.98	0.62	3.44	4.84
0	Dominican	0.00	100.00	0.51	0.01	16.65
0	Republic	0.00	100.00	2.31	0.01	10.03
9	Ecuador	79.02	20.98	10.41	23.81	25.48
10	El Salvador	0.00	100.00	0.30	1.45x10-6	0.33
11	Guatemala	83.25	16.75	1.77	0.85	1.39
12	Honduras	0.00	100.00	0.71	1.40x10-5	0.61
13	Mexico	85.68	14.32	6.67	9.27	11.93
14	Nicaragua	0.00	100.00	2.94	4.68x10-6	0.88
15	Panama	0.00	100.00	1.60	0.08	-
16	Paraguay	0.00	100.00	0.12	0.09	-
17	Peru	40.17	59.83	10.98	2.83	29.49
18	Uruguay	0.00	100.00	0.34	5.65x10-7	0.21
19	Venezuela	91.13	8.87	24.80	41.75	51.96
	Average LA-20	64.36	35.64	5.81	7.44	18.38

Table 35. The loss of mineral wealth in 2013 for LA-20 (Source: [68]).

Majority of the countries with higher production of fuel minerals had higher differences between the sales and loss of their mineral wealth, as the ratios LBP/GDP_{total} and UBP/GDP_{total} are higher than GDP_{extractive} / GDP_{total}. This is the case, for instance, for Bolivia, Venezuela, Argentina, Mexico and Ecuador, whose share of fuel mineral production in 2013 was higher than 71%. An exception is Guatemala, with a high production of fuel minerals (more than 80%), but its GDP_{extractive/total} was higher than UBP/GDP_{total}.

On the contrary, in countries with higher production of non-fuel minerals (higher than 85%), such as, Chile, Costa Rica, Honduras, Nicaragua, Panama, Paraguay, and Uruguay, the loss of mineral wealth was compensated by the sale of non-fuel minerals, as GDP_{extractive}/GDP_{total} is higher than UBP/GDP_{total}. But that was not the case of Brazil and

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Dominican Republic, where the income generated by the minerals was lower than the monetary value associated with that loss of mineral capital.

In 2013, LA-20 was the region mainly based on fuel minerals production, with a share of 64% of the total extraction. The average values of LBP/GDP_{total}, UBP/GDP_{total} were 7.44, 18.38, respectively. Additionally, the GDP_{extractive}/GDP_{total} average value for LA-20 was 5.81. Therefore, the recovery of minerals would be between one and three times higher than the economic benefit of the mineral sales if this recovery was carried out with the lowest and highest energy sources, respectively. Therefore, performing a comparison of these indicators (LBP/GDP_{total}, UBP/GDP_{total}) with GDP_{extractive}/GDP_{total} for 2013, shows that the economic revenues of the mineral sales did not compensate the loss of mineral wealth in LA-20.

9.6. Effects of new ERCs on the loss of mineral wealth

As mentioned in the concluding remarks in sections 5.5, 6.5 and 7.5, the ERC values reported by Valero and colleagues vary in orders of magnitude in comparison to the corresponding ones obtained through modeling in HSC. If they are listed in descending order both lists agree, **Table 36**. It means that even though quantitatively they differ, the message on the importance of the "free bonus" by Nature is the same. Therefore, from a conservative approach values of the previous ERC can be used for the assessment of loss of mineral wealth. However, if a more accurate estimation is required, the new ERC from HSC should be used. Therefore, more models with HSC are needed for the rest of minerals.

Within the timescale of the Thesis, these three representative minerals were modeled in HSC software. As for the assessment of the LMW in a country or region all minerals produced have to be considered as previously described in section 9.5, the evaluation with the new ERCs was not possible. However, as shown in **Table 36**, the "New ERCs" vary considerably in comparison to the previous ERCs. The highest difference exists for the precious metal gold, two orders of magnitude higher than the previous ERC. Only for iron, the new ERC was three times lower than the previous one. But, the difference in orders of magnitude in the new ERC of gold and copper are considerably higher than the change between the new and previous ERC for iron.

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Minoral (unita)	From HSC-model	Previous ERC	
Mineral (units)	Assumptions	New ERC	[12]
Gold (GJ/t-Au)	Wi=15 kWh/t and P80=75µm	6.17E+07	5.5E+05
Copper (GJ/t-Cu)	Wi=15 kWh/t and P80=34µm	6576	292
Iron-ore (GJ/t-Fe)	Wi=14 kWh/t and P80=40µm	5.6	18

Table 36. Comparison of specific energy from the results of the HSC-model and developed by Valero et al.

From these three new ERC values, the recovery in Equation (9) will increase in orders of magnitude as the new ERCs for gold and copper have increased. The ratio of LBP/GDP_{total} and UBP/GDP_{total} will also rise in comparison to the GDP_{extractive} / GDP_{total}. Hence, the LMW will be higher with the new ERC from HSC. With these arguments, it is seen the LMW in **Table 35** corresponds to a very conservative approach. With this, the results of the LMW for LA-20 in 2013 are astonishing.

9.7. Concluding remarks

For a proper evaluation of the loss of natural stock, a tonnage assessment alone is not enough, as it would be like adding "apples with oranges" trying to compare one ton of gold with one ton of iron, therefore disregarding important aspects of the commodities. One of those aspects is quality, which can be assessed using the exergy replacement cost (ERC), a concept which accounts for the physical characteristics of minerals, considering their scarcity in the crust of the Earth. Accordingly, a ton of iron has a significantly lower ERC than a ton of gold, as the first appears more concentrated and is more easily extracted from the mines.

Additionally, combined with material flows analysis, this approach has enabled us to identify more precisely destinations of high-quality minerals. For instance, from 1995 to 2013 in LA-20, iron production represented 72% of the total production in tons, while in Mtoe it only represented 13%, and the contrary was observed for aluminum. Thus, the loss of natural stock of LA-20 was mainly caused by aluminum and not by iron extraction, along with zinc and copper, commodities which also contributed highly to the loss of the natural stock in the region. It was also observed that in 2013 more than half of the mineral production in LA-20 was destined only to exports. Moreover, the loss of natural stock was also due to exports of higher quality minerals, such as gold or silver.

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China and North America (mainly the United States) were key commercial partners for LA-20 in 2013. Routes of exports by destination showed that 32% and 22% of the total exports in ERC terms were destined for these countries, respectively.

The results have vastly shown the importance of quantifying minerals not only in mass (ton), but also taking into account their quality through the concept of ERC. Precious metals like gold and silver, are always masked by other elements in conventional MFA, because of their low values in mass terms. Still, they are even more critical not only from an economic point of view, as gold is closely linked with the monetary market, but also from a scarcity perspective.

Additionally, when analyzing in detail the material trade of Chile, Brazil, and Mexico, another problem related to mineral extraction and statistics was revealed. In some cases, there were negative values of domestic material consumption (domestic extraction + imports – exports) caused by illegal and artisanal mining of precious metals. Illegal mining also entails that the burdens and impacts associated with mineral extraction increase even more as in the case of the latter, there are no social, legal, or environmental criteria being followed. Alongside ecological problems, such as deforestation, the uncontrolled dumping of hazardous wastes in soils or rivers, can cause health damage. This also evidences that more efforts should be made by the local governments to improve the traceability of extracted minerals. Additionally, LA-20 mining statistics are not always complete or present disaggregated data that can be used to calculate the impacts of the mining sector by metal. There are still other statistics services, such as BGS and USGS, who provide useful data, but improvements should be made towards a more transparent and thorough method of reporting mineral data.

Along with other publications [227,229–231,260–263], this study intends to raise awareness of mineral production in Latin-American. Currently, the extraction rate of mineral stock continues to increase, as it did to fuel the growth of European countries in the past and to power the booming of China during recent years. This extraction, especially in the case of scarcer minerals, entails a loss related to the quality of mineral resources. This loss will presumably increase in the coming future, which raises the question whether income received from mineral exports in Latin America truly

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compensates the loss of natural mineral stock and the environmental burdens left in the region. It can also be used as a wake-up call to national and local authorities in Latin America to look at mineral resources from a more sovereign position for equal trading in a global market.

This methodology was used to compare the revenues coming from the sales of minerals, through the indicator GDP_{extractive} / GDP_{total}, with the recovery process of the minerals to its initial conditions, using local lowest and highest primary energy sources prices. This approach is represented by two ratios LBP/GDP_{total} and UBP/GDP_{total}, respectively. By comparing these indicators, it is possible to conclude whether the extraction of minerals and the consequent mineral loss for the territory, was compensated or not by their sales. Just doing a qualitative comparison between the previous and the new ERC values, if considering them, the LMW will be considerably higher.

Chapter 10. Conclusions / Conclusiones

10.1. Conclusions

Minerals are essential in modern society. For decarbonization of the atmosphere, a considerable share of energy would have come from green technologies. They will undoubtedly require a significant amount of minerals. Some of them are currently considered as critical for industrialized economies according to governmental institutions, mainly in the US and European Union.

The southern hemisphere is a key supplier of important non-fuel minerals for keeping northern hemisphere economies, as well as for the manufacture of green technologies. Latin America and the Caribbean, for this Thesis, coined as LA-20, plays an important role as a supplier of metals. In this sense, the proper evaluation of non-fuel minerals is essential in a modern world eager for more metals. In the Thesis, it has been analyzed the pros and cons of methods currently used for quantifying minerals according to their tonnage (mass-based approach) or US\$ per ton (market-price approach). As studied in Chapter 3, both methods fail in properly evaluating non-fuel minerals. The current price of minerals, based on the cost of extraction plus profit, does not provide a sustainable approach to assessing the loss of mineral patrimony. To overcome this issue, other methods should be considered. One option could be considering the replacement costs as one of the parameters used to set-up the physical value of minerals. The ERC represents the energy required to concentrate minerals with current technologies from an ideal state of mineral dispersion. This state is coined as Thanatia and approximates to the average Earth's concentration. In that sense, ERC becomes a valuable indicator because it qualitatively estimates how much effort it is saved because of having minerals concentrated in mines and not dispersed throughout the crust.

As explained in Chapter 4, the methodology for the estimation of the ERC has some weak points. Therefore in this Thesis, a new approach was proved for the enhancement of Exergoecology. With the use of specialized software, HSC Chemistry, it was possible to estimate three new ERC for iron, copper, and gold. With the new approach, it was possible to accurately examine from an engineering perspective routes of mineral concentration starting from Thanatia. To analyze the validity of results, some parameters

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were compared to the respective ones already published. With this comparison, it was proved that results from the models were logical and reliable.

Due to the complexity regarding the number of elements and uncertainty on the need of hardness and which final particle size would be needed, the results are shown through a sensitivity analysis. For the three, the stage with demands higher energy is the comminution, which agrees with current processes. Two assumptions were made to estimate the "New ERC from HSC model". The first one was established based on the most abundant mineral in Thanatia, the quartz, and it was taken its typical hardness. Second, by assuming that metal will be extracted with typical final sizes from Thanatia, it was established a Bond index. With them, it was establishing new values for the ERC. These values should be used with care and also referring to the assumptions made, as shown in **Table 36**. The new ERC contrast considerably to the previous ones. This is due to mainly the difference in methodologies. While the previous ERCs were determined from a merely theoretical perspective, the new ones are based on a metallurgical perspective. The highest difference exists for the precious metal gold, two orders of magnitude higher than the previous ERC. Only for iron, the new ERC was three times lower than the previous one.

Furthermore, with a model in HSC, it was studied the effect of the ore-grade decline on the specific energy. Until now, only through analytical equations or from a life cycle assessment approach, it was proved such effect. With the model, it was possible to verify the exponential growth in the energy for metal processing while the ore grade declines. It is revealed the vast energy efforts that future generations will need to invest in mining in lower ore grades.

The new ERCs and the effect of ore-grade decline over time show the importance to give more value to current mineral deposits, since the fact that of having minerals concentrated in mines represents an energy saving factor for metal production. So, the analysis of the loss of mineral wealth (LMW) for twenty countries in Latin America and the Caribbean (LA-20) was done for 2013. For this task, a methodology was developed based on the exergoecology principles and applying ERC. According to the methodology described in section 9.5, it was necessary the use of previous ERC values

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since the whole mineral production is evaluated. The ERC concept has made the importance of scarcer minerals for the assessment of mineral trading in Latin America stand up, as the production of these high-quality minerals also means a higher loss of natural stock in the region. A comparison of these values revealed that, in 2013, the economic revenues of the sales of minerals was far from equal when compared to the costs of recovering them using the local lowest or higher energy price. Hence, the data shows that the sales of mineral in 2013 did not compensate fairly the loss of mineral wealth in LA-20, indicating a requirement for the shift in the paradigm of assessing fuel and non-fuel minerals and posing the question of what would be a fairer price of commodities. Although some governments have taken direct action to increase the price of commodities, a new scheme is required for metal prices.

Just making a qualitative comparison between the previous and the new ERC values, if considering them, the LMW will be considerably higher. Hence, the results of the LMW for LA-20 are very conservative, even though they are unforeseen. They intended to raise awareness among policy makers and local authorities in Latin America about an urgent need on the establishment of a fairer scheme on trading towards more sustainable paths for the production of non-fuel mineral resources in the region.

For these reasons, the Thesis attempts to promote a deeper discussion on the importance of the quality of minerals, incorporating the thermodynamic approach in conventional material flow analysis. This would imply following a new path by going beyond the traditional tonnage perspective.

10.2. Contributions

The main contributions are:

- During the Thesis, the concept of the ERC was upgraded, and Exergoecology principles were strengthened by supporting the theory with mineral processing through modeling with the specialized software HSC Chemistry. Accordingly, the Thesis was able to quantitatively assess the energy saving in the metallurgical process because of having minerals concentrated in mines instead of being dispersed throughout the Earth's crust.
- The use of this software allowed to change every parameter and so assess the impact they have on the final energy consumption. This cannot be carried out with conventional LCA analyses, which consider metal production as a "black box".
- With the computational models, it was possible to point out some key considerations of metal processing of iron, copper, and gold when dealing with low ore-grade deposits. For example, the use of additional stages of re-cleaners for flotation to concentrate copper and iron.
- The Thesis has established a baseline to upgrade exergy replacement costs and thermodynamic rarity values for other minerals. They are vital concepts in exergoecology for the proper evaluation of mineral resources.
- A model which can be used to forecast the impact of the ore grade decline in mines on the energy consumption was developed for gold, but the basis is established for extending the analysis to more metals.
- The role of Latin America and the Caribbean as a critical player in the globalized market of mineral commodities was portrayed for the first time through the analysis of mineral exports according to their physical quality.
- The results of the analysis of the loss of mineral wealth (LMW) in Latin America and the Caribbean reveal the need to search for a fairer price of minerals to compensate for the loss of mineral endowment of Nature.

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10.3. Outlook

Several pieces that have remained outside the scope of this Thesis which could complement the work are:

- A further step of this research is to continue with other models in HSC software for other minerals to compare and update ERC values previously obtained.
- Out of the scope of the thesis were processes of drilling, blasting, remediation, and reclamation. A procedure for their estimation can be developed.
- The models for iron-ore and copper can be used to estimate their thermodynamic rarity and compare them with the previous ones.
- The models in HSC with some additional stages of processing for the tailings can be used for the proper cost allocation in the field of Thermoeconomics.
- The establishment of a framework towards a fairer price of non-fuel minerals based on new ERCs could be developed.

10.4. Conclusiones

Los minerales son esenciales en la sociedad moderna en la que vivimos. Para la descarbonización de la atmósfera, un porcentaje considerable de la energía debería ser producida por las tecnologías verdes. Las que requerirán sin duda alguna una cantidad considerable de minerales. La mayoría de estos minerales son considerados como críticos para las economías industrializadas según instituciones gubernamentales principalmente en Estados Unidos y en la Unión Europea.

Los países del Hemisferio Sur son proveedores clave de importantes minerales para mantener las economías del Hemisferio Norte, así como para la fabricación de las tecnologías verdes. América Latina y el Caribe, en esta Tesis denominado como LA-20 juega un rol importante como proveedor de metales. En este sentido la evaluación adecuada de los minerales es esencial en un mundo moderno ansioso cada vez de más metales.

En la Tesis, fueron analizadas las ventajas y desventajas de los métodos actualmente empleados para la cuantificación de los minerales según su tonelaje (enfoque en masa) o US\$ por tonelada (enfoque en función del precio). En el Capítulo 3, fueron estudiados de manera detenida ambos métodos y los dos fallan en la evaluación adecuado de los minerales. El precio actual de los minerales, fundamentados en el costo de extracción más ganancia económica no provee un enfoque sostenible para evaluar la pérdida de capital mineral.

Como se explicó en el Capítulo 4, la metodología para la estimación del ERC tiene algunos puntos débiles. Por lo tanto, en esta Tesis se probó un nuevo enfoque para la mejora de la exergoecología. Con el uso de un software especializado, HSC Chemestry, fue posible estimar tres ERC nuevos para hierro, cobre y oro. Con el nuevo enfoque, fue posible examinar con precisión desde una perspectiva de ingeniería las rutas de concentración de minerales a partir de Thanatia. Para analizar la validez de los resultados, se compararon algunos parámetros con los respectivos ya publicados. Con

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esta comparación, se demostró que los resultados de los modelos fueron lógicos y confiables.

Los resultados se muestran a través de un análisis de sensibilidad debido a la complejidad en cuanto al número de elementos y la incertidumbre sobre la dureza de roca y qué tamaño final de partícula sería necesaria. Para los tres, la etapa con mayor demanda de energía es la conminución, lo cual concuerda con los procesos actuales. Se hicieron dos suposiciones para estimar el "Nuevo ERC del modelo HSC". La primera se estableció a partir del mineral más abundante en Thanatia, el cuarzo, y se tomó su dureza típica. En segundo lugar, al suponer que el metal se extraerá con los tamaños finales típicos de Thanatia, se estableció un índice de Bond. Con ellos, se establecieron nuevos valores para el ERC. Estos valores deben usarse con cuidado y también en referencia a los supuestos realizados, como se muestra en Table 36. Los "Nuevos ERC" contrastan considerablemente con los ERC anteriores. Esto se debe principalmente a la diferencia en las metodologías. Mientras que los ERC anteriores se determinaron desde una perspectiva meramente teórica, los nuevos se fundamentan en una perspectiva metalúrgica. La mayor diferencia que existe es para el oro, un metal precioso. Su diferencia es de dos órdenes de magnitud más alto que el ERC anterior. Solo para el hierro, el nuevo ERC fue tres veces más bajo que el anterior. Además, con un modelo en HSC, se estudió el efecto de la disminución de la ley de mina sobre la energía específica. Hasta ahora, esto solo había sido mostrado a través de ecuaciones analíticas o desde un enfoque de evaluación del ciclo de vida. Con el modelo fue posible verificar el crecimiento exponencial de la energía para el procesamiento de metales mientras que la ley de mina disminuye. Se revelan los vastos requerimientos de energía que las generaciones futuras deberán invertir en la minería en depósitos con leyes de mina más bajas.

Los nuevos ERC y el efecto de la disminución de la ley de mina a lo largo del tiempo muestran la importancia de dar más valor a los depósitos minerales actuales. El hecho de tener minerales concentrados en minas representa un factor de ahorro de energía para la producción de metales. Por lo tanto, se realizó el análisis de la pérdida de capital mineral (LMW por sus siglas en Inglés) para veinte países de América Latina

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y el Caribe (LA-20) en el año 2013. Para esta tarea se desarrolló una metodología fundamentada en los principios de exergoecología y la aplicación de ERC. De acuerdo con la metodología descrita en la sección 9.5, fue necesario el uso de valores ERC anteriores, ya que se evalúa toda la producción mineral. El concepto de ERC ha permitido resaltar la importancia de los minerales más escasos durante la evaluación de las exportaciones de los minerales en América Latina. La producción de estos minerales de alta calidad también significa una mayor pérdida de capital mineral en la región. Una comparación de estos valores reveló que, en 2013, los ingresos económicos por las ventas de minerales estaban lejos de ser iguales en comparación con los costos de recuperarlos utilizando el precio de energía local más bajo o más alto. Por lo tanto, los resultados muestran que las ventas de mineral en 2013 no compensaron de manera justa la pérdida de capital mineral en LA-20. Esto muestra que es necesario un cambio en el paradigma de evaluación de los minerales, y plantea la pregunta de cuál sería un precio más justo para las "commodities". Aunque algunos gobiernos han tomado medidas directas para aumentar el precio de las "commodities", se requiere un nuevo esquema para los precios de los metales.

Solo haciendo una comparación cualitativa entre los valores ERC anteriores y nuevos, el LMW será considerablemente más alto. Por lo tanto, los resultados de la LMW para LA-20 son muy conservadores, aunque son reveladores. Su intención es la de sensibilizar a los responsables de la formulación de políticas y las autoridades locales de América Latina sobre la necesidad urgente de establecer un esquema más justo en el comercio de las "commodities". Hacia caminos más sostenibles para la producción de metales en la región.

Por estas razones, la Tesis intenta promover una discusión más profunda sobre la importancia de la calidad de los minerales, incorporando el enfoque termodinámico en el análisis convencional de flujo de materiales. Esto implicaría seguir un nuevo camino yendo más allá de la perspectiva tradicional de tonelaje.

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10.5. Contribuciones

Las principales contribuciones son:

- Durante la Tesis, el concepto de ERC se actualizó y los principios de exergoecología se fortalecieron al respaldar la teoría con el procesamiento de minerales mediante el modelado con el software especializado HSC Chemistry. En consecuencia, la Tesis fue capaz de evaluar cuantitativamente el ahorro de energía en el proceso metalúrgico debido a tener minerales concentrados en minas en lugar de dispersarse por toda la corteza terrestre.
- El uso de este software permitió cambiar todos los parámetros y evaluar el impacto que tienen en el consumo final de energía. Esto no puede llevarse a cabo con análisis de LCA convencionales, que consideran la producción de metales como una "caja negra".
- Con los modelos computacionales, fue posible señalar algunas consideraciones clave sobre el procesamiento de metales de hierro, cobre y oro cuando se trata de depósitos de baja ley. Por ejemplo, el uso de etapas adicionales de re-limpiadores para flotación para concentrar cobre y hierro.
- La Tesis ha establecido una línea de base para actualizar los costos de reposición de exergía y los valores de rareza termodinámica para otros minerales. Son conceptos vitales en exergoecología para la evaluación adecuada de los recursos minerales.
- Se desarrolló un modelo que se puede usar para pronosticar el impacto del declive del mineral en las minas sobre el consumo de energía para el oro, pero se establece la base para extender el análisis a más metales.
- Se mostró el rol de América Latina y el Caribe (LA-20) como un actor vital en el mercado globalizado de productos minerales a través del análisis de las exportaciones de minerales de acuerdo con su calidad física.
- Los resultados del análisis de la pérdida de riqueza mineral (LMW) en América Latina y el Caribe revelan la necesidad de buscar el precio más justo de los minerales para compensar la pérdida de la dotación de minerales de la Naturaleza.

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10.6. Perspectivas

Una serie de piezas que han quedado fuera del alcance de esta Tesis que podrían complementar el trabajo son:

- Como paso adicional de esta investigación es continuar con otros modelos en el software HSC para que los valores de HSC se actualicen y puedan ser comparados con valores previos.
- Fuera del alcance de la tesis fueron los procesos de perforación, voladura, remediación y recuperación. Se puede desarrollar un procedimiento para su estimación.
- Los modelos para el hierro y el cobre se pueden usar para estimar su rareza termodinámica y compararlos con los anteriores.
- Los modelos en HSC con algunas etapas adicionales de procesamiento para los relaves se pueden usar para la asignación adecuada de costos en el campo de la termoeconomía.
- Se podría desarrollar el establecimiento de un marco para un precio más justo de los minerales no energéticos basados en los nuevos ERC.

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Appendix

The present thesis is based on a compilation of different published manuscript. The

impact factors and scope of the corresponding journals are listed below:

A.1. Palacios, J.-L., Fernandes, I., Abadias, A., Valero, A., Valero, A., & Reuter, M. A. (2019). Avoided energy cost of producing minerals: The case of iron ore. Energy Reports, 5, 364–374. https://doi.org/10.1016/J.EGYR.2019.03.004

Received 15 October 2018, Revised 20 February 2019, Accepted 7 March 2019, Available online 14 March 2019.

Impact Factor: 1.16 (SJR 2017, Q1 Energy (miscellaneous))

Scope: overview of methods for the assessment of mineral resources, review of the calculation of the exergy replacement cost (ERC), overview of mineral processing of iron, development of a computational model in HSC for the concentration of iron from Thanatia.

A.2. Palacios, J., Abadias, A., Valero, A., Valero, A., & Reuter, M. A. (2019). Producing metals from common rocks: The case of gold. Resources, Conservation & Recycling, 148(February), 23–35. https://doi.org/10.1016/j.resconrec.2019.04.026

Received 1 February 2019, Revised 29 March 2019, Accepted 24 April 2019, Available online 14 May 2019

Impact Factor: 5.228 (JCR 2017, Q1 Waste Management and Disposal)

Scope: review of the calculation of the exergy replacement cost (ERC) and thermodynamic rarity (ERC), overview of mineral and metal processing of gold, development of a computational model in HSC for the production of gold from thanatia

A.3. Palacios, J., Abadias, A., Valero, A., Valero, A., & Reuter, M. A. (2019b). The energy needed to concentrate minerals from common rocks: the case of copper ore. Energy, 181, 494–503. https://doi.org/10.1016/j.energy.2019.05.145

Received 8 February 2019, Revised 18 April 2019, Accepted 20 May 201, online 24 May 2019

Impact Factor: 5.582 (JCR 2017, Q1 Energy (miscellaneous))

Scope: review of the calculation of the exergy replacement cost (ERC)), overview of mineral and metal processing of copper, development of a computational model in HSC for the concentration of copper ore

A.4.Palacios, J.-L., Calvo, G., Valero, A., & Valero, A. (2018a). Exergoecology Assessment of Mineral Exports from Latin America: Beyond a Tonnage Perspective. Sustainability, 10(3), 723. https://doi.org/10.3390/su10030723

Received 27 November 2017, Revised 28 February 2018, Accepted: 3 March 2018, Published 6 March 2018

Impact Factor: 2.075 (JCR 2017, Q2 Geography, Planning, and Development)

Scope: revision of mineral exports from 20-countries in Latin America and the Caribbean from a tonnage perspective, translation of these exports into the physical quality of minerals based on Exergoecology principles, identification of routes of exportation of high-quality minerals

A.5.Palacios, J.-L., Calvo, G., Valero, A., & Valero, A. (2018b). The cost of mineral depletion in Latin America: An exergoecology view. Resources Policy. https://doi.org/10.1016/j.resourpol.2018.06.007

Received 28 October 2017, Revised 20 May 2018, **Accepted 13 June 2018**, Available online 30 June 2018

Impact Factor: 2.695 (JCR 2017, Q1 Waste Management and Disposal)

Scope: Review of the production of minerals of 20-countries in Latin America and the Caribbean, development of a methodology by applying Exergoecology principles of the exergy replacement cost to estimate the loss of mineral capital in the region for 2013

A.6. Palacios, J. L., Abadías Llamas, A., Valero, A., Vallejo, M. C., & Reuter, M. A. (2019). Simulation-based approach to study the effect of the ore-grade decline on the production of gold. In 32 nd International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems (ECOS). Wroclaw.

Article accepted 14 April 2019

Impact Factor: The international conference ECOS has a great reputation in the field of Thermodynamics and is carried out for more than 30 consecutive years.

Scope: To estimate the behavior of the energy consumption for the production of gold as function of the ore grade by means of a computational model in HSC software.

A.1 Paper I

Palacios, J.-L., Fernandes, I., Abadias, A., Valero, A., Valero, A., & Reuter, M. A. (2019). Avoided energy cost of producing minerals: The case of iron ore. Energy Reports, *5*, 364– 374. https://doi.org/10.1016/J.EGYR.2019.03.004

Received 15 October 2018, Revised 20 February 2019, Accepted 7 March 2019, Available online 14 March 2019.

Impact Factor: 1.16 (SJR 2017, Q1 Energy (miscellaneous))

Scope: overview of methods for the assessment of mineral resources, review of the calculation of the exergy replacement cost (ERC), overview of mineral processing of iron, development of a computational model in HSC for the concentration of iron from

Contribution to the work:

- To describe in brief the most common methodologies for the assessment of mineral resources and their disadvantages
- To explain how the exergy replacement cost (ERC) for iron was determined with its weak points
- To develop a new approach to estimate the new ERC of metals based on mineral processing criteria
- To develop a computational model with HSC software to concentrate high-iron minerals from Thanatia
- To estimate the new value of the ERC for iron with HSC and draw a comparison with the previous ERC

• To determine the importance of the development of computational models in HSC to estimate more accurate values of ERC for the rest of metals.

Contents lists available at ScienceDirect

Energy Reports

journal homepage: www.elsevier.com/locate/egyr



Research paper Avoided energy cost of producing minerals: The case of iron ore

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ABSTRACT

There is growing concern about the decline of the ore grade in mines and the increased energy usage for processing and refining metals. In the limit, where no concentrated deposits exist, minerals must be obtained from bare rock. A method for quantitatively assessing the "free bonus" granted by nature in providing concentrated minerals in mines and thus assessing the quality of the different resources is estimating how much energy is needed to concentrate the minerals, as they are already in mines, from bare rock. This bonus granted by nature reduces the costs of human mining and metallurgical processes, as well as the mining effort required of future generations. In this study, the concentration of high-iron-content minerals in common rocks was investigated via a computational model developed using the HSC software. As expected, the range of results for the specific energy for the concentration of iron from common rocks was considerably higher than the energy required by modern processes. This reveals the need to value current iron deposits and the challenge of developing sustainable methods of metal production to satisfy the needs of the present and future generations.

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1. Introduction

The development of nations has required an enormous amount of materials, with metals being essential, and nature has suffered the consequences. Concern regarding the decline of high-oregrade deposits has been expressed by many authors, such as Mudd Mudd (2007a,b, 2008, 2007c, 2010), Craig et al. Craig et al. (2014), Norgate Norgate and Jahanshahi (2010), and Calvo et al. Calvo et al. (2016). Even though iron is one of the most abundant minerals in Earth's crust Skinner (1979), the rich deposits have already been exploited owing to the massive consumption of metals by humans. Thus, new deposits must be found in remote locations, and the energy expenditure for not only handling the ore but also processing metals has increased Calvo et al. (2016). Steel - a carbon-iron alloy - is fundamental in the modern world. Although iron has one of the highest recycling rates among metals Graedel et al. (2011), in 2015, iron-ore production was 2.2 billion tons, which is 233% higher than that in 1990 Matos (2015), U.S. Geological Survey (2018). According to historical

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i.belo-fernandes@hzdr.de (I. Fernandes), a.abadias@hzdr.de (A. Abadias), aliciavd@unizar.es (A. Valero), valero@unizar.es (A. Valero), m.reuter@hzdr.de (M.A. Reuter). global statistics from the U.S. Geological Survey (USGS) Matos (2015), U.S. Geological Survey (2018), the leading iron-ore producers from 1900 to 2015 were China (38%), Australia (19%), and Brazil (17%). This high production of iron ore implies a loss of natural minerals in these countries Calvo et al. (2015), Valero and Valero (2014), Gabriel Carmona et al. (2015).

Additionally, a decarbonized society implies the use of renewable-energy technologies Sawyer et al. (2016), International Energy Agency (2010), World Steel Association (2017). These technologies require a considerable amount of metals, and steel is extensively needed; however, iron production is only economically feasible when ores with high concentrations of iron are available.

Because minerals are essential in modern society and rich mines are increasingly being depleted, the assessment of mineral resources is necessary. This can be done via three approaches: evaluation based on the mass, market prices, and the physical quality of the minerals. The first approach disregards essential aspects, such as the scarcity of the minerals in Earth's crust Valero and Valero (2014), Domínguez and Valero (2013), Palacios et al. (2018). For instance, in this approach, one ton of iron is considered equal to one ton of gold, even though iron is more abundant than gold and the energy required to extract the metal from the ore (embodied energy) is higher for gold than for iron.

Regarding the second approach, metal prices are influenced by many factors and are thus volatile Henckens et al. (2016). One of



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these factors is the difficulty of extracting metals from ores (cost of extraction) Valero and Valero (2014), Henckens et al. (2016). Another factor is speculation related to the physical reality of the commodities. According to historical data regarding commodity prices from the USGS Kelly and Matos (2016), the price of iron ore was lowest in 1901 (1.71 US\$/t) and highest in 2012 with (116.48 US\$/t). This shows the variability in iron-ore prices.

The third approach for the assessment of mineral resources involves the Second Law of Thermodynamics. Valero and Valero established the concept of the exergy replacement cost (ERC) for the evaluation of mineral resources Valero and Valero (2014), Valero et al. (2013). The ERC represents the energy needed to concentrate minerals at an average ore grade from Thanatia, which is an ideal illustration of mineral dispersion in Earth's crust Valero and Valero (2014). Thanatia symbolizes the common rock from which minerals would be concentrated. This idea is aligned with the research of Henckens et al. Henckens et al. (2016), who mentioned that the maximum cost of extraction of commodities would be set up as their mining would come from low-concentration deposits, common rocks, and seawater Henckens et al. (2016). Skinner reported that extraction from common rocks is technically feasible but requires more energy than extraction from rich metal ores Skinner (1976). Investigations by Harmsen et al. Harmsen et al. (2013), Bardi Bardi (2014), and Norgate and Jahanshahi Norgate and Jahanshahi (2010) reinforced the position of Skinner regarding the increment of the specific energy for the extraction of metals from low-concentration deposits. In research by Steen and Borg Steen and Borg (2002) on the direct costs of production of metals from Earth's crust through sustainable methods, considerable increments for metal concentrates, such as copper, cadmium, and manganese, were reported.

ERC values have been calculated according to an analysis of statistical trends, good estimations, or mathematical models. In this study, we estimate the specific energy needed to concentrate minerals from Thanatia via a more rigorous approach than the one used previously. The methodology developed for this endeavor relies on a computational model using the HSC Chemistry software Garcia et al. (2018), which is a specialized software for mining and metallurgical processes that is commonly used in industry. The aim is to provide accurate values regarding the amount of energy needed if no more concentrated ironore deposits exist. This exercise, which has not been previously performed with such detail, reveals the tremendous amount of energy savings due to having minerals concentrated in mines and not dispersed throughout the crust. Our study provides valuable insight regarding the sustainable production of metals, considering the loss of minerals experienced by modern nations. All of the aforementioned researchers based their methodologies on good estimations and assumptions, rather than rigorous metallurgical analysis of the energy needed in each process.

2. ERC and Thanatia

The ERC allows the quantitative evaluation of minerals. Exergy is a thermodynamic property of a system–environment combination that represents the minimum amount of work that a system can produce when it is brought into equilibrium with its surrounding environment Valero and Valero (2014), Cengel and Boles (2008), Bejan et al. (1996), Moran et al. (2011). When fossil fuels are burned, their liberation of energy is associated with their high heating value (HHV) Valero and Valero (2012a,b). Conversely, non-fuel minerals are noncombustible; thus, the association of the HHV and exergy is not valid. A common approach for assessing non-fuel minerals employs their chemical exergy. In an influential paper, Szargut published the chemical exergy of different elements Szargut (1989). The chemical exergy of elements has been used by other authors, such as Ayres Ayres (2016), Dewulf et al. Dewulf and Van Langenhove (2006), and Szargut et al. Calvo et al. (2015), Szargut et al. (2015, 2002), to evaluate mineral resources.

Nevertheless, chemical exergy is not effective for accurately assessing non-fuel minerals, as stated by Domínguez et al. Domínguez and Valero (2013). The chemical exergy of gold is 60 kJ/mol, and that of aluminum is 796 kJ/mol. Gold is scarcer than aluminum, and its chemical exergy does not adequately reflect this. Exergoecology was postulated by Valero Valero and Valero (2010) for the proper evaluation of mineral resources. Physical geonomics – one division of exergoecology – considers the application of exergy in the assessment of non-fuel minerals. The exergy of non-fuel minerals has two components; the first one is related to their chemical composition (chemical exergy), and the second one is associated with their relative concentration in Earth's crust (concentration exergy). The assessment with both components is more accurate than that the chemical exergy.

Nature provides a "free bonus", as minerals are concentrated in deposits rather than dispersed throughout Earth's crust. This "free bonus" significantly reduces the costs associated with the mining and concentration of mineral commodities. This free concentration of minerals can be seen as an "avoided cost" with regard to mineral processing and refining. When high-ore-grade mines are depleted, as is currently happening Calvo et al. (2016), there is a reduction in this free bonus. This leads to extensive exergy consumption for extracting a similar quantity of metal from a lower-ore-grade mine. The ERC is thus a measure of the "free bonus" provided by nature and quantitatively determines the loss of minerals for nations Calvo et al. (2015), Palacios et al. (2018), Valero et al. (2015).

The ERC is interpreted as the energy needed to extract and concentrate a mineral from a completely dispersed state (x_c) to the conditions of concentration and composition found in a mine (x_m) using available technology. Thanatia comes from the Greek word "Thánatos", which means death, and is an idealization of a "commercial death planet" in which all minerals have been mined and dispersed into the crust, and all fossil fuels have been burned Palacios et al. (2018), Valero et al. (2017). It is the baseline for calculating the concentration exergy of a mineral resource. The concept of Thanatia was developed by Valero and Valero Valero and Valero (2014) and represents a state of total mineral dispersion into Earth's crust (x_c) . It is made up of 324 species, 292 minerals, and 32 diadochic elements Valero and Valero (2014), Valero et al. (2011). In our model for the concentration of high-iron-content minerals, we use Thanatia as a common rock. Because Thanatia has many minerals, only those with an iron content of >15% (by weight) are shown in Fig. 1. A complete list of the substances in Thanatia considered in the present study, along with their chemical formulas and percentages by weight, can be found in Valero and Valero (2014, p. 304). Owing to the high iron content of magnetite in Thanatia and because hematic deposits are highly valued for iron production, e.g., Carajás in Brazil. Hematite and magnetite are considered for concentration in our computational model.

The ERCs of different minerals were computed by Valero et al. Valero et al. (2013) by examining the behavior of ore decline and the energy consumption required for the concentration of cobalt, copper, gold, nickel, and uranium. Analysis of these data revealed that as the ore grade decreases, the energy for concentration increases exponentially Valero et al. (2013). Valero et al. proposed a general equation for estimating the energy consumption according to the ore grade:

$$E_{(X_m)} = A \cdot X_m^{-0.5},\tag{1}$$

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Table 1				
ERC for iron	ore in GJ per ton o	of the element (a	dapted from Cal	vo et al. (2017)
Mineral	Mineral ore	$x_c(g/g)$	$x_m(g/g)$	ERC (GJ/t)
Iron ore	Hematite	9.66E-04	7.30E-01	18

where $E_{(X_m)}$ is the energy for the concentration and extraction of minerals at the ore grade (x_m) , and the coefficient *A* is determined for each mineral. In the methodology of Valero et al., the ERC of each element is calculated under the assumption that the element is obtained from a single type of ore (usually the most common one). Hence, for the case of iron, the ERC was obtained under the assumption that iron is only obtained from hematite ores, which have a crustal concentration of 9.66 E-04 g/g, as shown in Table 1. A complete and updated list of the exergy required for concentrating minerals from Thanatia (x_c) to the average concentration (x_m) for different minerals based on the methodology of Valero et al. was presented by Calvo et al. Calvo et al. (2017).

Table 1 presents the ERC value of 73% hematite (Fe₂O₃) required for concentration from Thanatia (x_c) to the average concentration in mines (x_m).

3. Methodology

The purpose of this study is to develop a model for concentrating iron-bearing minerals, mainly magnetite and hematite, from Thanatia until a concentration in equivalent-iron content similar to the one published in the ERC for hematite (Fe_2O_3) is reached. This indicates a starting concentration of 3.6% iron in Thanatia (x_c) and an ending concentration of approximately 50% iron in the mine (x_m). The latter comes from the stoichiometric conversion of the iron content in 70% hematite reported for the ERC of hematite, as shown in Table 1.

The concentration of minerals involves the transportation of the rocks from the mine to the concentration plant and different processes of mineral concentration Rankin (2011). Thus, the total specific energy for concentrating iron ore at the average ore grade $(\sim 50\%$ iron) from Thanatia (3.63\% iron) was considered as the sum of the energy for the ore-handling process and the energy for concentration. In our model, the minerals for concentration are obtained from Earth's crust; surface mining is assumed. As reported by Chapman and Roberts Chapman and Roberts (1983), ore transportation plays an important role in the total energy requirement of the ore-handling process. This is why the energy requirement for drilling and blasting is considered to be negligible in our model, in comparison with the energy for ore-handling and concentration. The ore-handling process involves the transportation of the ore from an open pit to the concentration plant, generally using haul trucks. At the facility, comminution and concentration are performed.

For the ore handling, a minimum distance between the mine and the facility was assumed, so that the fuel consumption per ton of ore prevailed over distance. Then, taking into account the iron concentration in the feed stream of 3.63 Fe%, the specific energy per ton of iron ore was calculated (see Fig. 2).

Because Thanatia is an ideal ore, the stages of comminution and concentration at the facility were designed according to an extensive literature review and analyses of different flowsheets of iron concentration plants. The fundamentals of iron-ore processing and the layouts of processing plants were adapted from Lu Lu (2015) and Sousa de Sousa et al. (2002). Technical reports of iron-ore projects were also studied Gignac et al. (2017), Tanghavel and Batista (2014), de Souza (2010), Sampaio et al. (2001). Publications by Houot Houot (1983) and Filippov Filippov et al. (2014) regarding the beneficiation of iron were reviewed, as well as papers regarding the flotation of iron ores by Frommer Frommer (1967) and Araujo et al. Araujo et al. (2005). The use of collectors and reagents for iron ores was examined according to the results of Schulz and Cooke Schulz and Cooke (1953), and a lifecycle assessment (LCA) of iron ore mining performed by Ferreira et al. Ferreira and Leite (2015) was considered.

The experience of the research group with regard to mineral processing was important for the final design of the model using the software HSC Chemistry version 9.5.1 Garcia et al. (2018). In the model, many variables were considered, but only the most important ones are described herein. For the simulation, an Intel core i7-6600 2.60 GHz central processing unit with 32 GB of random-access memory was used.

On the basis of the analysis of technical reports of iron projects Gignac et al. (2017), Tanghavel and Batista (2014), de Souza (2010), Sampaio et al. (2001), the study of the layouts in Lu (2015), and previous works on models by Abadías et al. Abadías Llamas et al. (2019), the ore feed for the model was assumed as 2,500 tons per hour with a top size of 600 mm. To illustrate the model, Fig. 3 depicts the main stages for the concentration of iron from Thanatia.

Three circuits in the comminution were considered for the model: crushing, grinding, and two regrinding stages for liberating the maximum amount of metal from Thanatia. The 80% passing through the primary crusher (F80) 264 mm is fed into the comminution circuit. Crushing is performed by a gyratory crusher and a cone crusher, with the particle-size output (P80) set as 200 and 60 mm, respectively. A screen with a cut size of 32 mm is placed in a closed circuit with the cone crusher. The screen reports to the grinding circuit, which consists of two ball mills. The sizes of the passing particles (P80) for these mills are 4000 and 75 μ m, respectively. A cyclone between the ball mills with a cut particle size of 1000 μ m is considered. The combination of the ball mill with the cyclone yields a particle size of approximately 75 μ m.

A fundamental equation for computing the specific energy required for the mill during the comminution process is Bond's equation Wills and Napier-Munn (2006), Skarin and Tikhonov (2015):

$$W = 10W_i \left(\frac{1}{\sqrt{P_{80}}} - \frac{1}{\sqrt{F_{80}}}\right) EF_x,$$
 (2)

where *W* is the specific energy consumption of the mill (kWh/t), *W_i* is the work index (Bond index) measured in a laboratory mill (kWh/t), and P80 and F80 are the 80% passing sizes of the product and the feed (-m), respectively. *EF_x* is the product of the Rowland efficiency factors, which depend on the mill, size, type of media, type of grinding circuit, etc. Wills and Napier-Munn (2006), Skarin and Tikhonov (2015), King (2001), Rowland (1982, 2002). The theoretical power draw by the mill (kW) is calculated as W × T, where T is the throughput tonnage (t/h) Wills and Napier-Munn (2006).

Eq. (2) was used to determine the theoretical power draw during the comminution stages. Both the feed (F80) and product (P80) passing sizes were obtained using the HSC model. The work index (W_i) for an unidentified iron ore can vary from 4 to 31 kWh/t Lindroos and Keranen (1985). For the first calculation of the specific energy consumption (W), a representative value of 14 kWh/t was considered. A similar value for this conversion (61.22 kJ/kg) was employed by Valero and Valero Valero and Valero (2012a) to calculate the exergy of comminution and concentration for different minerals.

To reduce the complexity of using the Rowland efficiency factors (EF_x) in Eq. (2), the procedure proposed by Will and Finch (Wills and Napier-Munn, 2006, Ch. 7) was followed for the selection of mills. Accordingly, a value of 1 for EF_x was



Fig. 1. Iron-bearing minerals in Thanatia. The left axis (in black) indicates the content of the minerals in Thanatia. The right axis (in gray) indicates the content of iron in the minerals.



Fig. 2. Conceptualization of the total energy needed to concentrate iron ore from Thanatia as the sum of the energies for the handling and concentration processes.

assumed, and the specific energy consumption (W) for every mill was computed. According to the W values for the mills and information from catalogs provided by the manufacturers, models of mills were selected. Then, the number of mills was estimated. Data published in Metso (2010, 2008) for primary gyratory and cone crushers were considered. For the grinding and re-grinding ball mills, we considered a survey of data regarding the specific energy (7.82 kWh/t) for these tumbling mills reported by Latchireddi and Faria Latchireddi and Faria (2013). For classification, the power of spirals and low and high magnetic separators were taken from Metso (2015). The power required for the flotation process of the main iron-bearing minerals was obtained directly from the HSC model Garcia et al. (2018). The specific energy per ton of iron was determined according to the feed flow rate (2500 t/h) and the iron concentration in Thanatia (3.63% iron).

After the start of the classifying process in comminution, highiron-content minerals are separated from the unwanted minerals because of their higher specific gravity (SG) and magnetic susceptibility. Thus, the comminution process reports to two spiral concentrators, where low-SG minerals, such as quartz and silicates, are partially separated. To ensure the separation of unwanted minerals, a combination of three classifying cyclones separates fine particles (low SG) from coarse ones (high SG). The overflow of the cyclones undergoes a low-high magnetic separation process to remove iron minerals with low and high densities. The high iron minerals are transferred to the final concentration stage.

On the other hand, the underflow of the cyclones reports to a combination of low and high magnetic separators to upgrade the iron content. Magnetite is removed from the low-magnetic intensity separators owing to the high magnetic susceptibility. From the circuits of the rougher, scavenger, and cleaner of high intensity and magnetic gradient separators (SLon), hematite is recovered. Both the magnetite and hematite retrieved from the magnetic separation circuits are employed in the reverse flotation process.

Before the reverse flotation process, regrinding in a ball mill to 40 μ m is required. The flotation process consists of two stages: arrangements of rougher, scavenger, and cleaner cells and a recleaner stage. The feed to the first stage of reverse flotation is approximately 23% iron, which is a common iron content in concentration plants. The combination of the steps of reverse flotation, recirculation, cleaners, and re-cleaners assures that the iron content at the end of the flotation is 63.63%. Then, this stream is mixed with another stream coming from the classifying stage having a high magnetite content. For the flotation process, fast kinetics constants (kf) are set up following those reported by Saleh Saleh (2010). The volume and number of cells for the



Fig. 3. Flowsheet of concentration and tailings from Thanatia to iron ore.

flotation tanks are established according to typical values of cells per bank from manufacturer data published by Weiss Lindroos and Keranen (1985) and Wills and Finch Wills and Napier-Munn (2006).

The arrangement of the equipment for the comminution and concentration processes described above is shown in Appendix.

4. Results and analysis

In this section, the results of the simulation are presented. The results are validated through a comparison of the key parameters of the comminution and concentration process with those in the literature. Finally, according to the methodology, the calculation of the specific energy through a sensitivity analysis is presented.

4.1. Simulation results

For the developed model, the direct results were the particle size for the feed (F80) and output (P80) of the crushers and mills in the comminution process, as shown Table 2. The reduction ratio (Rr) is the particle size of F80 divided by that of P80. The

Table 2

Feed (F80), product size (P80), reduction ratio, and specific energy (W) for every mill for the comminution process.

Stage	Equipment	F80 (-m)	P80 (-m)	Reduction ratio (Rr)
Crushing	Primary crusher	245631	200000	1
	Secondary crusher	215737	60000	4
Grinding	1st ball mill	11695	2400	5
	2nd ball mill	796	75	11
Re-grinding	3rd ball mill	60	50	1
	4th ball mill	66	40	2
Total				436

Table 3

Retention time and power draw for the flotation proce

Stage	Retention time (min)	Power (kW)
Rougher (RG)	28	90
Scavenger (SCV)	17	44
Cleaner (CL)	26	74
Scavenger 1	36	44
Cleaner 1	8	22
Cleaner 2	7	22

Table 4

The total specific energy of the comminution process according to the HSC model and the literature.

Stage	Equipment	Source	Specific energy (kWh/t)
Cruching	Primary crusher	Metso (2010)	0.27
Crushing	Secondary crusher	Metso (2008)	0.57
Crinding	SAG mill	Latchireddi and Faria (2013)	10.26
Gilliullig	Ball mill	Latchireddi and Faria (2013)	16.27
Re-grindingHIG mill		Wills and Napier-Munn (2006)18.72
TOTAL			27.36
Crushing an	d grinding iron ore	Bleiwas (2011)	20-30

total reduction ratio is the product of every mill, as indicated in Metso (2015). For the flotation process, the direct results were the retention time and power consumption, as shown in Table 3.

The result of the flotation process was a product with a mass flow rate of 19.72 t/h and an iron content of 58.10%. The main minerals in the concentrate are shown in Fig. 4. Owing to the large number of iron-bearing minerals in Thanatia, as shown in Fig. 1, recovered product mainly compromised high-iron-content minerals (mainly magnetite and hematite). This is why the recovery of iron was only 12.62% in our model. On the other hand, the recovery of hematite and magnetite was 25.13% and 79.06%, respectively.

4.2. Validation of model

To validate the HSC model, key values obtained using the model were compared with corresponding values in the literature. An important parameter for the comparison was the total specific energy of the comminution process. The selection of the models and capacities of every mill was performed as explained in Section 1. This procedure involves the use of information provided by the developed HSC model and catalogs from manufacturers. Under these assumptions, Table 4 shows the total specific energy of the comminution process.

The total specific energy based on the HSC model shown in Table 4 has the same order of magnitude as the values published by Bleiwas Bleiwas (2011) (for the electricity used in the crushing and grinding for the production of iron and steel in sub-Saharan Africa).



Fig. 4. Minerals in the concentrate at the end of the reverse flotation.

Table 5

Power draw for the comminution and concentration processes.

Stage	Power demand (MW)	Power demand (%)
Crushing	2	1.9
Grinding	71	87.1
Re-grinding	9	10.6
Classifying	0.06	0.1
Reverse flotation	0.52	0.4
TOTAL	81	

Table 6

Specific energy for the concentration of iron minerals from Thanatia in kWh per ton of ore.

	Iron concentration	Flow rate	Specific energy
	(wt-%)	(t/h)	(kWh/t)
Feed ore	3.63	2500	33

The retention time for the HSC model, as shown in Table 3, is in the expected range of values reported by Lu (2015), Lindroos and Keranen (1985), Fuerstenau et al. (2007). For the rougher, cleaner, and scavenger 1, retention times of >30 min were obtained owing to the need for recirculation in the flotation circuits.

Considering the complexity of Thanatia as a mixture of lowcontent minerals and the uniqueness of the flowsheet developed in the present study, the results of the HSC model are logical and reliable.

4.3. Specific energy for iron concentration

As indicated by Eq. (2), the specific energy consumption W of the mill necessary to calculate the power demand is based on the work index (W_i). In a first attempt to determine the specific energy, a value of 14 kWh/t was considered, as mentioned in Section 3. With these considerations and others previously explained for the model setup, the power demand for the flotation plant was estimated, as shown in Table 5.



Fig. 5. Specific energy for the concentration of high-iron-content minerals from Thanatia with respect to the total reduction ratio (Rr) and Bond work index (W_i)

As shown in Table 5, most of the power demand was due to the comminution process (>99%), with grinding accounting for the largest power consumption. Using the methodology described in Section 2, we calculated the specific energy for the concentration of high-iron-content minerals from Thanatia, as shown in Table 6.

To estimate the specific energy required for ore handling, consumption of 2.2 kg/t was considered, as reported by Norgate and Haque Norgate and Haque (2010) in their work based on LCA for iron ore and other minerals. The specific energies for the ore handling, which involves the transportation of ore from the mine to the concentration plant, and concentration, including the stages of crushing, grinding, re-grinding, and reverse flotation, for a W_i of 14 kWh/t are shown in Table 7.

Table 7

Specific energy for the concentration of iron-ore from Thanatia in GJ per ton of the element

Specific energy (GJ/t-Fe)
2.3
3.2
5.6

Table 8

Total reduction ratios of the mills for the sensitivity analysis.

	5 5
Scenario	Total reduction ratio (Rr)
1st	436
2nd	491
3rd	574
4th	657
5th	739
6th	844
7th	958
8th	1145
9th	1433
10th	1943

4.4. Sensitivity analysis

Because Thanatia represents a complex ore, its Bond index W_i cannot be accurately determined for a large number of minerals. Thus, it is appropriate to estimate the specific energy through a sensitivity analysis. This analysis is based on the variation of W_i from 4 to 31 kWh/t – a possible range for iron ores – as described in Section 1. The values considered for the sensitivity analysis were: 4, 9, 14, 21, and 31 kWh/t. According to the developed HSC model and the methodology described in this work, the specific energy required for concentrating iron minerals from Thanatia is accurately represented by the variation of the parameters of the comminution process, the highest energy consumption stage, and the hardness of the rock. These parameters are represented by the total reduction ratio (Rr) and the Bond work index (W_i) . In essence, the sensitivity should be taken as the uncertainty of the required final particle size needed to liberate the iron metal from unwanted minerals and the hardness values of the rock. Table 8 shows the range of total reduction ratios considered for the sensitivity analysis.

Similarly, as reported in Table 7, Fig. 5 shows the specific energy for the concentration of minerals with high content of iron from Thanatia. In the analysis, the total reduction ratio (Rr) was changed, as shown in Table 2, to represent the different particle sizes required for extracting iron from the minerals in Thanatia.

The results for the specific energy in Fig. 5 were obtained under the assumptions made in Section 3, with the layout of mills, classifiers, magnetic separators, flotation cells, and recirculation circuits shown in Appendix.

As shown in Fig. 5, the specific energy increases as the total reduction ratio (Rr) increases. There is a proportional relationship between the specific energy and the Bond work index, as indicated by Eq. (2).

The result based on the HSC model is compared with the ERC value converted into iron content (through molecular weights) and the embodied energy (mining and concentration) of iron reported by Calvo et al. Calvo et al. (2017). The energy spent on loading and crushing reported in Norgate and Haque (2010) is used to draw a comparison. In the model, the values of the

Comparison of the specific energy (in GJ per ton of element) between the present work and other reported values.

	Specific Energy (GJ/t-iron)	Source
ERC based on HSC	3.3-14.1	Present work
PIEVIOUS EKC	10	Calvo et al. (2017)

specific energy can vary according to Rr and W_i . For the lowest Rr (436) and softest rock ($W_i = 4 \text{ kWh/t}$), the energy required was 3.3 GJ/t-Fe. For the highest Rr (1943) and hardest rock ($W_i = 4-31 \text{ kWh/t}$), the energy required was 14.1 GJ/t-Fe.

Table 9 summarizes the results and compares them with previously reported values, under the assumptions explained in Section 3.

The previous ERC has the same order of magnitude of the specific energy as the present work with a combination of the finest particles (Rr = 1943) and the hardest iron ore (Wi = 31 kWh/t). Importantly, in our model, minerals with a high iron content were concentrated. The mathematical calculation of the ERC for iron by Valero et al. corresponds to only hematite, as shown in Table 1.

As shown in Fig. 5, the specific energy for the concentration of iron minerals depends on the hardness of the rock (W_i) and the final particle size (represented by Rr). As shown in Table 7, for $W_i = 14$ kWh/t, which was also considered by Valero and Valero Valero and Valero (2012a) as a common value for different minerals, and a common final size of P80 = 40 μ m (Rr = 436) for iron ore, the specific energy for the concentration is 5.6 GJ/t-Fe. This value can be considered as a "New ERC for iron from HSC", assuming that Thanatia exhibits behavior similar to that previously described ($W_i = 14$ kWh/t and Rr = 436).

In summary, the previous and new ERCs for iron differ considerably in the method of estimation. While the previous one was determined only according to mathematical and analytical analysis, the new one has strong support from a metallurgical viewpoint. For the previous ERC for iron, it was roughly assumed that only hematite could be concentrated from Thanatia. On the other hand, from a more realistic perspective, minerals with a high iron content in Thanatia, such as magnetite and hematite, are easily concentrated, and their separation is difficult. Additionally, in the case of the previous ERC, the processing of iron to obtain pellets or lumps for producing pig iron implies an additional expenditure of energy. This is because in the calculation of the previous ERC, the separation process (crushing and grinding) was not even considered. In contrast, further treatment for the iron ore of the new ERC allows energy saving because the ore is already ground to P80 = 40 μ m.

5. Conclusions

This study was the first attempt to rigorously assess the hypothetical energy needed to extract minerals from common bare rock. The assessment is fundamental for understanding the mineral capital of nations and the implications of the depletion of high-grade mines for future generations. Nature provides minerals concentrated in mines rather than dispersed throughout the crust, which saves a large amount of energy. However, as minerals become depleted, this free natural bonus decreases, and energy expenditures increase. In the ultimate limit, the calculated energy costs are not hypothetical but real. Accordingly, assessing the "free energy bonus" allows the mineral patrimony of nations to be measured in a physical manner.

Theoretical and academic analyses to assess this bonus were previously performed for various minerals. These analyses involved assumptions and extrapolations that may be valid for determining the orders of magnitude but are not accurate enough. With the help of HSC software and the team at Helmholtz Institute Freiberg for Resource Technology (HIF), we for the first time simulated a real mining and the metallurgical process starting with Thanatia, and hence obtained accurate values for iron production.

The computational model was developed by studying different layouts of iron-ore concentration plants and leveraging the experience of the members of the research team at HIF and the Research Centre for Energy Resources and Consumption (CIRCE Institute).

To validate our results, we compared the parameters obtained from the model with others obtained from a literature review. Furthermore, we performed a sensitivity analysis by changing two key parameters for the concentration of iron minerals. The first parameter characterizes the uncertainty of the final particle size before the reverse flotation processes, because of the requirement to liberate iron metal present in a very low concentration in Thanatia. This is represented by the variation of the particle size in the comminution process (Rr). The second parameter in the sensitivity analysis denotes the variation of hardness in Thanatia according to the Bond index. From the model, a "New ERC for iron" of 5.6 GJ/t-Fe can be obtained by assuming that Thanatia exhibits behavior similar to that previously described (W_i = 14 kWh/t and Rr = 436). This value is three times lower than the previous one (18 GJ/t). The values differ with regard to the method of calculation. While the previous value was estimated via mathematical and analytical analysis, the new one has strong support from an engineering viewpoint, as it was obtained using the specialized software HSC Chemistry.

In future research, additional models will be developed for other minerals to compare and update the previously obtained ERC values. The results of this study highlight the need to value high-ironcontent deposits, particularly in countries where the iron ore is vastly extracted. Although steel is the most extensively recycled metal, its consumption is expected to increase significantly in the coming years with the need for renewable-energy technologies. Thus, sustainable methods for the production of metals that satisfy the needs of the present and future generations are necessary. Additionally, the loss of natural patrimony in nations where minerals are extracted should be taken into account. The roles of these nations in a globalized economy should be reconsidered.

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Author contributions

Palacios, J.L performed the literature review, model construction, and simulations and wrote the first parts of the paper. Fernandes, I. and Abadias, A. supported the modeling and simulation. Valero, An. and Valero, Al. supervised the research on the calculation of the energy consumption for upgrading the ERC for copper. Reuter, M. provided metallurgical advice and supervised the modeling and results.

Conflict of interest

The authors declare no conflicts of interest

Appendix



Comminution stage





From Thanatia to Iron (Fe) Reverse Flotation

Reverse flotation stage

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A.2 Paper II

Palacios, J., Abadias, A., Valero, A., Valero, A., & Reuter, M. A. (2019). Producing metals from common rocks: The case of gold. Resources, Conservation & Recycling, 148(February), 23–35. https://doi.org/10.1016/j.resconrec.2019.04.026

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Scope: review of the calculation of the exergy replacement cost (ERC) and thermodynamic rarity (ERC), overview of mineral and metal processing of gold, development of a computational model in HSC for the production of gold from thanatia

Contribution to the work:

- To describe in brief the most common methodologies for the assessment of mineral resources and their disadvantages
- To explain how the exergy replacement cost (ERC) and the thermodynamic rarity /TheRy) for gold was determined with its weak points
- To develop a new approach to estimate the new ERC of metals based on mineral processing criteria
- To develop a computational model with HSC software to produce gold from Thanatia
- To estimate the new value of the ERC and TheRy for gold with HSC and draw a comparison with the previous ERC
- To determine the importance of the development of computational models in HSC to estimate more accurate values of ERC and TheRy for the rest of metals.

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Producing metals from common rocks: The case of gold



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ABSTRACT

The depletion of the mineral capital is a topic of concern because the worldwide demand for minerals is rapidly increasing. Moreover, since the energy consumption increases as ore grades decline, there is growing stress on energy resources and the environment associated with mining activities. The energy costs associated with the exhaustion of mineral deposits is ruled by the entropy law through a negative logarithmic pattern, in which as the ore grade tends to zero, the energy tends to infinity. This study analyzes through a model developed in HSC Chemistry software, the energy that would be required to produce gold from common bare rock. In this way, we evaluate the maximum energy consumption with current technologies, to obtain gold at the final ore grade, i.e., when all mineral deposits were completely exhausted until reaching crustal concentration. The final theoretical concentration of gold is assumed to be that of the model of Thanatia, which is a resource exhausted Earth with the most abundant minerals found at crustal concentrations. The results are then compared to theoretical values obtained in previous studies for gold and serve to update with a more accurate methodology, the so-called thermodynamic rarity of minerals, as a way to assess the avoided mining energy for having minerals concentrated in mines and not dispersed throughout the crust. This then serves to assess the mineral capital and its degradation velocity from a thermodynamic point of view.

1. Introduction

Because of its extraordinary properties, such as electrical conductivity, stability at environmental conditions and meaning of nobleness in ornaments. Due to its stability, gold has a number of applications in medical implants as reported in (Higby, 1982; Pricker, 1996; Dykman and Khlebtsov, 2011), and activity in catalysis as investigated in (Hashmi and Hutchings, 2006; Gold-Catalyzed Organic Reactions, 2007; Yang and Hashmi, 2014; Pflästerer and Hashmi, 2016; Asiri and Hashmi, 2016). Therefore, gold has been exploited for centuries. In 2015, main gold producers were: China 20%, Australia 12%, Russia 11% and Canada 7%. Peru, South Africa, and Mexico had 6% of world mine production. In Fig. 1, the production of gold from 1998 to 2015 by country is shown based on statistics and reports of the US Geological Survey (USGS) (Matos, 2019; U.S. Geological Survey Mineral commodity summaries, 2018).

The evolution of the decline of high-grade deposits has been investigated by different authors, such as Mudd (2007a, 2007b, 2007c, 2008, 2010; Craig et al. (2014); Norgate and Jahanshahi (2010) or Calvo et al. (2016). In this respect, and although the recycling of gold accounted for approximately one-third of the total supply from 1995 to 2014 (Hewitt et al., 2015), Mudd (2007a) observed a clear decline tendency of the ore grades (Mudd, 2007a) of gold-producer countries, such as Brazil, Australia, South Africa, Canada, and the United States,. For instance, in Australia in 1859 ore grades in gold deposits were 37 g/ t and nowadays the concentration is found at 2 g/t.

The need for renewable energy technologies for a decarbonized society will imply the use of more metals (Sawyer et al., 2016; International Energy Agency Energy Technology Perspectives, 2010; World Steel Association Steel's contribution to low carbon future and climate resilient societies - worldsteel position paper, 2017). In a recent publication by Valero et al. (2018) on material restriction for the manufacture of renewable energy technologies, it was pointed out that moving towards a low carbon economy would cause a deeper reliance on non-fuel minerals.

Minerals are essential for keeping today's standard of living (United Nations (UN) Plan of Implementation of the World Summit on Sustainable Development Contents, 2019), and high metal-content

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Fig. 1. World mine production of gold by country.

deposits are gradually being depleted. As a consequence, today, man needs to go deeper and to more remote places to satisfy the increasing societal need for raw materials. Therefore there is an urgent necessity to manage the mineral capital effectively, and to do that; the first step is to assess it accurately. This assessment can be performed merely on a tonnage perspective. When the evaluation of minerals is done on a tonnage approach, substantial aspects of minerals are ignored, such as scarcity in the Earth's crust (Valero and Valero, 2014; Domínguez and Valero, 2013; Palacios et al., 2018). For instance, one ton of iron is equal to one ton of gold, on a mass basis, however iron is more abundant than gold, and the energy required for the processing and refining of the metal from the ore (embodied energy) is higher for gold than for iron. This comparison reveals that a tonnage approach is no longer valid for the proper evaluation of minerals.

Another way to assess minerals is considering their market prices. Metal prices are linked to the effort made to extract metals from ores and extraction costs (Valero and Valero, 2014; Henckens et al., 2016). Nevertheless, prices are strongly influenced by many other factors, such as, supply-demand, geopolitics or speculation, that is why its behavior is volatile (Henckens et al., 2016), as can be seen in Fig. 2, where historical gold prices since 1900 are shown (Kelly and Matos, 2019).

Alternatively, minerals can be assessed considering their physical quality through the Second Law of Thermodynamics. Valero and Valero proposed the concept of the exergy replacement cost (ERC) and thermodynamic rarity for the evaluation of mineral resources (Valero and Valero, 2014; Valero et al., 2013). The ERC characterizes the energy required to concentrate minerals at an average ore-grade found in Thanatia until the concentration currently located in the mines, while thermodynamic rarity is the sum of the ERC and current mining and beneficiation energies for obtaining the different mineral commodities. Thanatia is an idealization of complete mineral dispersion in the Earth's crust (Valero and Valero, 2014) and represents the common rock from which minerals would be concentrated when mineral deposits no longer exist. The ERC can be seen as an avoided cost that man saves for having minerals concentrated in mines and not dispersed throughout the crust. In the limit, this free bonus would become lost, and mining would need



Fig. 2. Historical gold market price. Source (Kelly and Matos, 2019).

to take place directly from common rocks. Several authors also examined the idea of crustal mining as a limit. Henckens et al. stated that the maximum cost of extraction of commodities would be achieved when mining would come from low concentration deposits, common rocks and seawater (Henckens et al., 2016). Skinner mentioned that the extraction from common rocks is technically feasible, but it would require more energy than from rich metal ores (Skinner, 1976). Authors like Harmsen et al. (2013), Bardi (2014), supported Skinner's statement about the increment of specific energy for the extraction of metals from low-ore grade deposits. Steen and Borg published considerable increases in the production cost of metal concentrates, such as copper, cadmium, manganese, etc. (Steen and Borg, 2002).

Valero and Valero (2014) made an in-depth analysis of such crustal mining energy values characterized by ERC. This was estimated by analysis of statistical trends, estimations or mathematical models, supported by thermodynamic assessments considering that the energy consumption as a function of the ore grade is ruled by the entropy law and hence as the ore grade tends to zero, the energy consumption tends to infinity.

In this research, we show a novel method to estimate the specific energy needed to produce metals; in this case, gold, from Thanatia. The methodology is based on a computational model with HSC Chemistry software (Garcia et al., 2018) and hence is more exact than the values provided by Valero and Valero (2014). Our investigation aims to contribute to a deeper discussion about the sustainable production of metals and the loss of the natural patrimony of nations.

2. Production of gold from Thanatia

In the first part of this section, the concepts of thermodynamic rarity and exergy replacement costs are explained. Moreover, the main features of the production of gold for our model are described. Finally, the procedure to estimate the energy required to produce gold from Thanatia is explained.

2.1. The thermodynamic rarity and tThanatia

Thermodynamic rarity (TheRy) has been established for a more accurate assessment of minerals. TheRy is defined as the amount of exergy required to obtain a mineral commodity from a state of total mineral dispersion coined as Thanatia. TheRy is defined as the sum of the exergy replacement cost (ERC) and the energy for concentration and refining (Valero and Valero, 2014; Calvo et al., 2017). The exergy replacement cost (ERC) enables the quantitative assessment of mineral resources, as is a measure of the mineral bonus granted by Nature in the form of concentrated mineral deposits. Exergy is an extensive thermodynamic property of a system-environment combination that defines the minimum amount of work that a system can produce when it is brought into equilibrium with its surrounding environment (Valero and Valero, 2014; Cengel and Boles, 2008; Bejan et al., 1996; Moran et al., 2011). When fossil fuels are burned and hence brought to equilibrium with the environment, they liberate exergy which is associated with their high heating value (HHV) (Valero and Valero, 2012a, b).

In contrast, non-fuel minerals are not combustible, and the link between the HHV and exergy is not valid. A traditional approach to evaluate non-fuel minerals has been through their chemical exergy. Szargut made a substantial contribution to the assessment of minerals with exergy. In a seminal paper, Szargut published chemical exergy of different elements (Szargut, 1989) which have been widely used for research done by many different authors such as Ayres (Ayres and Energy, 2016), Dewulf et al. (2006) and Szargut and colleagues (Calvo et al., 2015; Szargut et al., 2015, 2002). However, only chemical exergy does not assess non-fuel minerals accurately, as demonstrated by Domínguez and colleagues. In their work, Domínguez et al. (Domínguez and Valero, 2013) made a comparison between the chemical exergy of gold (60 kJ/mol) and aluminum (796 kJ/mol). The authors pointed out that even though gold is scarcer than aluminum this fact is not adequately reflected by chemical exergy. That is why Valero and Valero postulated Exergoecology for the proper assessment of mineral resources (Valero and Valero, 2010). In this regard, Physical Geonomics, one division of Exergoecology, deals with the use of exergy for the evaluation of non-fuel minerals. According to this postulate, exergy of non-fuel minerals cannot only be computed with the chemical exergy, but also with the concentration exergy. This should reflect the relative concentration of the mineral in the Earth's crust and hence is a measure of the mineral's scarcity.

As previously explained, the fact of having minerals concentrated in deposits represents a "free bonus" provided by Mother Nature. This "free bonus" reduces significantly the costs associated with mining, concentration, and refining of metals. This cost-free concentration of minerals in deposits can be seen as an "avoided cost" concerning mineral processing and refining. When high-grade deposits become depleted, a reduction of this free bonus occurs. This results in an extensive exergy consumption to extract a similar quantity of metal from lowerore grade deposits. The loss of exergy replacement cost (ERC) can hence be used quantitatively to determine the loss of mineral patrimony of nations (Palacios et al., 2018; Calvo et al., 2015; Valero et al., 2015). ERC is inferred as the energy that would be required to extract and concentrate a mineral from a completely dispersed state (x_c) to the conditions of concentration and composition found in the mine (x_m) by using current technologies. Thanatia represents a state of total mineral dispersion into the Earth's crust (x_c) and is a model of exhausted crust composed of 324 species, 292 minerals and 32 diadochic elements (Valero and Valero, 2014; Valero et al., 2011). In our model, we will use Thanatia as a common rock. In Fig. 3 high-grade minerals in Thanatia are shown, they include native gold and two tellurides, sylvanite and calaverite. A complete list of the substances in Thanatia can be found in (Valero and Valero, 2014).

The exergy replacement cost (ERC) of different minerals were calculated by (Valero et al. (2013)) by observing the ore decreasing behavior and increase in energy consumption of cobalt, copper, gold, nickel, and uranium. Valero et al. suggested a mathematical equation to give an estimate on the energy consumption as a function of the ore grade, Eq. (1).

$$E_{(X_m)} = A \cdot X_m^{-0.5}$$
(1)

Where $E_{(X_m)}$ is the energy for the concentration and extraction of minerals at the ore grade (x_m) , and coefficient A is a constant determined for each mineral.

In a publication, Calvo et al. (2017) updated from Valero and Valero (2014) the exergy required to concentrate minerals from Thanatia (x_c) to the average concentration in mines (x_m). For the interest of this research, Table 1 shows the ERC and TheRy of gold. As previously explained, the thermodynamic rarity (TheRy) is computed as the sum of ERC and the energy required for the production of metals obtained from mines (energy for mining, concentration, and smelting and refining).

2.2. The energy needed to obtain gold from Thanatia

The purpose of this study is to obtain gold from Thanatia in order to upgrade the previous value of TheRy reported by Calvo and colleagues (Calvo et al., 2017). It means that the first step is to estimate the ERC to concentrate gold from Thanatia's composition (x_c) to the average gold content in mines (x_m) and then with additional processing to obtain gold. Fig. 4 better explains the idea to estimate the energy needed to get gold from a disperse state, Thanatia.

Due to the low concentration of gold in deposits, it is usually measured in grams per ton. Ore-grades for open pit mines (1-4 g/t) is generally lower than underground mines (8-10 g/t) (Calvo et al., 2016; World Gold Council The Authority on Gold, 2019). The production process of gold depends upon the ore composition (Rankin, 2011;



Fig. 3. Gold-bearing minerals in Thanatia in wt-%. The arrows above each column show the wt-% of each mineral.

Table 1

The exergy replacement cost (ERC) and thermodynamic rarity (TheRy) for gold in GJ per ton of element.

(adapted from (Calvo et al., 2017)).

Metal	$x_c (g/t)$	<i>x_m</i> (g/t)	ERC (GJ/t)	TheRy (GJ/t)
Gold	1.28E-03	2.24	5.53E+05	6.63E+05

Marsden and House, 2019, 2006). In our case, Thanatia constitutes the orebody (x_c). As can be seen in Fig. 3, most of the gold is in native form, followed by tellurides, such as calaverite and sylvanite. In that sense, our model considers processing stages for the production of gold from native and telluride ores.

To determine the ERC, exergy needed to concentrate gold from

Thanatia concentration to average mine, it was considered the energy for ore-handling and concentration. For the ore-handling, it was assumed a minimum distance between the mine and the facility, so that the fuel consumption per ton of ore prevailed over the distance. Because of the nature of Thanatia, the concentration of minerals involves stages of comminution and flotation. Comminution is performed to liberate gold-bearing minerals from the unwanted ones. During comminution, particles are reduced in size through crushing and grinding until one that metal can be released during the concentration process (Szargut et al., 2002; Valero and Valero, 2010). Theoretical and empirical equations to determine the energy required during comminution have been postulated by Rittinger, Kick and Bond (Jankovic et al., 2010; Wills and Napier-Munn, 2006). However, Bond's method has been used extensively and has become the standard (Wills and Napier-Munn,



Fig. 4. Conceptualization of the total energy required to obtain gold from Thanatia. Thermodynamic rarity (TheRy) as the sum of exergy replacement cost (ERC) and additional processing.



Fig. 5. Flowsheet for the processing of gold from Thanatia.

2006; Gupta et al., 2006; Skarin and Tikhonov, 2015), Eq. (2). Others methods, like Morell (Morrell, 2016) can be used for the same purposes, but they require as input in their equations values coming from laboratory testing works. Since Thanatia is an ideal state of mineral dispersion, it is not possible to collect samples. Therefore, the specific energy estimated in this work will correspond to a very conservative approach.

$$W = 10 W_i \left(\frac{1}{\sqrt{P_{80}}} - \frac{1}{\sqrt{F_{80}}} \right) EF_x \tag{2}$$

where W is the specific energy consumption of the mill (kWh/t), Wi is the work index measured in a laboratory mill (kWh/t) and represents the hardness of the ore. The P80 and F80 are the 80% passing sizes of the product and the feed (µm), respectively. Finally, EFx in the product of the Rowland efficiency factors which depend upon mill, size, and type of media, type of grinding circuit, etc. (Wills and Napier-Munn, 2006; Skarin and Tikhonov, 2015; King and Ronald, 2001; Rowland, 1982, 2002). Then, theoretical power draw by the mill (kW) is calculated by W x T, where T is the throughput tonnage (t/h) (Wills and Napier-Munn, 2006). A typical particle size after comminution for gold concentration facilities is about $75 \mu m$ (Marsden and House, 2019; Christine et al., 2014; Lipiec et al., 2016). Due to the high difference in density between gold and other minerals, often gravity concentration is widely used for its concentration (Wills and Napier-Munn, 2006; Lipiec et al., 2016; Carrasco, 2016).

Because of the presence of tellurides as gold-bearing minerals in Thanatia (Fig. 3), the concentration of the gold-telluride is necessary through flotation as suggested in (Marsden and House, 2019; Ellis and Deschênes, 2016a; Zhang et al., 2010). On this stage, the gold-tellurides are selectively separated from the gangue. Then roasting is necessary to break-down the bonding of the tellurides by heating between 600 °C–700 °C and gold is liberated (Marsden and House, 2019; Ellis and Deschênes, 2016a). Then, a refining stage is followed by cyanide leaching. Meanwhile, for the native gold, cyanide leaching was also used for refining. Finally, to obtain high-content gold, electrowinning is required. These stages of treatment and refining of the native and telluride stream follow the guidelines proposed by (Marsden and House, 2019) Taking into account the gold concentration in the feed stream (x_c) the specific energy per ton of gold was calculated.

3. Methodology

Due to the nature of Thanatia, the design of different processes to obtain gold has been done based on a literature review and an in-depth analysis of flowsheets. Basics about gold processing were studied from publications by Marsden and House (2019), Yannopoulos (1991), and mineral processing by Wills and Finch (Wills and Napier-Munn, 2006). Technical reports for gold processing plants were also studied, such as Éléonore Project in Canada (Christine et al., 2014), Fruta del Norte in Ecuador (Lipiec et al., 2016), Peñasquito in Mexico (Redmond et al., 2015), and Pueblo Viejo in Argentina (AMC Consultants, 2019). Investigations about the gravimetric concentration of gold were also analyzed, such as works by Carrasco (2016), and Valdivieso et al. (1999). The metallurgical recovery of gold was examined based on investigations by Sen (2010), Muir et al. (1985), Beyuo and Abaka-Wood (2016), Brandon et al. (1987) and Adams (1994). Publications by Elis and Deschênes (Ellis and Deschênes, 2016b), Zhang and colleagues (Zhang et al., 2010), as well as the layout of Emperor mines in Fiji published in Marsden and House (2019), were studied for processing of tellurides ores. The energy consumption in gold mines was derived from the research by Ballantyne and Powell (2014), and modeling and simulation of processing plants for recycling of gold from that of Reuter and van Schaik (2016).

Based on the experience of the research group about mineral processing the model with HSC Chemistry-version 9.7.1 software (Garcia et al., 2018) was set up. For the model, many variables were considered because of an extensive literature review and many runs of the model during the simulation campaign, yet due to its high number, only the important ones are written in the next lines. Computational requirements for the model and simulation can be found in Appendix A.

Because of the features of Thanatia and the analysis of technical reports about open-pit gold mines (Redmond et al., 2015; AMC Consultants, 2019; Tripp et al., 2015) and information about telluride ores (Marsden and House, 2019; Ellis and Deschênes, 2016a), the feed for the model was assumed to 6000 tons per hour with a top size of 600 mm. These figures were chosen based on the simulation campaign in HSC as appropriate feed for processing and sizing of the flotation tanks. Fig. 5 shows the main stages for the concentration of gold from Thanatia.

During ore handling, it was assumed consumption of 0.6 l/ton of rock as fuel consumption as reported in (Calvo et al., 2016) for open pit mines. For this, it was assumed that the facility was located in the nearby of the mine so that the distance did not profoundly influence fuel consumption. The set-up of the 80% participle size output (P80) in crushers and mills was selected according to fair values of reduction ratios as reported in (Metso Basics in minerals processing, 2019).

Accordingly, for the concentration, three circuits in the comminution were set up: crushing, grinding and regrinding. The 80% of particle size passing through the primary crusher (F80) 200 000 um is fed in the comminution circuit. Crushing is carried out by a cone crusher, control for particle size output (P80) is set-up for the crushers to 60 000 um. A screen (Screen 1) with a cut size of 100 mm is placed in a closed circuit with the cone crusher. Then, Screen 1 reports to the grinding circuit made up with a Semi-Autogenous Grinding mill (SAG) and two ball mills. Screen 2, which has a cut size of 20 mm, is connected in closed circuit with the SAG mill. The control for the particle size output (P80) for the SAG mill is 6000 um. Screen 2 feeds the circuit of the two ball mills (Ball Mill 1 and 2). Control of the passing particle size (P80) for these mills were 500 μ m and 75 μ m, respectively. Cyclone 1 is located between both ball mills with a cut particle size of 150 µm. Cyclone 2, placed after Ball Mill 2 separates due to the high density of native gold from tellurides. The cut size in this cyclone was $19 \,\mu m$.

In order to determine the theoretical power draw during comminution, Eq. (2) was used. The feed (F80), as well as the product (P80) passing sizes were obtained from the HSC model. The work index (Wi) for a gold ore may vary from 3 to 42 kW h/t (Weiss, 1985). In a first trial to estimate the specific energy consumption (W) a representative value of 15 kW h/t was considered. A slightly lower value with this corresponding conversion (16.3 kW h/t) was assumed by (Valero and Valero (2012a)) to calculate the exergy of comminution and concentration of different minerals.

To simplify the complexity of using Rowland Efficiency factors (EFx) in Eq. (2), the procedure explained by Will and Finch in (Wills and Napier-Munn, 2006) for the selection of mills was followed. Hence, a value of 1 for EFx was assumed, then the specific energy consumption (W) for every mill was computed. With W for every mill and together with the information in catalogs by the manufactures, models of mills were selected. The power required for the flotation process was obtained directly from the HSC model (Garcia et al., 2018). The specific energy per ton of gold was determined with the feed flow rate (6000 t/ h) and its concentration in Thanatia ($x_c = 1.28E-3 \text{ g/t}$).

After Cyclone 2, two streams are split because of the difference in density: one with native gold (high density) and the other containing gold-bearing tellurides (low density). Each stream will have different treatments. Due to the high density of gold, only gravity concentration is necessary for the native gold stream. Information regarding continuous gravity concentrators (Falcon Falcon Continuos Concentrators, 2019) was used to determine the energy spent on this stage. With the processing of the native gold stream, the concentration in mines (x_m) named in Fig. 4 as "gold ore" was reached. Hence the ERC was computed by adding the energy of the processes involved in its production, such as ore-handling, comminution, grinding and gravity concentration. To produce gold, it is necessary to continue with further processing (coined as "additional processing" in Fig. 4) of the native gold stream through a metallurgical process. Since cyanidation is widely used for the production of gold (Rankin, 2011; Marsden and House, 2019; Adams, 1994), leaching was considered to recover gold from this stream.

On the other hand, after Cyclone 2 the stream with tellurides requires a different treatment to extract as much gold as possible. For tellurides, the first process consists on a re-grinding up to $12 \,\mu$ m. The latter was chosen and a finer size due to inconvenient for the treatment of ultrafines in flotation (Zhang et al., 2010; Fuerstenau et al., 2007). Subsequently, flotation is required to separate sulfides and other unwanted minerals. The flotation process consists of two stages of arrangements of rougher, scavenger and cleaner. The combination of stages of flotation, recirculation, and cleaners guarantees the appropriate concentration of gold before the process of roasting. The volume and number of cells for the flotation tanks were established upon common values of cells per bank on manufactures data published by Weiss (Lindroos and Keranen, 1985), and Wills and Finch (Wills and Napier-Munn, 2006). Through roasting, most of the gold contained by the tellurides is liberated. For the model, data from (Marsden and House, 2019) about roasters was considered. The consumption of natural gas was assumed for the roaster to be 0.35 GJ/t Au as reported by Norgate et al. (Norgate and Haque, 2012) on a publication about the assessment of environmental impacts of gold production. Then, leaching through cyanidation is required for the processing of this stream of gold. According to the study of technical reports of Éléonore Project in Canada (Christine et al., 2014), Fruta del Norte in Ecuador (Lipiec et al., 2016), Peñasquito in Mexico (Redmond et al., 2015), and Pueblo Viejo in Argentina (AMC Consultants, 2019), the cyanide consumption was considered in the range of 0.3 to 0.4 g/l. Electricity consumption during leaching was taken as reported in (Norgate and Haque, 2012) and equal to 1.4 kW h/t ore.

Finally, electrowinning for the refining of both streams, native and gold-tellurides is needed to produce high-purity gold. The specific energy for these stages ("additional processing") is calculated from the concentration of gold ore (x_m). For the electricity consumption in electrowinning, a value of 3100 kW h/t Au was taken as reported by Norgate et al. (Norgate and Haque, 2012). It is important to note that, for the production of gold from common rocks understood from "gold ore," additional grinding is not required because the particles are already in the accurate size for concentration. This means an energy saving factor to estimate the total specific energy for the production of gold from Thanatia.

The thermodynamic rarity (TheRy) entails the energy required to produce gold from Thanatia. Hence it adds the specific energy to concentrate gold ore (from Thanatia to gold ore) and the energy required for additional processing to produce pure gold.

Circuits of comminution, concentration, and metallurgy of the model in HSC described above to produce gold from Thanatia can be seen in Appendix B.

4. Results and analysis

In this section results from the modeling and simulation campaign are shown. The validation of results is determined through a comparison of main parameters, such as energy for the comminution process and flotation with those found in the literature. Finally, from the methodology presented in this work, the calculation of the specific energy to produce gold from common rocks, Thanatia, is shown accompanied by a sensitivity analysis.

4.1. Results of the simulation

Results are shown according to the description in subsection 2.2, mainly in Fig. 4 and the methodology in section 3.

4.1.1. From Thanatia to gold-ore

For the concentration of gold-ore from Thanatia direct results of the computational model in HSC entails the processes of comminution, grinding and gravity concentration. The particle size for feed (F80) and output (P80) for comminution are shown in Table 2. For gravity and concentration, four continuous concentrators were assumed, and their power draw is shown in Table 3.

4.1.2. From the ore to gold

For the production of gold, no additional grinding is needed, only

Table 2

Feed	(F80)	and	product	size	(P80)	for	the	comminution	process
rccu	(100)	anu	product	SILC	(100)	101	unc	communution	process

Stage	Equipment	F80 (µm)	P80 (µm)
Crushing	Primary crusher	245,631	200,000
	Cone crusher	249,916	60,000
Grinding	SAG mill	39,439	6,000
	Ball mill 1	2,253	500
	Ball mill 2	127	75

Table 3

Power consumption for the gravity concentration.

Equipment	Power (kW)
Rougher	3,000
Cleaner	750
Re-cleaner 1	150
Re-cleaner 2	30

Table 4

Additional gravity concentration to produce gold from Thanatia.

Equipment	Power (kW)
Conc. 1	7.5
Conc. 2	7.5

two other concentrators, flotation, and metallurgy must be added. The results from the model are shown in the next tables as follows: gravity concentration in Table 4 and flotation in Table 5.

The retention time from the model in HSC, Table 5, was in the range of values reported by (Fuerstenau et al., 2007; Lindroos and Keranen, 1985; Lu, 2015), this fact constitutes a first step on the validation of results. Although Thanatia is a complex ore as an idealization of mineral dispersion and despite the singularity of the flowsheet for this research, the results from the model in HSC were logical and reliable.

4.2. Specific energy from Thanatia to gold ore

Since the specific energy depends upon the work index (Wi) and final size (P80) as written in Eq. (2), the validation of the model was done for a representative work index of 15 kW h/t and final size of (P80) $75 \mu\text{m}$. With the methodology described above and other assumptions for the model set-up previously explained, the power demand and specific energy, based on the feed of 6000 t/h and concentration of 1.28E-3 g/t, are shown in Table 6.

As can be seen in Table 6, comminution represents more than 90% of the power demand. Therefore, a key parameter for the validation of the model is a comparison of the specific energy for comminution. This value was in agreement with figures for energy requirements for beneficiation reported by (Chapman and Roberts (1983)).

Then, taking into account the ore handling and the previous values for comminution and gravity concentration, hereafter concentration, the total specific energy per ton of element is calculated Table 7.

4.2.1. Sensitivity analysis

Because of the complexity of Thanatia, where its work index Wi cannot be accurately predicted because of the large number of minerals, it is necessary to estimate the specific energy using a sensitivity analysis. In this analysis, Wi is varied from 3 to 42 kW h/ as reported in (Weiss, 1985). For the sensitivity analysis, five working indexes were considered, such as 5, 7, 15, 21 and 42 kW h/t. The specific energy required to concentrate gold until an average representative concentration in mines from Thanatia would be more precisely denoted by the variation of a parameter of the comminution process, and hardness of the rock. These parameters have been represented by the final particle size (P80) at the end of the comminution and work index (Wi).

Table 5	
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Retention time and power draw for the flotation process.

Stage	Retention time (min)	Power (kW)
Rougher (RG)	5	528
Scavenger (Sca)	10	1000
Scavenger 1 (Sca 1)	5	320
Cleaner (CL)	6	320

Table 6

Power demand and specific energy for comminution and concentration processes from Thanatia to gold-ore.

Stage	Power Demand (MW)	Specifc Energy (kWh/t)
Comminution	102	17.03
Gravity concentration	4	3.67
TOTAL	106	20.7

Table 7

Specific energy for the concentration of gold from Thanatia in GJ per ton of element.

	Specific Energy (GJ/t)
Ore handling	1.62E + 07
Concentration	4.54E + 07
TOTAL	6.17E + 07

Fig. 6 shows in logarithmic scale the total specific energy to concentrate gold from Thanatia as a function of the final particle size (P80) with five working indexes.

As can be observed in Fig. 6 for the five working indexes, the specific energy for comminution increases as the final size decreases. Also, when the ore is harder (higher work index), more energy is required for its processing. For visual comparison purposes, the value of ERC for gold from Valero and Valero as reported in (Calvo et al., 2017) (assuming that it had been calculated with 75 μ m) is also shown in Fig. 6, the difference in orders of magnitude is highlighted in this figure. Values of specific energy can vary from 3.3E + 07 GJ/t-Au to 3.8E + 08 GJ/t-Au for 80% final size (P80) from 75 μ m to 10 μ m and Wi = 5 and 42 kW h/t, respectively.

By making a comparison of the specific energy necessary to concentrate gold ore from Thanatia with the HSC model as shown in Table 8. with the exergy replacement cost (ERC) of gold reported in (Calvo et al., 2017), it can be seen that they differ in two orders of magnitude. This discrepancy is due to the difference in procedures to calculate both values, while the current work is based on a mineral processing model developed in HSC, the one published by (Calvo et al., 2017) is based on assumptions of Valero and colleagues about the analysis of ore-grade decline and increase of energy for processing expressed by Eq. (1).

In a benchmark for energy consumption in comminution for the processing of copper and gold ores in Australia, Ballantyne et al. (Ballantyne and Powell, 2014) reported an average value of 0.353 MW h/ozAu. If this is converted into the same units of the specific energy herein stated, most of the energy is due to comminution; a comparison is valid. This comparison shows a difference of three orders of magnitude. It means that the concentration of gold-ore from common rocks, Thanatia, would imply a consumption of three orders of magnitude higher than the current expenditure of energy for comminution.

By taking $75 \,\mu\text{m}$ as the final particle size for comminution, the different stages for the concentration of gold can be represented in a graph for different work indexes, Fig. 7.

By analyzing Fig. 7, it is appreciated that the highest energy consuming stage during the concentration of gold from Thanatia is the crushing and grinding processes. Ore handling and gravity concentration remain stable because the same amount of ore would be moved and concentrated regardless of its work index. Also, it is seen how the specific energy increases as the ore become harder (higher Wi). An exponential trend in energy consumption is shown when the ore becomes harder. This effect is again evidence of the entropic nature of mining processes.

4.3. Specific energy from Thanatia to gold

As explained in the methodology section, and depicted in Fig. 4 by doing additional processing, gold can be obtained from Thanatia. The specific energy to produce pure gold from Thanatia based on the model in HSC would be equivalent to the thermodynamic rarity (TheRy) of gold reported in (Calvo et al., 2017) postulated by Valero and Valero (2014). Accordingly, the energy required for additional processing to produce gold from the ore with Wi of $15 \,\text{kW} \,\text{h/t}$ and 80% passing through of $75 \,\mu\text{m}$ is shown in Table 9.

As it was expected most of the energy to produce gold from Thanatia corresponds to the ERC. As seen in Table 9 the difference in orders of magnitude between the ERC and additional processing are considerable (three orders of magnitude). Within the additional processes, the highest energy consumer was the leaching process, because no additional grinding is needed in this stage as explained in the methodology section. In comparison to the thermodynamic rarity for gold published in (Calvo et al., 2017) (6.6E + 05 GJ/t), there is a difference of two



Fig. 6. Total specific energy to concentrate (in the log. scale) gold from Thanatia as a function of the final particle size (P80) and different working indexes. For comparison purposes the value of ERC for gold of 5.5E + 05GJ/t Au reported in (Calvo et al., 2017) is also shown.

Table 8

Comparison of the specific energy to concentrate gold from Thanatia with other reported values in GJ per ton of element.



Fig. 7. Specific energy for the concentration of gold from Thanatia for $P80 = 75 \,\mu\text{m}$ for different work indexes (Wi).

Table 9 Specific energy to produce gold from Thanatia

	Specific Energy (GJ/t)
ERC	6.17E+07
Additional processing	
Concentration	4.80E + 02
Roasting	3.50E-01
Leaching	7.70E+03
Cyanidation	1.90E + 03
Electrowinning	9.6E+00
TOTAL	6.17E+07

orders of magnitude because of the ERC difference previously obtained.

5. Conclusions

With the methodology described in this paper based on a computational model developed with HSC Chemistry software, it has been possible to estimate the specific energy that would be required for the production of gold from common rocks. Since Thanatia has been an idealization of mineral dispersion in the Earth's crust, it has been selected as our common rock. Due to this fact, the specific energy was determined by applying Bond's equation, and not by other more precise methods which require some laboratory testing that is not possible having Thanatia as the starting point. Therefore, our results correspond to a very conservative approach.

The analysis of different flowsheets for the production of gold and the experience of the research group at the Helmholtz Institute Freiberg for Resource Technology and the Research Centre for Energy Resources and Consumption (CIRCE Institute) allowed the development of the computational model of this research. Drawing a comparison of main parameters obtained from the model in HSC and those available in the literature, the results from the model were logical and reliable. Due to the low concentration of minerals in Thanatia and the uncertainty regarding the hardness of its ore, a sensitivity analysis by varying two parameters were needed to obtain more accurate results. The first parameter was the final size of comminution and the second parameter representing the variation of hardness in Thanatia, its work index.

Our results were compared to two values developed by Valero and colleagues, the exergy replacement cost (ERC) and the thermodynamic rarity (TheRy). The first one represents the effort made by Mother Nature to have minerals concentrated in mines, and the latter the energy required to obtain metals from Thanatia. In comparison to the ERC, our results differ in two and three orders of magnitude for the softest and hardest ore, respectively. Comminution demands the most significant energy consumption during the processes of the concentration of gold from Thanatia. In comparison to an average figure for current comminution processes reported in the literature, our values varied in three orders of magnitude. This fact shows that the concentration of gold-ore from common rocks would require consumption of three orders of magnitude higher than the current expenditure of energy for comminution. Drawing a comparison with the TheRy, the result of our model shows a difference of two orders of magnitude with the one of Valero's. It means that the fact of having minerals concentrated in deposits is a representative factor of energy saving in the production of metals. The "free bonus" provided by Nature for having gold concentrated in deposits saves a huge amount of energy in the gold production process. In the limit, when ore grades decline until crustal concentrations, these ultimate costs will be required to mine and refine minerals, thereby making them unaffordable.

These results lead to reconsider the adequacy of the value currently granted to mineral deposits, especially in those countries were metals are highly extracted. With the apparent booming of renewable energy technologies for the decarbonization of the society, the increasing need for purer metals, and particularly gold, will be imminent. With the exhaustion of ore-rich deposits, recycling and more sustainable production processes are urgently required for keeping today's standard of living and the expectations of a better future of the coming generations. While a globalized economy is eager for the consumption of more and more metals, the natural patrimony of nations with rich mineral deposits will be drastically diminished. This is why fair global accountability of the mineral capital and its degradation velocity is required.

Author contributions

Palacios, J.L. performed the literature review, model, and simulation campaign and writing the first stages of the paper. Alejandro Abadias supported stages of modeling and simulation. Valero, An. and Valero, Al. supervised the research on the calculation of energy consumption to upgrade ERC for copper. Reuter, M. contributed with metallurgical advice and supervision of the model and results.

Appendix A

Table A1.

The authors declare no conflict of interest.

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Table A1Computational requirements for modeling and simulation.

Processor	Intel(R) Core (TM) i7-6600 U CPU 2.60 GHz
RAM memory	32 GB
System type	64-bit
Operating system	Windows 10 Pro

Appendix B

Comminution Flotation Gravity Concentration Metallurgy

From Thanatia to Gold Minerals (Au)

Comminution



Comminution



Flotation

From Thanatia to Gold Minerals (Au)

Gravity Concentration

Total Solids Flow (t/h) Gold_Tha (g/t) Total Liquid Flow (t/h) Au (g/t)



Gravity Concentration

From Thanatia to Gold Minerals (Au)



Metallurgy

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A.3 Paper III

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Scope: review of the calculation of the exergy replacement cost (ERC)), overview of mineral and metal processing of copper, development of a computational model in HSC for the concentration of copper ore.

Contribution to the work:

- To describe in brief the most common methodologies for the assessment of mineral resources and their disadvantages
- To explain how the exergy replacement cost (ERC) for iron was determined with its weak points
- To develop a new approach to estimate the new ERC of metals based on mineral processing criteria
- To develop a computational model with HSC software to concentrate copper ore from Thanatia
- To estimate the new value of the ERC for iron with HSC and draw a comparison with the previous ERC for copper
- To determine the importance of the development of computational models in HSC to estimate more accurate values of ERC for the rest of metals.

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The energy needed to concentrate minerals from common rocks: The case of copper ore



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ABSTRACT

A way to assess today's mineral patrimony is to evaluate how much mining energy is saved today because of having concentrated mines instead of finding the minerals dispersed throughout the crust. This can be assessed through the so-called exergy replacement costs (ERC), which are a measure of the exergy required to extract and concentrate minerals from barerock. Previous studies evaluated such exergy using a theoretical approach. In this paper, from a mineral processing point-of-view through a model developed with HSC Chemistry 9.4.1, we calculated the energy needed to concentrate copper from common rocks at average crustal concentrations. In the model, current state-of-the-art technologies for copper concentration were considered. The results were then compared to the theoretical value obtained before for the ERC of copper and helped to update it. The updated ERC value is of one order of magnitude greater than the original one. This difference in magnitude enhances, even more, the issue of ore grade decline in terms of the associated spiraling energy required for mining. It also reveals the importance of valuing properly the mineral heritage of nations and the effort that should be placed for increasing secondary metal production.

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1. Introduction

The extraordinary properties of copper, such as high electrical conductivity, heat conduction, antibacterial behavior, etc. have made copper a preferred mineral for a variety of applications: from a plain penny, domestic uses, like in doorknobs until high-tech usage as a semiconductor in silicon chips for energy-efficient microprocessors [1,2]. That is why copper consumption has increased significantly in the last years. In order to meet this growing demand copper extraction rapidly increased. As stated by Meinert et al. [3], in just ten years (from 2005 to 2015), copper production was equivalent to one-quarter of the total copper mined in human history.

Mine-copper production from 1900 to 2014 by country derived

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from statistics and reports of the US Geological Survey (USGS) [4,5,6,7] is shown in Fig. 1. During this period, the main producers of copper mine were: Chile, the United States, and Peru with an average of 4.0, 1.5 and 0.8 million tons per year.

Many authors have analyzed the issue of copper ore grade decline, this fact has been supported by publications based on analyses of historical data by Mudd [8,9,10,11,12], Craig et al. [13] and Norgate [14]. Findings of a study by Calvo et al. [15] investigated the decline of ore grades in 25 mines found in Chile, Australia and Peru (representing around 32% of the world copper production). On average, about 25% in ore grade decline was observed during ten years (2003–2013). This decline was accompanied by an increase of 46% in energy consumption. Another key finding in this publication was related to the close relationship between the decrease of ore-grade and the increment of specific energy, which followed an exponential behavior. This was revealed for the case of copper and zinc [15]. Publications by Harmsen et al. [16], Bardi [17], Norgate and Jahanshahi [14] also stated an increment in specific energy while the ore-grade decline.



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Fig. 1. World copper mine production by country. Other means the total production of countries whose average individual production was lower than 430 million tons per year. (Source: [4,5,6,7]).

The maximum extraction cost to mine copper, as pointed out by Henckens et al. [18] would be achieved if production would come from common rocks or seawater, where copper concentration is extremely low compared to current deposits. In this respect, Skinner, already in 1976, stressed that extraction of copper from the common rock was technically feasible, but it would require ten times more energy than the extraction from copper ore [19]. More recently, Steen and Borg by analyzing sustainable paths of production of metals from the earth's crust with an idealized process reported a rise of 90% for the production cost of copper from the common rock in comparison with copper-market prices [20].

As a way to assess the value of minerals through non-monetary approaches, Valero and Valero defined the concept of the exergy replacement cost (ERC), by considering their physical quality [21,22]. The ERC establishes the energy required to concentrate minerals at the current average ore-grade from a state of mineral dispersion coined as Thanatia [21]. Thanatia represents a scenario of total mineral dispersion in the Earth's crust and is for the authors the common rock from which minerals could be eventually concentrated. An updated list of ERC values for different minerals has been recently published [23].

The ERC values published so far have been based on estimations, trends of statistical analysis and mathematical models. In this paper, as similarly done in recent publication [24,25], we propose a new approach to estimate the specific energy for the concentration of copper from a state of mineral dispersion, Thanatia, with a computational model developed with HSC Chemistry 9 and HSC Sim software [26]. The aim is to provide a more accurate value than that obtained in the past by Skinner [19], Steen and Borg [20] and in particular by Valero and Valero [24].

2. The concept of the exergy replacement cost

One way to assess minerals is through the market price of commodities. However, prices are unstable and depend on many factors, such as market fluctuations [18]. Besides, the physical quality of minerals, like geological scarcity is not necessarily considered through market prices.

Another way to quantitatively evaluate minerals is through the use of the Second Law of Thermodynamics. Exergy is an extensive thermodynamic property that establishes the minimum amount of work that a system can deliver when it is brought into equilibrium with its surrounding environment [21,27–29]. In the case of fossil fuels, when they are burned, the liberation of energy is associated with their high heating value (HHV) [30,31]. On the other hand, since non-fuel minerals are not combustible, the HHV is not applicable. A traditional way to treat them has been by using their chemical exergy. Szargut published the chemical exergy of different elements [32], a value that was updated later by Valero, Stanek and Valero [33]. These values have been used by Ayres [34], Dewulf et al. [35] and Szargut et al. [36,37] to evaluate mineral resources. However, this approach is very removed from a societal appreciation of the value of minerals. Domínguez et al. [38] portrayed this fact by showing that the chemical exergy of precious metal gold is 60 kJ/mol, while aluminum exhibits 796 kJ/mol. To overcome this issue, Exergoecology was postulated by Valero [39] for a more accurate assessment of natural resources. Physical Geonomics, one of Exergoecology's division, deals with the application of exergy for the evaluation of non-fuel minerals. In this branch, exergy of minerals has two components: one is related to chemical composition (chemical exergy) and the other associated with the relative concentration of the mineral in the Earth's crust (concentration exergy). Concentration exergy is, in fact, closer to the societal perception of value. Nature provides a "free bonus" for having minerals concentrated in mines and not dispersed throughout the Earth's crust. This "free bonus" significantly reduces the costs associated with mining. When high-ore grade mines become depleted, a reduction in this free bonus takes place, leading to an extensive exergy consumption to extract a similar quantity of metal. The bonus provided by nature can be measured through the

concept of the exergy replacement cost (ERC).

ERC is defined as the energy that would be required to extract and concentrate a mineral from a completely dispersed state at a crustal concentration (x_c) to the conditions of concentration and composition found in the mine (x_m) using available technology. Thanatia represents a state of total mineral dispersion into the Earth's crust. Thanatia's composition is made up of 324 species, 292 minerals and 32 diadochic elements included in the crystal structure of other elements [21,40].

The exergy required to concentrate minerals from a concentration found in Thanatia (x_c) to the average concentration (x_m) for different minerals has been reported by Calvo et al. [23]. For the interest of this paper, Thanatia would represent a mixture of orebearing minerals, among these, chalcopyrite, at low concentration in the Earth's crust (x_c). The concept of ERC accounts for the energy required to have copper concentrate at an average ore-grade (x_m) from Thanatia at the crustal concentration (x_c).

The exergy replacement cost (ERC) in GJ/t of element was calculated by Valero et al. [22] based on the observation of the decline of ore grade and growth in energy consumption of cobalt, copper, gold, nickel, and uranium. They suggested a mathematical equation to give an estimate on the energy consumption as a function of the ore grade, Equation (1).

$$E_{(X_m)} = A \cdot X_m^{-0.5}$$
 (1)

where $E_{(X_m)}$ is the energy for the concentration and extraction of minerals at the ore grade (xm), and coefficient A is a constant determined for each mineral.

In the case of copper, Valero et al. [22] made different assumptions, some of the main ones were: concentration of copper in the Earth's crust $x_c = 6.64 \times 10^{-5}$ g/g or 0.006% from chalcopyrite (CuFeS₂) [41], and average ore grade assumed $x_m = 1.67 \times 10^{-2}$ g/g or 0.5% Cu [42], Table 1. Also, the authors considered that 60% of the total energy was utilized for the mining and concentration processes [22].

3. Overview of the concentration of copper

A typical copper ore-grade in open-pit mines is 0.5% and 1% or 2% in underground mines [43]. To extract the valuable metal, the processing route depends upon the type of ore. Two main ore types can be found, sulfides and oxides. For both ores, the comminution process is common. During this stage, particles are reduced in size through crushing and grinding until one that metal can be liberated during the concentration process [44,45]. The main route for sulfide ores includes the concentration through a flotation process [44]. A concentrate is produced with 20%-30% copper. Afterward, a pyrometallurgical process which includes smelting and refining is performed. The outcome is cathodes with 99.9% copper concentration. For oxides, the preferred concentration process is by leaching and then via a hydrometallurgical process that entails solvent extraction and electrowinning. The result of this route is copper with impurities with a concentration lower than 20 ppm [43-47].

Schlesinger et al. [42] report that a vast majority (80%) of copper is obtained from sulfide ores and only a small amount (20%) via a

 Table 1

 The exergy replacement cost (ERC) for copper in GJ per ton of element (adapted from Ref. [23]).

Mineral	Mineral ore	$x_{c}(g/g)$	$x_{m}\left(g/g\right)$	ERC (GJ/t-Cu)
Copper	Chalcopyrite	6.64E-05	1.67E-02	292

hydrometallurgical process. The most common sulfide ore is chalcopyrite (CuFeS₂) [48].

The purpose of this study is to upgrade the previous value of ERC for copper. Therefore the same conceptual scheme will be applied. Accordingly, our target is to concentrate copper from its ore, chalcopyrite, available at Thanatia's composition ($x_c = 0.006\%$) to the average copper content in mines ($x_m = 0.5\%$).

In the next line, explanations of the main aspects of modeling the processes for concentration of copper ore from Thanatia are described. Fig. 2 depicts the stages of comminution and concentration for the computational model.

During the comminution process, a pivotal equation to compute the specific energy required for the mill is Bond's equation [44,49] Equation (2):

$$W = 10 W_i \left(\frac{1}{\sqrt{P_{80}}} - \frac{1}{\sqrt{F_{80}}} \right) EF_x$$
(2)

where W is the specific energy consumption of the mill (kWh/t), W_i is the work index measured in a laboratory mill (kWh/t), P80 and F80 are the product and feed passing sizes (μ m), respectively. Finally, EF_x is the product of the Rowland efficiency factors, which depend upon the mill, size and type of media, type of grinding circuit, etc. [44,49–52]. Then, theoretical power draw by the mill (kW) is calculated by W x T, where T is the throughput tonnage (t/h) [44]. A common particle size after the comminution process is usually below 100 μ m [45,49,53–56].

Froth flotation (hereafter flotation) is a concentration process that takes advantage of natural or induced surface properties of mineral ores. As mentioned before, sulfide ores are typically concentrated by this process. In flotation, hydrophobic (waterfearing) particles are separated from the hydrophilic (easily wetted by water) particles. The valuable metal is then collected from the froth [44,45,57,58]. Flotation occurs in cells where the product obtained is named as a concentrate, which has a higher concentration of the desired metal and tailings as residues. There are different types of arrangements of cells in series or parallel and combinations. In these arrangements, it is common to find the socalled rougher and scavenger cells. The former ones are those where the main step of concentration occurs, and the latter is used to recover minerals from rougher tailings. Different layouts for concentration plants are designed according to the best recovery of metal [44,45,59]. Another parameter to consider in flotation is the retention time, which is the time required for the process to form the froth from which the metal will be separated [44,47,57]. Recovery of the desired metal from the ore is a parameter to evaluate the performance of the metallurgical process [44,54].

4. Methodology

In this section, the conceptualization for the calculation of the specific energy and the steps followed for the model set-up in HSC Sim 9 [26] software are described.



Fig. 2. Stages of modeling and simulation. The comminution process consists of crushing and grinding. The concentration is based on froth flotation.

4.1. Energy for copper concentration from Thanatia

The total specific energy to concentrate copper to an average ore grade of 0.5% Cu from Thanatia was calculated as the energy in the ore handling process plus the energy required in its concentration, Fig. 3. The ore handling process included transportation of the ore with Thanatia composition to the concentration plant. In the concentration facility processes of comminution and flotation were assumed to be performed. A complete list of 324 substances from Thanatia, with the corresponding chemical formulas and the percentage by weight considered for the study can be found in Ref. [40].

The ore-handling phase was considered to involve the transportation of ore from an open pit mine to the concentration plant. For this, it was assumed a minimum distance between the mine and the concentration plant, so that the fuel consumption per ton of ore prevailed over distance. Then, taking into account the copper concentration in the feed stream of 0.003%, the specific energy per ton of copper was calculated.

The comminution was assembled into three circuits, crushing, grinding and regrinding. During crushing the reduction of particle size was carried out in a primary and secondary crusher. The grinding stage was achieved by semi-autogenous (SAG) and ball mills. As Thanatia represents a complex ore mine (a mixture of different low-content minerals), a regrinding stage was also considered.

In order to determine the theoretical power draw during comminution. Equation (2) was used. Both. feed (F80) and product (P80) passing sizes were obtained from the HSC Sim 9 [26] model. The work index (W_i) for copper ore may vary from 4 to 30 kWh/t [45]. An average value of 14 kWh/t was considered for the calculation of the specific energy consumption (W). This value was also taken by Valero and Valero [30] to compute the exergy of comminution and concentration of different minerals. To reduce the complexity of using Rowland Efficiency factors (EFx) in Equation (2), the procedure explained by Will and Finch in [43, Ch. 7] for the selection of mills through manufacturer's data was followed. In this procedure, EFx with a value of 1 was assumed, then the specific energy consumption (W) for every mill was computed. With the W value of every mill and information by manufacturers, models were selected and the number of mills was estimated. Accordingly, for primary and secondary crushers, information published in Refs. [60,61] for gyratory and cone crushers was considered. For grinding, we regarded data of specific energy for SAG and ball mill reported by Latchireddi and Faria [53]of 10.26 kWh/t and 7.59 kWh/ t, respectively. Technical data for the HIG mill published in Ref. [44] was utilized. Subsequently, with the nominal power available for every mill, the power draw in comminution was calculated. The power required on the flotation process of copper was obtained directly from the HSC Sim 9 [26] model. Then, with the feed flow rate (4500 t/h) and its copper concentration (0.003% Cu) the specific energy per ton of copper was determined. Fig. 4 illustrates the stages for the calculation of the specific energy for concentrating copper from Thanatia.

4.2. Model set-up

The starting point for the design of a concentration plant is the analysis of the ore type in the laboratory. On the basis of these analyses and best practice of other similar facilities, the appropriate flowsheet for the plant was designed. In our case, due to the lack of experimental data of Thanatia, the computational model was done based on an extensive literature review of copper-concentration plants and experience of the research group.

For the development of the model with HSC Chemistry-version 9.4.1 software [26], different references were studied to analyze both flowsheets and state-of-the-art technologies for copper concentration [14,43–45,62–67]. In addition, the work by Abadias et al. [68] about modeling of copper processes from a circular-economy perspective was considered. For the model, many variables were considered for the comminution and flotation process. Due to the high number of variables for the model, only some are described. The circuits in the comminution and flotation processes modeled with HSC Sim 9 software [26] are shown in Fig. 5. For the simulation, an Intelcore i7-6600 2.60 GHz central processing unit with 32 GB of random-access memory was used.

Based on an analysis of operating data for copper flotation mills published in Ref. [45], and information of a low-ore grade mine available in Ref. [67], a flow rate of 4500 tons per hour was assumed as the input for the concentration plant. A top size in the ore feed of $600\times105~\mu m$ was considered. Three circuits in the comminution were assumed for the model: crushing, grinding and regrinding. The raw material with $260 \times 105 \ \mu m$ (F80) size was the feed in the crushing circuit. Crushing was carried out by a gyratory and cone crushers as primary and secondary crushers. Controls for particle size output (P80) were set-up for the crushers, 175000 µm, and 45000 µm, respectively. Between the primary and secondary crushers, a classifier with a cut size of $45000 \,\mu\text{m}$ was placed. It was considered the output of the classifier reports to the grinding circuit. The latter was made up of SAG and ball mills with controls for particle size output (P80) of 5000 and 145 µm, respectively. After the SAG mill a classifier with a cut size of $2300 \,\mu m$ was placed. The conjunction of classifiers, mixer, and hydrocyclone in the crushing and grinding circuit allowed to achieve a particle size in the



Fig. 3. Conceptualization of the total energy required to concentrate copper ore from Thanatia as the sum of energies for handling and concentration processes.



Fig. 4. A flowchart illustrating the methodology to determine the specific energy per ton of copper from common rock (Thanatia). Dashed lines indicate the steps developed with HSC Sim 9 software [26].

comminution process of about 100 µm.

The hydrocyclone overflow reported to the flotation circuit. The first stage consisted of conjunction of rougher and scavenger cells. Taking into account that Thanatia represents a complex ore, a regrinding stage was also considered. A high-intensity grinding mill (HIG) was selected for this task with a control for the output particle size of $34 \,\mu$ m. Concentrates from the rougher and scavenger cells were assumed as the feed into the HIG mill. The output of the HIG mill reported to the second arrangement of cleaner and scavenger cells. Tailings from the scavenger of the first and second concentration stages were conducted to the final tailings thickener. To achieve the required concentration of copper, the overflow of the latter stage was the input in a pack of flotation tanks, re-cleaner 2.

For the flotation process, fast kinetics constants (kf) were set up for chalcopyrite, the main copper carrier, in the range of 1–2.5. These values were in accordance with those reported by Dua et al. [69] and Fuerstenau et al. [47]. The volume and number of cells for the flotation tanks were established upon usual values of cells per bank on manufactures data published by Weiss [45], and Wills and Finch [44]. With these considerations, the model was set up for the comminution and flotation processes. In the layout, the arrangements between flotation cells and recirculation circuits were made to achieve the target of 0.5% copper.

5. Results and analysis

In this section results from the simulation, campaign are shown. The validation of results is determined through a comparison of critical parameters of the comminution and concentration processes with those found in the literature. Finally, based on the methodology previously described, the calculation of the specific energy is presented.

5.1. Simulation results

From the model developed, direct results were particle size for feed and output of the crushers and mills in the comminution process, Table 2. The reduction ratio (Rr) is determined by dividing F80 to P80 for every mill, and the total reduction ratio is the product of every mill as indicated in Ref. [63]. In this case, the total reduction ratio is 480.

For the flotation process, direct results were retention time and power consumption, Table 3. The result of the flotation process was a product with a mass flow rate of 19.81 t/h with a copper concentration of 0.5%. During the concentration process of copper from Thanatia, its recovery was 87%. Along with copper other elements were recovered, their recovery rates are shown in Fig. 6.



Fig. 5. The flowsheets from HSC Sim software of concentration and tailings from Thanatia to copper ore (a) Comminution process and (b) Flotation process.

 Table 2

 Feed and product size and reduction ratio for the comminution process.

Stage	Equipment	F80 (µm)	P80 (µm)	Reduction ratio (Rr)
Crushing	Primary crusher	264032	175000	2
	Secondary crusher	219797	45000	5
Grinding	SAG mill	16145	5000	3
	Ball mill	1204	145	8
Re-grinding	HIG mill	84	34	2

Table 3

Retention time and power draw for the flotation process.

Stage	Retention time (min) Power (k	
Rougher	7	960
Scavenger	5	660
Cleaner	29	1540
Scavenger	37	1540
Re-cleaner 1	13	450
Scavenger	15	450
Re-cleaner 2	16	264



Fig. 6. Recovery of elements from the concentration of copper from Thanatia.

5.2. Validation of the model

The validation of the model consisted in the comparison of the results obtained from the model for the comminution and concentration processes with values reported in the literature. For the comminution, a parameter to consider was the particle size. As previously mentioned, common particle size is below 100 μ m. From the simulation, the value obtained from comminution (crushing and grinding) was 145 μ m (Table 2). To reduce further the particle size, a regrinding stage was included in the model, identified by HIG mill in Fig. 7. The particle size after regrinding was 34 μ m (Table 2).

Another parameter for validation was the retention time in flotation (see Fig. 6). In [44, Ch. 10] retention time for the roughing circuit was in the range of 13–16 min. In comparison with those of the model, for Rougher 1 and 2 were in this range. However, the retention time of Rougher and Cleaner were shorter and larger, respectively. Therefore, it is expected to have a lower concentration of copper in the first rougher, considering that Thanatia was a complex ore. That is why a shorter time was obtained in Rougher. In the case of the Cleaner, recirculation produced an increment in retention time. Recirculation circuits were necessary to achieve the final concentrate with 0.5% Cu. A key parameter for the validation of

the model was final recovery. Haque et al. [54] modeled pyro and hydrometallurgical low-grade copper deposits. In that publication, the recovery of copper was assumed to have a yield between 86% and 89%. The recovery obtained from the simulation campaign in this paper was 87%, which was in the range of the expected recoveries.

Even though Thanatia is a mixture of primary minerals in the Earth's crust with low concentration, the results from the model developed in HSC Sim 9 software [26] under the assumptions described in Model set-up, were logical and reliable as shown above.

5.3. Specific energy for copper concentration

With the considerations for the model set-up previously explained in Section 2.2, the power demand for the flotation plant was estimated, Table 4.

As can be appreciated in Table 4, most of the power demand in the concentration process was due to the comminution process (c.a. 97%). Within this process, the grinding circuit was the largest consumer. This agrees with an investigation by Abadias et al. [68] in which from an exergy point-of-view, the comminution process had the highest energy consumption for the production of copper.

By following the methodology previously explained, the specific energy for the concentration process was calculated, Table 5.

The energy required for the concentration of copper from Thanatia can be assessed per ton of ore, as was done by Valero and colleagues and reported in Ref. [21], or per metal concentrate. The first is useful for comparison purposes with previously obtained ERC values, while the latter is the way commonly found in the literature [55,70]. The specific energy was equivalent to 151 MJ/t of ore. This figure was more than twice the average value of electricity consumption at a concentration copper plant in Chile for 2015 (80.8 MJ/t ore) as reported in Ref. [71]. If the specific energy is expressed by a ton of metal concentrate, this value was 34278 MJ/t. This represents one order of magnitude greater than the specific energy required in current copper-concentration processes reported by Norgate and Haque [54] and almost twice the value reported by Rankin in Ref. [70].

In order to compare our value with the corresponding one reported by Valero, it is necessary to consider the flow rate of 4500 t/ h and the copper concentration of 0.003%. With the methodology in Section 2.1, the specific energy for the concentration of copper from Thanatia was computed. For the ore-handling stage, a value of 1.2 L of diesel per ton of rock was considered for the specific fuel consumption. This was a figure reported by Calvo at al [15]. as an average value for the energy consumption in the Chuquicamata open-pit mine. The specific energy for the concentration of copper from Thanatia is shown in Table 6.

For the current work, the ore-handling phase accounted for 24% of the total specific energy in the concentration process of copper. This agrees with figures reported by Norgate and Haque [55].

The result of specific energy in Table 6 was obtained under the assumptions made in the Model set-up. The second stage for the recleaner in the layout should be thought for the requirement to concentrate copper from very-low copper ore (Thanatia). The regrinding circuit in the layout should be interpreted as the need to reduce the particle size to get metal from the complex ore (Thanatia). This agrees with the study by Norgate and Haque [55] that illustrated that the most energy-intensive stage when decreasing ore-grades in copper was mineral processing.

5.4. Sensitivity analysis

Due to the complexity of Thanatia to determine which particle



Fig. 7. Specific energy for the concentration of chalcopyrite from Thanatia by changing the total reduction ratio (Rr) and Bond's work index (Wi).

Table 4

Power draw for comminution and concentration processes.

Stage	Power Demand Power Der (MW) (%)	
Crushing Grinding Re-grinding Concentration	3.8 174.9 4.1 5.9	2.0 92.7 2.2 3.1
TOTAL	188.6	100

Table 5

Specific energy to concentrate copper from Thanatia based on the power demand of 189 MW.

	Cu concentration	Flow	Specific	Specific
	(wt-%)	rate (t/h)	Energy (kWh/t)	Energy (MJ/t)
Feed Ore	0.003	4500	42	151
Conc. metal	0.5	19.8	9522	134278

size will be optimum to recover as much chalcopyrite as possible, a sensitivity analysis was to be performed. In the analysis, two parameters were considered as independent variables to estimate the specific energy. The first parameter represented the possible hardness of Thanatia during the comminution process. For this, it

Table 6Specific energy for the concentration of copper from Thanatia in GJper ton of element.

Phase	Specific Energy (GJ/t)
Ore handling	1546
Concentration	5030
TOTAL	6576

was deemed that Bond's work index (W_i) varies in the range written in Section 4.1. In that sense, it was assumed that the values of W_i were: 4, 9, 20 and 30 kWh/t. The other parameter that is key in the estimation of the specific energy is the total reduction ratio (Rr). Values of reduction ratios for the sensitivity analysis for the current study are shown in Table 7.

By considering the variation in reduction ratios (Rr) and Bond work index (W_i), *Fig.* 7 shows the specific energy for the concentration of chalcopyrite from Thanatia.

In order to have a scheme of comparison with the current energy required for copper concentration processes, the average energy intensity for the Chuquicamata mine for 2000 to 2013 published by Calvo et al. [15] was converted into GJ per ton of copper (Table 8).

The lowest value of the specific energy calculated from the simulation is one order of magnitude higher than the previously obtained ERC for copper. To put this huge amount of energy into perspective, it represents about 74 times more the energy usage at the Chuquicamata mine.

In Fig. 7 it can be seen that the specific energy for the

Table 7
The total reduction ratio of the mills for the sensitivity analysis.

Scenario	Total reduction ratio (Rr)
1st 2nd	480 626
3rd	766
4th	953
5th	1260
6th	1758
7th	2667
8th	4081
9th	6247
10th	11637

Table 8

Comparison of the specific energy of the current work with other reported values in GJ per ton of element.

	Specific Energy (GJ/t-Cu)	Source
Based on HSC-model	3100 - 30890	Current work
ERC copper	292	[23]
Chuquicamata	42	[15]

concentration of copper from Thanatia depends upon the reduction ratios (Rr) and the Bond work index (W_i). If the same work index used by Valero and Valero [30] is considered, W_i = 14 kWh/t, and assuming that Rr = 480 (P80 = 34 μ m), then the specific energy obtained is 6576 GJ/t-Cu (Table 6). This value can be considered as the "New ERC for copper from HSC". Here, it is important to stress that the previous and the new ERC values are different because of the calculation methods used. The previous ERC was approximated by extrapolating existing mining data assuming that the specific energy would follow a given exponential behavior with ore grade decline. By way of contrast, the new ERC for copper has been more accurately estimated using a mineral-processing perspective with a specialized software HSC [26].

6. Conclusions

While the use of metals has become more important in modern society, their consumption has increased drastically. This has produced that rich mineral deposits have been already exploited and the decline of ore grade is becoming a serious issue. The assessment of mineral resources is thus playing a more important role for economic, environmental and societal reasons. One way to assess mineral resources is by estimating the natural bonus for having minerals concentrated in mines. In this study, we undertook the calculation of specific energy required for the concentration of copper at an average ore grade from common rocks. For that purpose, the chemical composition of Thanatia was considered as the common rock. The research was done through the development of a computational model with HSC Chemistry 9 and HSC Sim 9 software. For this endeavor, the simulation campaign was performed with data from the literature, and no experimental testworks were done. The layout was established upon an extensive literature review of different copper concentration facilities and experience of the research group. The outcomes of the model were in the range of parameters published by other authors; hence the results of the model were considered logical and reliable.

The specific energy for the concentration of copper from Thanatia is a function of the hardness of the ore, represented by the Bond Index (Wi) and the reduction ratio of the process (Rr). By assuming Wi = 14 kWh/t and Rr = 480 (P80 = 34 μ m), the "new ERC from HSC" value obtained was 6576 GJ/t-Cu. This is one order of magnitude greater than the previous ERC value reported by Valero and colleagues. This difference obeys to the method of calculation. While the previous ERC was calculated by extrapolating existing mining data assuming that the specific energy would follow a given exponential behavior with ore grade decline, the new one results from a robust analysis from a mineral-processing perspective with a specialized software HSC. The main advantage of using HSC is that each process for the concentration of copper was modeled based on state-of-the-art technology.

An important conclusion of the study is that if humankind were to reconcentrate dispersed minerals throughout the crust back again into their initial concentrations found in the mines, the energy would be even higher as thought. This also helps to learn about the importance of the mineral heritage of nations, currently being exploited and sold without considering the vast energy efforts that future generations will need to invest when ore grades decline. For the case of copper, mining countries especially located in South America should reconsider the significance they already have in the global commodity market.

Another key message of this study is the relevance of increasing the recycling rate of metals because, in energy terms, secondary production is or soon will become more competitive than primary production as ore grades decline.

The methodology and results of the current study may be considered as an update of the exergy replacement cost (ERC) for copper and will be used for other metals in the future. In a forthcoming paper, the authors will analyze the effect of ore-grade decline on the energy for processing, using a similar procedure.

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A.4 Paper IV

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Scope: revision of mineral exports from 20-countries in Latin America and the Caribbean from a tonnage perspective, translation of these exports into the physical quality of minerals based on Exergoecology principles, identification of routes of exportation of high-quality minerals

Contribution to the work:

- To make an overview of the methods for the evaluation on non-fuel minerals.
- To highlight the advantages of considering the physical quality of non-fuel minerals respect to mass-based approaches
- To determine the route of minerals exports of twenty countries in Latin America and the Caribbean.
- To identify the importance of high-quality minerals which are not identified through the use of mass-based approaches



Article



Exergoecology Assessment of Mineral Exports from Latin America: Beyond a Tonnage Perspective

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Abstract: Latin America has traditionally been a raw material supplier since colonial times. In this paper, we analyze mineral exports from an exergoecology perspective from twenty countries in Latin American (LA-20). We apply material flow analysis (MFA) principles along with the concept of the exergy replacement cost (ERC), which considers both quantity and thermodynamic quality of minerals, reflecting their scarcity in the crust. ERC determines the energy that would be required to recover minerals to their original conditions in the mines once they have been totally dispersed into the Earth's crust, with prevailing technology. Using ERC has helped us identify the importance of certain traded minerals that could be overlooked in a traditional MFA based on a mass basis only. Our method has enabled us to determine mineral balance, both in mass (tonnes) and in ERC terms (Mtoe). Using indicators, both in mass and ERC, we have assessed the self-sufficiency and dependency of the region. We have also analyzed the mineral exports flows from Latin America for 2013. Results show that half of the mineral production from LA-20 was mainly exported. High-quality minerals, such as, gold, silver, and aluminum were largely exported to China and the United States. Extraction of high-quality minerals also implies higher losses of natural stock and environmental overburdens in the region.

Keywords: Latin America; material flow analysis; exergy replacement cost; mineral trade; mineral exports; domestic material consumption

1. Introduction

Since colonial times, Latin America has traditionally been an exporter of raw materials [1]. Before World War I, the region was the main supplier of primary products in the world [2], and was also a significant supplier of primary products to foster the industrial revolution in Western European countries [3]. In recent years, the region has also been a key supplier of raw materials for China's booming society [4–6]. Nowadays, the region is characterized for its importance in the global market. In 2014, exports of fossil fuels and mining products from South and Central America to Asia, North America, and Europe accounted for \$89, \$77, and \$37 billion USD, respectively [7].

A useful way to study flows and patterns of resource use across regions is through Material Flow Analysis (MFA) [8]. Indeed, MFA offers a complete and systematic description of a specified system to support policymakers [9]. It provides data regarding the extraction and trade of materials, hence offering useful information for the establishment of sustainable schemes [10–14]. Moreover, this approach has been used to show the dependence of a region on mineral imports. To that end, Schaffartzik et al. [12] analyzed patterns and trends of materials extraction, trade, and consumption of 177 countries in the world, which were grouped in six regions, from 1950 to 2010. They stated the

importance of Latin America and the Caribbean as metal producers, especially for copper, silver, tin, and iron, supplying 12% of world's metal demand. Other prominent studies have analyzed material flows focusing only on Latin America. For instance, country-specific MFA were undertaken by Vexler et al. for Chile [15], by Perez-Rincon for Colombia [16], by Vallejo for Ecuador [17], Tanimoto et al. for Brazil [4], and Walter et al. for Argentina [18].

On a multi-country perspective, in 2007 a report published by the United Nations Environmental Programme (UNEP) on material flows and resource productivity, analyzed ten countries of South America and the Caribbean: Argentina, Plurinational State of Bolivia, Brazil, Chile, Colombia, Ecuador, Guatemala, Mexico, Peru, and the Bolivarian Republic of Venezuela [19]. The main conclusion of this study was that growth in demand of resources of other regions can have effects on Latin America's material flows. Thus, MFA for Latin America are crucial in a globalized economy.

In another study, Russi et al. [20] analyzed the consequences of neoliberal economic reforms on natural resources of Chile, Ecuador, Mexico, and Peru through MFA from 1980 to 2000. This study demonstrated that domestic material extraction had increased in these four countries as a consequence of economic reforms. In a similar way, West and Schandl [21] analyzed material use and efficiency in 22 countries in Latin America and the Caribbean. Material flows from 1970 to 2008 were studied, and a remarkable conclusion was that these countries were less efficient in gaining economic profit by means of selling their natural resources. A similar conclusion was made in the study by Giljum and Eisenmenger [22], which observed "an unequal environmental distribution" at global level between the distribution of environmental goods and environmental burdens between the North and the South. The North, such as the European Union [23], which is mostly resource dependent on southern countries, sells high-value products to the South, while leaving the negative environmental impacts that are associated to raw material extraction in the South [22].

It is a fact that mining activities can result in important environmental damages. Web platforms, such as the Environmental Justice Atlas [24] and information by Bottaro and Sola-Alvarez [25], give an overview of the effects on the environment caused by mining activities in Latin America. The Observatory of mining conflicts in Latin America (OCMAL) reported in its database 229 conflicts, most of them in Peru, Mexico, Chile, and Argentina [26]. More specifically, problems that are related to water usage in mining were analyzed by Aitken et al. [27] in the north of Chile. Himley [28] in turn, raises questions regarding sustainable development and the role of large-scale mining industries through a study in a gold mine in Peru.

Neither environmental damages nor the loss of natural stock caused by mining activities are reflected in conventional MFA, which are commonly made using tonnage as the unit of measure. M, a tonnage-based assessment leaves out the quality of commodities. To overcome this issue, the loss of natural stock can be quantitatively analyzed through an indicator based on the Second Law of Thermodynamics, called exergy replacement costs (ERC) [29,30]. As it will be explained in the methodology section, using ERC instead of tonnage we can assign a greater value to scarcer and difficult to obtain minerals thereby avoiding the problem of "adding apples with oranges". Note that this same study could be done on a monetary basis. Nevertheless, prices rarely take into account the physical reality of minerals, such as geological scarcity. They are volatile by nature since they are subject to market fluctuations [31].

Thus, to have an order of magnitude for the loss of natural stock in Latin America due to mineral extraction, and to identify where such valuable minerals ended up, this paper undertakes a material flow analysis (MFA) based on the Second Law of Thermodynamics. A total of 20 countries in Latin America have been analyzed: Argentina, Bolivia, Brazil, Chile, Colombia, Costa Rica, Cuba, Dominican Republic, Ecuador, El Salvador, Guatemala, Honduras, Mexico, Nicaragua, Panama, Paraguay, Peru, Uruguay, Venezuela, and Haiti (hereafter LA-20). For this purpose, the mineral balance for LA-20 was examined, using indicators that can help evaluate the self-sufficiency or dependency of the region and evaluating exports by destination. With the mineral balance, both in mass and ERC terms, mineral production from 1995 to 2013 was assessed and differences between both approaches were explored.

Mineral exports by destination were examined for a particular year to see which countries benefit from the natural stock loss of LA-20. To that end, we have followed the exergoecology method proposed by Valero et al. [32] and guidelines of investigations published by Calvo et al. [33–35] and Carmona et al. [36]. In these studies, the ERC concept was used to develop a MFA for European countries (EU-28) and for Colombia in 2011. Alongside these studies, we seek to demonstrate that considering the thermodynamic quality of minerals through ERC would further improve the potential of MFA, especially when dealing with non-fuel minerals. The final aim is to contribute to a deeper discussion on the search for sustainable paths on mineral production in Latin America.

2. Methodology

2.1. Research Framework

Exergy has been traditionally used to measure any energy source, and is defined as the minimum amount of work that may be theoretically performed by bringing a system into equilibrium with its surrounding environment. It is a property of a system-environment combination and is helpful in recognizing and evaluating consumption of non-renewable resources, especially fuel minerals [37–39]. The exergy content of fuel minerals is associated to their chemical composition and can be approximated with no significant error to their High Heating Value (HHV), which can be obtained from [40]. Yet, non-fuel minerals cannot be evaluated using this same approach as they are not combustible. This is why non-fuel resources have been traditionally assessed through their chemical exergy content. The latter, in turn, can be obtained from the Gibbs free energy of the given substance $\Delta G_{f,i}$ and the chemical exergy of the elements that form the substance, as expressed in Equation (1):

$$b_{chi} = \Delta G_{f,i} + \sum_{j} n_{j,i} \times b_{ch,j} \tag{1}$$

where b_{chj} is the standard chemical exergy of the elements $n_{j,i}$ that compose substance *i*. Gibbs free energy indicates the thermodynamic potential available for usage until a system reaches chemical equilibrium at a constant pressure and temperature [41,42]. Commonly, the chemical exergy of the elements is usually taken from the values obtained by Szargut [43] and the Gibbs free energy can be obtained from chemical databases, or, alternatively, estimated with different calculation procedures [44,45].

This way of assessing the exergy of substances, including mineral resources, has been used by different authors including Szargut et al. [33,46,47], Ayres [48], or Dewulf et al. [49]. Yet, as demonstrated by Domínguez et al. [50], assessing minerals solely with chemical exergy disregards important aspects that make minerals valuable. As an example, the chemical exergy of precious metal gold is 60 kJ/mol, whereas that of aluminum is 796 kJ/mol. In this respect, exergoecology has been established for the evaluation of natural resources and one division of this discipline is Physical Geonomics, which investigates how the exergy concept can be applied to the assessment of non-fuel minerals. In addition to the chemical exergy, minerals have an important physical feature that makes them valuable, mainly their relative concentration in the crust. The fact of having minerals concentrated in mines and not dispersed throughout the crust represents a "free bonus" provided by Nature, which allows for significantly reducing the costs that are associated with mining. When mines become depleted, this free bonus is reduced, meaning that more energy is required to extract the same amount of metal. Such a bonus can be assimilated to a hidden or avoided cost that can be quantified through the so-called exergy replacement costs (ERC). These are defined as the exergy costs that would be needed to extract and concentrate a mineral from a completely dispersed state to the conditions of concentration and composition found in the mine using prevailing technology. ERC values are, thus, related to the scarcity degree of a given mineral, which can be reflected through the concentration exergy (b_{ci}) , as calculated with Equation (2).

$$b_{ci} = -RT^0 \left[lnx_i + \frac{(1-x_i)}{x_i} \right] ln(1-x_i)$$
(2)

where b_{ci} represents the minimum theoretical work, exergy, which required to concentrate a substance *i* from an ideal mixture of two components; x_i can be either the average concentration in the mines measured in g/g (x_m) or the concentration in the Earth's crust (x_c); *R* is the gas constant (8.314 J/molK); and, T^0 is the absolute reference temperature (298.15 K).

The exergy (Δb_c) associated to the concentration of minerals from a dispersed state in the crust to that in a given mineral deposit is determined by the concentration exergy when $x_i = x_c$ and when $x_i = x_m$, thus Equation (3).

$$\Delta b_c(x_c \to x_m) = b_c(x_i = x_c) - b_c(x_i = x_m) \tag{3}$$

Since exergy only reports minimum values and man-made technology is very far removed from reversibility, we need to resort to exergy costs. Accordingly, the so-called exergy replacement costs (B^*) are computed with Equation (4):

$$B^* = k \times \Delta b_c(x_c \to x_m) \tag{4}$$

where variable *k* is a dimensionless constant called unit exergy cost. It is the ratio between: (a) the real cumulative exergy required to accomplish the process of concentrating the mineral from the ore grade x_m to the commercial grade x_r and (b) the minimum thermodynamic exergy required to accomplish the same process $\Delta b_c(x_m \rightarrow x_r)$ [30]. An implicit assumption in the methodology is, thus, that the same technology applies for concentrating a mineral from x_m to x_r as from x_c to x_m .

The aforementioned methodology is used to calculate the exergy replacement costs of the main mineral commodities that are currently used by industry on a global basis. It should be noted that for obtaining the global ERC of minerals, it is assumed that each commodity (i.e., copper) is obtained from a single type of ore (i.e., chalcopyrite). For each mineral, the average global ore grades were considered (x_m), mainly obtained from Cox and Singer [51], as well as the average energy values of state-of-the-art technologies in mining and beneficiation. The depleted ore grade (x_c) was obtained through a model of dispersed Earth, called Thanatia [29]. Thanatia comes from the Greek Thanatos that means death. In our perspective, Thanatia is a baseline for the exergy assessment of mineral resources and represents an idealization of the planet when all of the fossil fuels have been burned and all minerals have been totally dispersed into the continental crust [29,52]. Thanatia's crust is composed of the 300 most abundant minerals at average crustal concentrations [29]. Once exergy replacement costs of minerals are obtained (i.e., for chalcopyrite), those of the element (i.e., for Cu) are calculated through their corresponding molecular weights.

One key aspect that differentiates exergy replacement costs (ERC) from other thermodynamic properties is that ERC considers the scarcity degree of the commodities in the crust and the energy required to extract them. When a mineral is scarcer and its extraction and beneficiation processes are more difficult, its ERC value becomes higher. This is why, contrarily to what happens when only chemical exergy is used for the assessment, precious metals, such as gold and silver, exhibit higher values of ERC than more abundant ones, such as iron or limestone. Higher values of ERC thus represent a higher quality of minerals and would also mean a higher loss of the natural stock in a region if these become depleted.

These values have been taken from Valero et al. [40]. Due to the number of minerals that are considered in the current study, only selected ERC values of minerals have been listed in Table 1.

All the ERC values of minerals considered in the current study can be seen in Appendix A, but a complete list of all minerals with their corresponding ERC values can be found in [53].

	Mineral Ore	ERC (GJ/t)
Non-fuel minerals		
Gold	Native gold	553,250
Silver	Argentite	7371
Zinc	Sphalerite	1627
Copper	Chalcopyrite	292
Lead	Galena	37
Limestone	Calcite	3
Phosphate rock	Fluorapatite	0.4
Fuel minerals		
Crude Oil		46.3
Coal		24.3-31.6
Natural Gas		39.4

Table 1. Main exergy replacement costs for the current study in GJ per tonne of element (source: [54]).

Note: $1 \text{ GJ} = 2.39 \times 10^{-8} \text{ Mtoe.}$

2.2. Data Compilation

With the aforementioned methodology, the mineral balance of LA-20 from 1995 to 2013 was analyzed, taking into consideration several indicators that can be used to evaluate self-sufficiency or dependency of the region. Exports by destinations for 2013 were also analyzed. In all of the cases, 2013 was used as the last year analyzed as it was the most recent year for which there was information available for all LA-20 countries.

A total of 38 non-fuel minerals were considered in this paper: aluminum, antimony, barite, beryllium, bismuth, cadmium, chromium, cobalt, copper, fluorite, gold, graphite, gypsum, iron, lead, limestone, lithium, magnesite, manganese, mercury, molybdenum, nickel, niobium, platinum group metals (PGM), phosphate rock, potash, rare earth elements (REE), salt, selenium, silver, tantalum, tin, titanium, vanadium, wolfram, zinc, and zirconium. Additionally, fossil fuels were included in the study (oil, natural gas and coal).

The information needed for this study (extraction, imports, and exports) was gathered from different data sources for the 20 countries under study. Only data regarding bulk mineral production, imports, and exports were included, thus excluding semi-manufactured products, such as steel. This means that if a country extracts iron but exports steel, only iron was taken into account in the MFA. As suggested in economy-wide material flow accounts (EW-MFA) guidelines [55], the primary source of information was national databases and national agencies of each country. Brazil's mineral production, imports, and exports data were gathered from the Departamento Nacional de Produção Mineral [56]. Chilean mineral production was obtained from Servicio Nacional de Geología y Minería [57], imports and exports from Comisión Chilena del Cobre [58]. Production, exports, and imports of Colombia were retrieved from Sistema de Información Minero Colombiano [59]. Ecuador's mineral production was compiled from Agencia de Regulación y Control Minero [60], while exports and imports information from Banco Central del Ecuador [61]. Production, imports, and exports of Peru were provided by the Ministerio de Energía y Minas [62]. It was not possible to collect direct data from local agencies for Argentina, Costa Rica, Cuba, Dominican Republic, El Salvador, Guatemala, Honduras, Nicaragua, Panama, Paraguay, Uruguay, and Venezuela. Instead, mineral trade data of these countries were collected from British Geological Survey database [63], Economic Commission for Latin America and the Caribbean (ECLAC) [64] and the United Nations International Trade Statistics Database (UN Comtrade) [65]. The disaggregation level corresponding to mineral exports and imports was five digits (UN Comtrade license). To avoid double accounting, this database allows for treating a selected region, in our case, LA-20, as a single unit, therefore not taking into account exports and imports between each LA-20 country. For completing gaps and for cross-checking purposes, reports of the U.S. Geological Service [66] were also consulted. Due to the lack of information for Haiti in 2013, it was not possible to

include it in the assessment of exports by destination and material flow indicators. Regarding fossil fuels, all production, imports, and exports values were gathered from the Latin American Organization of Energy (OLADE) databases [67].

ERC is expressed in GJ per tonne of element, hence all mineral information expressed in metal content was taken from these data sources. This information was then converted into exergy terms by means of the ERC and different indicators were calculated. One of the indicators that was used in the study is domestic material consumption (DMC), defined as the amount of physical minerals that are consumed inside one region. Hence, DMC is calculated as the sum of minerals that are produced in the region (domestic extraction = DE) plus imports (I) minus exports (E). The term consumption in this paper refers to apparent consumption and not final consumption (i.e., goods are excluded for the analysis). Goods are not considered in this analysis for two reasons: first, because of important information gaps regarding semi-manufactured products exported and imported in the analyzed countries; and second, because this same approach was used in Calvo et al. [35] for EU-28, and so the results can be compared. These indicators were calculated both in mass and ERC. Subsequently, using this information, different ratios of domestic extraction (DE/DMC), imports (I/DMC), and exports (E/DMC) were obtained. The usefulness of these ratios is that they can provide information about the dependency and self-sufficiency of a region [35].

3. Results and Analysis

Results of the study are separated into three sections. First, the evolution of mineral production of LA-20 from 1995 to 2013 is analyzed using both mass terms (tonnes) and ERC terms (Mtoe). Additionally, Sankey diagrams are used to represent the mineral trade in 2013 of three selected countries (Brazil, Chile, and Mexico) both in mass and ERC. Then, ratios that show the dependency or self-sufficiency of the region are calculated for 2013. Last, the destinations of the exports of materials produced in LA-20 are studied to have a better knowledge of which countries are relegating in LA-20 the environmental burden associated to the mining industry.

3.1. Mineral Balance

Figure 1 shows non-fuel mineral production of LA-20 disaggregated by minerals, data was compiled from USGS statistics [68] and then compared to the information provided by national agencies to ensure maximum coherence and completeness.



Figure 1. Non-fuel mineral production in LA-20 from 1995 to 2013 in mass terms expressed in million tonnes (**left**) and in exergy terms expressed in Mtoe (**right**). Only the minerals that can be seen in the figures are shown in the legend.

Overall, in mass terms, the most extracted minerals in LA-20 from 1995 to 2013, were iron, aluminum, salt, limestone, and gypsum (average of 197, 28, 18, 12, and 9 million tonnes per year, respectively). When these data is translated into loss of natural stock in the region, through the ERC concept, the highest loss corresponded to aluminum (average value of 413 Mtoe), followed by

iron (84 Mtoe). In the period of analysis, iron production represented 72% as an average of the total production in tonnes, while in Mtoe it represented only 13%. On the opposite side, aluminum, which only represented 10% of the total production in tonnes, represented 66% in ERC. Hence, the loss of natural stock in LA-20 was mainly caused by aluminum rather than iron. The importance of taking into consideration quality and not only quantity of non-fuel minerals is revealed with this comparison.

The complete mineral balance disaggregated by mineral for LA-20 in 2013 in mass and ERC terms can be seen in the Appendixs B and C. Analyzing these data in detail, it can be observed that the most extracted fuel minerals in that year were crude oil and natural gas, with a share of 63% and 23% of the total fossil fuels, respectively. Regarding non-fuel minerals, iron, aluminum, and salt were the most produced in mass terms (69%, 9%, and 6%, respectively). When looking at consumption data, crude oil, and natural gas were largely consumed within LA-20, and regarding non-fuel minerals, iron, aluminum, limestone, and salt were mostly consumed internally. The cases of limestone and salt can be easily explained as usually industrial minerals, which have lower prices than other metallic or non-metallic minerals, are consumed internally, rather than exported to other countries.

As stated before, mineral trade can be represented using Sankey diagrams, with arrows showing the production, imports, exports, and domestic consumption proportional to flow quantities. As it was previously mentioned, domestic consumption referred to apparent and not final consumption. Therefore, and as opposed to conventional EW-MFA, semi-manufactured products (either entering or leaving the analyzed system) were not taken into account. In conventional EW-MFA, the composition of most traded goods is assessed using the main material component or the main raw materials used in the production. On the contrary, in our analysis if for example iron was used internally to produce steel, and this in turn, was exported, the corresponding iron was considered as a commodity consumed internally. This is why, according to the EW-MFA definitions, our results are only partial when analyzing imports and exports as we only consider bulk commodities.

Three countries have been selected for such purposes, Brazil, Chile, and Mexico (Figure 2). These countries have been chosen as an example as they approximately represent 65% of the total mineral trade in LA-20. All of the mineral commodities (38) along with natural gas, oil, and coal are represented in the diagram, but the legend only shows those that can be easily seen in the figure.



Figure 2. Sankey diagrams for Brazil, Chile, and Mexico for 2013 expressed in million tonnes (**upper row**) and in Mtoe (**lower row**) for selected substances.

In some countries, when calculating the domestic material consumption, negative values can be obtained for certain commodities, such as gold, silver, lead, or zinc, as exports are higher than production and imports combined. Illegal and artisanal mining are a serious problem in the region, especially in the case of precious metals, such as gold [69–72]. In 2013, it was estimated that 158 tonnes of gold were produced illegally, accounting for \$6.9 billion USD. Countries with higher illegal gold production rates in that year were: Venezuela, Colombia, and Ecuador [72]. Negative values of domestic consumption can also be explained by the lack of reported data by official authorities and variation in stocks that are not shown on mineral statistics. The difference between input and output flows was represented in the diagram as "imbalance". Still, this imbalance on average is quite low when compared to the remaining flows.

In Brazil in 2013, in mass terms, the most produced and exported commodity was iron, with a share of 57% of the total domestic production and 85% of the total exports, respectively. When analyzing that same information applying the ERC concept, the main commodity contributing to the loss of natural stock was aluminum, with a share of 66%. In a merely tonnage perspective there is almost no difference between total exports and total domestic consumption. On the other hand, in terms of quality, consumption of higher-quality minerals, such as aluminum, potash, and crude oil, was three times higher than exports.

As for Chile, the country imported large amounts of fossil fuels and principally produced copper, iron, and salt. Chile is a world leader in copper production, and in 2013 copper extracted represented one-third of the global copper production [73]. When transforming this information using ERC, it can be seen that copper plays a major role in exports as more emphasis is placed on its physical quality: it represents more than 90% of the total exports. Total exports in tonnes represent a fifth of the total outputs (exports plus domestic consumption) but when expressed in ERC they only account half.

As for Mexico, the most notable difference with the other two countries is that it mainly produces fossil fuels, along with small amounts of iron. It is also noteworthy that there was no major dependency on the external supply for internal consumption of minerals, as only small amounts of gas and coal were imported. In mass terms, Mexico's consumption was mainly dominated by natural gas and crude oil and was one order of magnitude higher than exports. In ERC terms, consumption was approximately two times higher than exports. A possible explanation for this value is the high fossil-fuel consumption in Mexico, as, for instance, in 2014 more than 59% of the total final energy consumption came from fossil fuels [74].

3.2. Mass and ERC Indicators

As stated before, different ratios were calculated: DE/DMC, I/DMC, and E/DMC, each considering domestic extraction, imports, and exports, respectively, when compared to DMC. These ratios only include material trade of the fossil fuels and non-fuel minerals listed in previous sections.

All of the ratios were calculated both in tonnes and in Mtoe for LA-20 for 2013 (Table 2). Absolute results are not comparable between both units of measure. Yet that is not the case when we assess ratios, such as DE/DMC, I/DMC, or E/DMC.

	LA-20 (2013 Data)			EU-28 (2011 Data)		
	DE/DMC	I/DMC	E/DMC	DE/DMC	I/DMC	E/DMC
Non-fuel minerals						
Mass	1.88	0.11	1.00	0.79	0.30	0.09
ERC	1.50	0.16	0.66	0.45	0.94	0.40
Fossil fuels						
Mass	1.36	0.24	0.59	0.52	0.62	0.13
ERC	1.35	0.22	0.57	0.41	0.76	0.17

Table 2. Comparison between LA-20 and EU-28.

When looking at DE/DMC ratios of non-fuel minerals, it is clear that LA-20 in 2013 produced more minerals than those it consumed internally. Imports were significantly lower than domestic consumption and exports were also significant, which is consistent with the image that LA-20 has

of being a net exporter territory. In the case of DE/DMC ratio, the value in mass is higher than in ERC. The explanation relays on the weight of iron, a very abundant element that has a low ERC value (18 GJ/t). When expressed in tonnes iron accounts for 68% of the total LA-20 mineral production but

in ERC this value is only for 13%. On the contrary, for the I/DMC ratio, the value in ERC is higher than in mass, meaning that the minerals imported have higher ERC values and are therefore more scarce, such is the case of potassium (665 GJ/t), which accounts for 79% of the total imports in ERC, but only 19% in mass.

The region produced more fossil fuels than those it consumed internally; analyzing the DE/DMC and E/DMC, it can be seen that a large amount of the fossil fuels produced in the region were exported. No high variation between ratios of DE/DMC, I/DMC, and E/DMC of fossil fuels can be appreciated when comparing the results in mass and ERC. This is related to the high importance of oil and gas in domestic extraction, as, as seen before, both represented approximately 85% of the total fossil fuels extracted in LA-20 in 2013. A higher variation would be perceived if coal would play a more important role. This is because coal has a comparatively lower HHV than oil or natural gas.

Calvo et al. [35] applied MFA with an exergoecology approach for twenty-eight European countries (EU-28) using 2011 as the reference year. Although the latter and current study differs by two years, a comparison among the indicators obtained in this study will give us an indication of mineral sufficiency and dependency for both regions.

In general, this comparison clearly shows a markedly difference between both regions, while DE/DMC is higher than 1 for LA-20 (i.e., exports are larger than imports), stating the relevance of domestic extraction and exports, for the EU-28 this value is considerably lower. This is understandable as EU-28 relies on minerals imports rather than on domestic extraction, therefore shifting the environmental burden of mineral extraction to other territories.

As expected, non-fuel mineral values of the ratio I/DMC for LA-20 were considerably lower than those for EU-28. This reveals that EU-28 had to rely on importing materials to meet its internal needs, while, in LA-20, domestic extraction was sufficient to cover most of its internal demand. In addition, the E/DMC ratio was higher for LA-20 than for EU-28, reflecting the importance of LA-20 as an exporter region.

Contrary to what happens in EU-28, which in 2011 was extremely dependent on fossil fuels, in LA-20 the import to DMC ratio was considerably lower and for the case of the exports ratio, it reflected the fossil fuel trade that takes place in the region.

Ratios of DE/DMC, I/DMC, and E/DMC, calculated in ERC terms only, for every country, except for Haiti due to a lack of data, are shown in Table 3. It is noteworthy that DMC values for Costa Rica and El Salvador are the only ones with negative figures. This is because, as it can be seen in the annexes, export values for these countries are higher than production and imports. The lack of mineral production official data, which can be incomplete or present gaps, can lead to lower values that do not reflect the reality of the country. This is even more notorious in ERC than in mass terms, because scarcer minerals have a higher weight.

Table 3. Ratios of domestic extraction (DE/DMC), imports (I/DMC), and exports (E/DMC) over
domestic material consumption for each country in exergy replacement cost (ERC) terms for fossil fuels
and non-fuel minerals in 2013.

Country	DMC (Mtoe)	DE/DMC	I/DMC	E/DMC
Argentina	73.90	1.07	0.16	0.23
Bolivia	15.22	2.29	0.00	1.29
Brazil	669.62	1.16	0.21	0.37
Chile	63.37	1.38	0.33	0.71
Colombia	37.52	3.27	0.05	2.32
Costa Rica	-6.64	0.00	-0.22	-1.22
Cuba	10.66	0.50	0.50	0.00
Dominican Republic	16.67	0.91	0.17	0.08

Country	DMC (Mtoe)	DE/DMC	I/DMC	E/DMC
Ecuador	10.71	2.91	0.00	1.91
El Salvador	-1.97	-0.46	-0.15	-1.61
Guatemala	0.11	1.00	0.00	0.00
Honduras	1.13	0.94	0.06	0.00
Mexico	148.05	1.59	0.18	0.78
Nicaragua	0.71	0.18	1.00	0.18
Panama	0.02	2.16	0.15	1.31
Paraguay	0.07	0.43	0.57	0.00
Peru	28.87	2.92	0.18	2.09
Uruguay	2.22	0.06	0.96	0.02
Venezuela	113.66	1.94	0.02	0.95
Average LA-20	62.31	1.43	0.19	0.62

Table 3. Cont.

Countries with a ratio DE/DMC higher than 1 in 2013 were: Colombia, Peru, Ecuador, Bolivia, Panama, Venezuela, Mexico, Chile, Brazil, and Argentina. Colombia, Ecuador, and Peru in 2013 produced three times more fuel and non-fuel minerals than their national consumption.

This classification also shows the importance of performing the analysis using ERC, since, until now, in a mass basis analysis, only a few countries, such as, Brazil, Venezuela, Mexico, and Chile, were considered as the most significant producers in the region because of their mining and oil tradition.

3.3. Exports by Destination

In this section, the destinations of the non-fuel minerals from Latin America were studied, not analyzing only quantities, as other studies previously did [12,19–22,75], but considering that minerals are more valuable from a quality point of view with the ERC approach.

Although all 38 non-fuel minerals previously mentioned before were considered in the analysis, in the graphs only those that can be seen appear on the legend. These graphs were based on data from UN Comtrade [65]. As explained before, this database allows for avoiding double accounting, being able to eliminate flows between LA-20 countries and only analyzing trade between LA-20 and the rest of the world.

The main exported minerals were aluminum, iron, zinc, copper, silver, and gold (139, 134, 117, 58, 32, and 23 Mtoe, respectively). As it can be seen in Figure 3, approximately one quarter of all the minerals produced in LA-20 ended in North America, mainly going to the United States, while the rest went to other territories. This share can be understood because proximity is a key factor in mineral trade and also because some companies that own mines in LA-20 have processing plants in other parts of the world.



Figure 3. Non-fuel minerals exported by destination in ERC terms (Mtoe) for 2013. Due to the scale, some minerals are not included in the legend.

High quality minerals, such as aluminum or gold, were exported mostly to North America (59 and 77%, respectively). The majority of copper produced in LA-20 was exported to China (38%), as well as silver (48%), while most of the zinc exports went to Russia (41%). Additionally, a not negligible 21% of

It can be observed that even using an ERC approach, iron still accounts for the vast majority of the exports as even if the ERC of iron is quite low when compared to other commodities, the extraction figures are so high that it masks other scarcer minerals. For this reason, some elements were removed from Figure 3 so other mineral flows can be seen (Figure 4).

gold went to Europe. More results disaggregated by mineral can be seen in Appendix D.



Figure 4. The remaining minerals exported by destination in ERC terms (Mtoe) for 2013. Due to the scale, some minerals are not included in the legend.

If those results were analyzed only in tonnes, it would seem that LA-20 only exports iron, aluminum, and salt, as these three elements alone represents 95% of the total exports to other countries. Still, between only Chile and Peru, they represented more than one third of the total copper production in the world, Chile alone has 6 of the 10 largest copper mines in the world, while two others are located in Peru and Mexico. Moreover, around 12% of gold is produced in LA-20, with some of the largest gold mines being located in Dominican Republic, Mexico, and Peru.

4. Discussion and Conclusions

Latin America has always played an important role in the production of mineral commodities at international level. In this paper, the production, imports, and exports of 41 fuel and non-fuel minerals of 20 countries has been analyzed. Then, the dependency or self-sufficiency of the region has been assessed, as well as exports by destination. Combining all of these approaches, the main goal was to analyze the impact of the loss of natural stock in the region.

For a proper evaluation of the loss of natural stock, a tonnage assessment alone is not enough, as it would be like adding "apples with oranges" trying to compare one tonne of gold with one tonne of iron, therefore disregarding important aspects of the commodities. One of those aspects is quality, which can be assessed using the exergy replacement cost (ERC), a concept that accounts for the physical characteristics of minerals, when considering their scarcity in the crust of the Earth. Accordingly, a tonne of iron has a significantly lower ERC than a tonne of gold, as the first appears more concentrated and is more easily extracted from the mines.

The ERC concept has made the importance of scarcer minerals for the assessment of mineral trading in Latin America stand up, as the production of these high quality minerals also means a

higher loss of natural stock in the region. Additionally, combined with material flows analysis, this approach has enabled us to identify more precisely destinations of high-quality minerals. For instance, from 1995 to 2013 in LA-20, iron production represented 72% of the total production in tonnes, while in Mtoe it only represented 13%, and the contrary was observed for aluminum. Thus, the loss of natural stock of LA-20 was mainly caused by aluminum and not by iron extraction, along with zinc and copper, commodities which also contributed highly to the loss of the natural stock in the region. It was also observed that in 2013 more than half of the mineral production in LA-20 was destined only to exports. Moreover, the loss of natural stock was also due to exports of higher quality minerals, such as gold or silver. China and North America (mainly United States) were key commercial partners for LA-20 in 2013. Routes of exports by destination showed that 32% and 22% of the total exports in ERC terms were destined to these countries, respectively.

The results have vastly shown the importance of quantifying minerals not only in mass (tonnes), but also taking into account their quality through the concept of ERC. Precious metals, like gold and silver, are always masked by other elements in conventional MFA, because of their low values in mass terms. Still, they are even more critical not only from an economic point of view, as gold is closely linked with the monetary market, but also from a scarcity perspective.

Additionally, when analyzing in detail the material trade of Chile, Brazil, and Mexico, another problem related to mineral extraction and statistics was revealed. In some cases, there were negative values of domestic material consumption (domestic extraction + imports – exports) that is caused by illegal and artisanal mining of precious metals. Illegal mining also entails that the burdens and impacts associated to mineral extraction increase even more as in the case of the latter there are no social, legal, or environmental criteria being followed. Alongside environmental problems, such as deforestation, the uncontrolled dumping of hazardous wastes in soils or rivers, can cause health damage. This also evidences that more efforts should be made by the local governments to improve the traceability of extracted minerals. Additionally, LA-20 mining statistics are not always complete or present disaggregated data that can be used to calculate the impacts of the mining sector by metal. There are still other statistics services, such as BGS and USGS, that provide useful data, but improvements should be made towards a more transparent and thorough method of reporting mineral data.

Along with other publications [4,19,20,22,27,28,76], this study intends to raise awareness on mineral production in Latin-American. Currently, the extraction rate of mineral stock continues to increase, as it did to fuel the growth of European countries in the past and powering the booming of China during recent years. This extraction, especially in the case of scarcer minerals, entails a loss that is related to the quality of mineral resources. This loss will presumably increase in the coming future, which raises the question whether income received from mineral exports in Latin America truly compensates the loss of natural mineral stock and the environmental burdens left in the region. It can also be used as a wake-up call to national and local authorities in Latin America to look at mineral resources from a more sovereign position for equal trading in a global market.

For this reason, this study attempts to promote a deeper discussion on the importance of the quality of minerals, incorporating the thermodynamic approach in conventional material flow analysis. This would imply following a new path by going beyond the traditional tonnage perspective.

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Appendix A

Table A1. Exergy replacement cost of non-fuel mineral for LA-20 in GJ per tonne of element. Source: [53].

No.	Mineral	ERC (GJ/t)	No	Mineral	ERC (GJ/t)
1	Aluminium (Gibbsite)	627	20	Mercury (Cinnabar)	28,298
2	Antimony (Stibnite)	474	21	Molybdenum (Molybdenite)	908
3	Barite	38	22	Nickel (Garnierite)	168
4	Beryllium (Beryl)	253	23	Niobium (Ferrocolumbite)	4422
5	Bismuth (Bismuthinite)	489	24	Platinum Group Metals (PGM)	4,491,690
6	Cadmium (Greenockite)	5,898	25	Phosphate Rock (Apatite)	0.4
7	Chromium (Chromite)	4.5	26	Potassium (Sylvite)	665
8	Cobalt (Linnaeite)	10,872	27	REE (Bastnaesite)	348
9	Copper (Chalcopyrite)	292	28	Sodium (Halite)	44.07
10	Fluorite	183	29	Selenium	2,235,699
11	Gold	553,250	30	Silver (Argentite)	7371
12	Graphite	20	31	Tantalum (Tantalite)	482,828
13	Gypsum	15	32	Tin (Cassiterite)	426
14	Iron ore (Hematite)	18	33	Titanium (Ilmenite)	4.5
15	Lead (Galena)	37	34	Vanadium	1055
16	Lime	2.6	35	Tungsten (Scheelite)	7430
17	Lithium (Spodumene)	546	36	Zinc (Sphalerite)	155
18	Magnesite	26	37	Zirconium (Zircon)	654
19	Manganese (Pyrolusite)	16			

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Appendix B

Country		Oil		~	Vatural Gas			Coal		No	m-Fuel Miner.	als		TOTAL	
-	Production	Imports	Exports	Production	Imports	Exports	Production	Imports	Exports	Production	Imports	Exports	Production	Imports	Exports
Argentina	28.20	0.38	1.97	35.60	9.45	0.07	0.07	1.67	0.001	8.00	2.43	0.89	71.90	13.90	2.93
Bolivia	2.95	·	,	15.70	,	12.60	,	,	,	0.52	0.00	0.20	19.20	$2.2 imes10^{-4}$	12.80
Brazil	101.00	19.60	19.80	20.80	12.80		6.86	25.00		436.00	6.43	293.00	422.71	63.83	210.20
Chile	0.34	8.84		0.71	2.87		2.18	9.27	0.89	24.50	0.20	5.85	27.70	21.20	6.75
Colombia	48.50		32.40	13.90		1.37	91.90		85.10	15.20	1.48	2.8×10^{-3}	169.00	1.48	119.00
Costa Rica										0.01	0.00	$4.7 imes 10^{-3}$	0.01	0.00	4.7×10^{-3}
Cuba	2.91	4.81		0.79				$3.0 imes 10^{-6}$		0.38			4.08	4.81	,
Jominican Republic	,	1.33			0.87			0.85		0.99	0.01	0.16	66.0	3.05	0.16
Ecuador	25.30		18.30	1.21						7.05		1.4×10^{-5}	33.60		18.30
El Salvador	0.50		0.44							0.21	0.01	0.68	0.71	0.01	1.11
Guatemala										0.10	0.01	$2.5 imes10^{-4}$	0.10		$2.5 imes 10^{-4}$
Honduras	,	,	,	,	,	,	,	0.12	,	0.08	,	,	0.08	0.12	,
Mexico	126.00		59.40	49.50	18.60	0.10	10.20	7.40	0.01	38.10	1.50	20.60	216.73	27.50	80.14
Nicaragua		0.64	,		,					0.04		$2.4 imes 10^{-5}$	0.04	0.64	2.4×10^{-5}
Panama										0.03	0.00	$1.4 imes10^{-4}$	0.03	$2.6 imes10^{-4}$	$1.4 imes 10^{-4}$
Paraguay			,		,					0.07	0.11		0.07	0.11	'
Peru	3.13	4.17	0.73	13.90	,	4.69	0.25	0.65	,	25.80	,	3.39	43.10	4.82	8.81
Uruguay		1.89			0.04			0.00		1.49	4.0×10^{-9}	$3.8 imes10^{-6}$	1.49	1.94	3.8×10^{-6}
Venezuela	144.00	0.61	96.30	20.80	1.55	,	1.08		0.80	16.20	13.60	3.23	182.00	15.80	100.00

Table A2. LA-20 mineral balance in 2013 (Unit: million tonnes).

Appendix C

Table A3. LA-20 mineral balance expressed using ERC for 2013 (Unit: Mtoe).

Country		Oil		z	atural Gas			Coal		No	n-Fuel Miner	als		TOTAL	
funno.	Production	Imports	Exports	Production	Imports	Exports	Production	Imports	Exports	Production	Imports	Exports	Production	Imports	Exports
Argentina	31.21	0.42	2.17	33.51	8.90	0.06	0.05	1.16	0.001	14.39	1.43	14.92	79.15	11.91	17.16
Bolivia	3.26	·	,	14.82	,	11.86	,	,	,	16.75	0.02	7.78	34.83	0.02	19.63
Brazil	111.64	21.71	21.86	19.57	12.09	,	5.18	18.92	,	702.60	85.51	268.79	778.47	138.23	225.38
Chile	0.37	9.77	,	0.67	2.70	,	1.51	6.44	0.62	84.97	1.87	44.32	87.53	20.78	44.94
Colombia	53.65		35.81	13.09	,	1.29	53.30		49.39	2.82	1.88	0.72	122.85	1.88	87.21
Costa Rica										0.01	1.43	8.07	0.01	1.43	8.07
Cuba	3.22	5.31	,	0.74	'	,				1.39			5.35	5.31	,
ninican Republic		1.47			0.81			0.49		15.16	0.10	1.38	15.16	2.89	1.38
Ecuador	28.01		20.25	1.14						1.99		0.18	31.14		20.43
El Salvador	0.55		0.49							0.35	0.30	2.68	0.90	0.30	3.17
Guatemala										0.11			0.11		
Honduras		,	,		'	,		0.07		1.06			1.06	0.07	'
Mexico	139.21		65.71	46.64	17.48	0.09	5.93	4.29	0.003	47.07	5.33	47.86	235.87	27.00	47.86
Nicaragua	,	0.71	,	,	,	I		,	,	0.13	,	0.13	0.13	0.71	0.13
Panama		,	,		'	,				0.04	0.003	0.03	0.04	0.003	0.03
Paraguay									•	0.03	0.04		0.03	0.04	•
Peru	3.46	4.61	0.81	13.12	,	4.42	0.19	0.49	,	67.42	,	55.19	84.19	5.10	60.42
Uruguay		2.09	0.00	0.00	0.04			0.00		0.14	0.0001	0.05	0.14	2.13	0.05
Venezuela	159.57	0.68	106.51	19.58	1.46	,	0.75	,	0.55	40.03	0.0003	1.36	219.94	2.14	108.43

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Appendix D



Figure A1. Mineral exports by destination (data expressed in %).

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A5. Paper V

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Scope: Review of the production of minerals of 20-countries in Latin America and the Caribbean, development of a methodology by applying Exergoecology principles of the exergy replacement cost to estimate the loss of mineral capital in the region for 2013

Contribution to the work:

- To make a balance of mineral production in twenty countries in Latin America and the Caribbean based on mass approach.
- To convert the mass balance into an energy balance through the use of the exergy replacement costs (ERC).
- To develop a methodology to estimate the loss of mineral wealth (LMW) in the region based on the ERC and GDP.
- To determine whether or not the revenues for selling minerals compensate the LMW in the region for a specific year.

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The cost of mineral depletion in Latin America: An exergoecology view *

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ABSTRACT

Latin America has always been a region of great interest not only for its rich-multicultural heritage, and diverse flora and fauna, but also for its natural resources that have become valuable commodities worldwide. In this paper an exergy-based analysis is used to investigate the cost of mineral depletion. By applying exergy replacement costs (ERC), a concept based on the Second Law of Thermodynamics, ERC determines the cost in exergy terms to recover minerals to its prior conditions with the current best available techniques when they have been completely dispersed after their usage. Such an assessment is a robust tool when evaluating natural resources in a country or region. We show that by using the above-mentioned methodology, it is possible to objectively quantify the loss of mineral wealth in Latin America associated to mineral extraction. Our study shows that the loss of mineral wealth in 2013 in the region was not compensated in comparison to the revenues obtained for the sale of minerals. Therefore, to establish a sustainable future scenario for the production of minerals in Latin America, a new framework for trading and management of fuel and non-fuel minerals is necessary.

1. Introduction

Modern living is heavily dependent on products obtained through mining activities. In fact the essential role of minerals for sustaining modern society was even accepted at the United Nations summit on Sustainable Development held in Johannesburg in 2002 (United Nations (UN), 2002). Accordingly, several studies have already been published (Calvo et al., 2017a; Graedel et al., 2015; Jin et al., 2016; Cunningham et al., 2008) on mineral availability and supply constraints from the perspective of industrialized nations and mineral analysis from a supply risk and economic importance perspective. For instance, the United States, through its National Defense Stockpile program published a report on Strategic and Critical Materials in 2015 (U.S. Department of Defense, 2015). In that report, among other things, aluminum oxide and antimony materials were identified for a shortfall from Latin American countries with Venezuela and Mexico supplying the above-mentioned materials, respectively. Additionally, in the latest Critical Raw Materials report published by the European Commission (2017a, 2017b), Mexico and Brazil, two of the largest countries in Latin America, were considered as key suppliers of niobium and fluorspar to European industries with a share of 71% and 38%, respectively.

Besides, due to the growing concern on climate change as also proclaimed in the amendments of the 21st Conference of the Parties (COP 21) in Paris (United Nations (UN) 2015) there have been discussions on generating different energy transition models (World Energy Council, 2013). In any case, low-carbon emission technologies require mineral extraction and processing (Calvo et al., 2017b; Grosjean et al., 2012; Henckens et al., 2016; Mohr et al., 2012; Ortego et al., 2018), as certain metals are essential for the proper operation of such low-carbon technological devices, and those minerals cannot be easily replaced by other substituents (Hurd et al., 2012; Stürmer, 2013; Zepf et al., 2014). Many of the elements and minerals classified as critical are available in Latin American countries, for example, Bolivia, Chile, and Argentina could be main sources of easily extractable lithium (Grosjean et al., 2012; Vara, 2015; Vikström et al., 2013; Gruber et al., 2011) useful in several energy devices.

Along with some elements mentioned above, in 2017, the Latin America region produced many important metals, such as, from a total global production stand point, 43% copper, 50% of silver, 21% of tin, 12% of nickel, and 11% of gold (USGS 2018). Additionally, exports of fuels and mining products generated about 277 billion US dollars in 2014; and the reserves of oil, natural gas and coal accounted for 20%,

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4%, and 2%, respectively, of the total world's proven reserves (World Trade Organization (WTO) 2015; Carrera et al., 2015).

As such, from above discussion, it is clear that Latin America is a key region which has been a subject of several studies performed using traditional material flow account methodologies focusing on extraction and trade of materials within and from Latin America (Giljum, 2008; Organisation for Economic Co-operation and Development (OECD) 2008; Wang et al., 2014; Schaffartzik et al., 2015). For example, Schaffartzik and colleagues (Schaffartzik et al., 2014) analyzed patterns and trends of materials extraction, trade and consumption of 177 countries from 1950 to 2010. In that study, the authors highlighted the role of Latin America and the Caribbean as metal producers, satisfying 12% of the metal demand of the world. Additionally, West and Schandl (2013) pointed out that Latin America and the Caribbean were less efficient in gaining economic profit because of the sale of natural resources. Giljum and Eisenmenger (2004) also suggested existence of "an unequal environmental distribution" between the North (OECD countries) and the South (non-OEDC countries). Additionally, studies with primary emphasis on economics, social or sustainability issues in which mining in South and Central America was directly or indirectly involved, have already been published (Bastida, 2002; Altomonte and Sánchez, 2016). Nevertheless, none of these studies have considered the quality of minerals when performing natural resource assessments of the region as a whole, material flow analyses do not portray either the environmental damage or the loss of mineral wealth caused by mining activities.

One way to quantitatively investigate the loss of mineral wealth is through an indicator based on the Second Law of Thermodynamics, the exergy replacement costs (ERC) (Valero and Valero, 2014). ERC takes into account the thermodynamic quality of minerals and assigns greater value to scarcer minerals which are, in turn, more difficult to produce.

In a recent study, Palacios et al. (2018) evaluated mineral exports by destination of twenty countries in Latin America in 2013 with the use of the ERC concept. Carmona et al. (2015), and Calvo et al. (2016) carried out investigations using ERC to analyze material flow in Colombia and Europe, respectively. In this paper, we apply the same methodology from a broader perspective, carrying a quantitative assessment of the impact that trading of fuel and non-fuel minerals in Latin America had in the mineral capital of the region. In this study the Latin America region is considered to be composed of 20 countries: Argentina, Bolivia, Brazil, Chile, Colombia, Costa Rica, Cuba, Dominican Republic, Ecuador, El Salvador, Guatemala, Honduras, Mexico, Nicaragua, Panama, Paraguay, Peru, Uruguay, Venezuela, and Haiti (hereinafter LA-20), which covers approximately one-eighth of the global surface area. Therefore, the main goal of this paper is to evaluate if in 2013 whether or not the revenues from the sale of minerals compensate the loss of LA-20's mineral wealth.

2. Evolution of metal prices

Like other metal producers, Latin America's economy has suffered ups and downs of commodity prices in the last few years (Rosales, 2015; Comisión Económica para América Latina y el Caribe (CEPAL) 2016c).

As stated by many authors, mineral commodity prices are very volatile (Henckens et al., 2016; Frankel and Rose, 2010; Li et al., 2012) and factors that influence this volatility can be attributed to stock variations, supply-demand interactions, geopolitics, market speculation, etc. (Stürmer, 2013; Frankel and Rose, 2010; Deaton and Laroque, Jan.J. 1992).

Information about mineral prices shown in Fig. 1 was compiled from (Kelly and Matos, 2016). To further decipher the volatility in mineral prices from 1960 to 2015, Fig. 1 has been split into four groups of minerals. At the upper left (a), the change in the price of gold can be seen. In 2010 its price was \$39.5 million USD/t and the last reported value was \$37.4 million USD/t in 2015. The most recent peak price for gold occurred in 2012 when its price reached \$53.8 million USD/t. At the upper right corner (b), the historical trend of silver price is shown, its price was \$1.13 million USD/t in 2011, and the last reported price was \$0.5 million USD/t in 2015. Nickel, at the lower left (c), oscillated between \$37.2 thousand USD/t in 2007 and \$11.8 thousand USD/t in 2015. Other minerals produced principally in Latin America can be found in the lower right corner (d). Iron ore-price decreased from \$99 USD/t in 2010 to \$81 USD/t in 2015, with a peak in 2012 of \$116 USD/t. For copper, prices varied from \$7.7 thousand USD/t to \$5.7 thousand USD/t, in 2010 and 2015 respectively, with a peak 2011 of \$8.9 thousand USD/t. Lithium price increased from \$3.8 thousand USD/t in 2011 to \$4.5 thousand USD/t in 2015.

A growing concern about the environmental effects of mining activities and social conflicts in Latin America has been stated as reasons for price fluctuations by many scholars (West and Schandl, 2013; Martinez-Alier, 2001; Gudynas, 2018). Gudynas pointed out that because of the need of public spending in South American countries and the booming prices of raw materials, the pressure for the exploitation of natural resources increased along with environmental damage (Gudynas, 2018). A publication by Martinez-Alier describes conflicts caused by mining activities in different countries, including some South American countries. The unfair treatment of lawsuits against mining companies between powerful and non-powerful nations was clearly pointed out by this author (Martinez-Alier, 2001).

A fairer price of commodities has been claimed as a necessity to tackle the long-lasting environmental and societal issues caused by the exploitation of natural resources, not only in Latin America but also in other regions (Temper et al., 2015; Childs, 2014; Hilson et al., 2016; Childs, 2014). The Fairtrade certification of gold in Latin America and sub-Saharan Africa could have been a better alternative, at least to overcome some issues faced by small-scale miners. However, some authors did a deeper analysis of this initiative (Childs, 2014; Hilson et al., 2016; Childs, 2014), and found that more actions were required, beyond a logo of Fairtrade, for better outcomes for miners. One way to face up to economic and environmental difficulties is through the direct intervention of governments. For instance, China, a world leader in the production of rare earths, nationalized and closed some rare earth mines for strategic reasons in 2011 (Bilsborough, 2012; Klossek et al., 2016; Schlinkert and van den Boogaart, 2015). Venezuelan Government in 2013 ignored intermediate negotiators and guidelines of the London Metal Exchange (LME) and imposed "fairer prices" for iron, steel, and aluminum (Oré and Antonioli, 2013). Nevertheless, both of the abovementioned direct governmental measures brought serious economic and geopolitical implications at national and international levels.

It is known that commodity prices are very volatile; but one objective way to evaluate mineral commodities from a fairer approach is by applying thermodynamics. Specifically, we refer to the second law of thermodynamics through the exergy replacement costs concept, which evaluates the quality of minerals and charges greater value to scarcer minerals, as will be explained below in Section 3.

3. Methodology

In this section, the methodology used for the analysis of mineral production in LA-20 is described, starting with the concept of the exergy replacement cost (ERC) and then establishing the necessary steps to quantitatively assess the loss of mineral wealth in the region.

3.1. The exergy replacement cost

One way to overcome the issue of proper evaluation of mineral resources is through the Second Law of Thermodynamics. Exergy has been traditionally used to measure any energy source and is defined as the minimum amount of work that may be theoretically performed by bringing a system into equilibrium with its surroundings. It is a property of a system-environment combination (Cengel and Boles, 2008) and is helpful in recognizing and evaluating environmental impacts and



Fig. 1. Mineral price variation of different non-fuel mineral commodities mainly produced in Latin America since 1960 presented in four graphs for better visualization. a) gold and platinum, b) silver only, c) and d) mineral commodities whose higher price was 70 and 35 thousand USD/t, respectively.

consumption of non-renewable resources (Yazdi et al., 2015; Athari et al., 2015; Akbari and Mahmoudi, 2014), especially in the case of fuel minerals (Bejan et al., 1996; Sato, 2005; Dincer and Rose, 2013). Thermodynamically, non-fuel minerals have been traditionally evaluated through their chemical exergy, which is usually obtained from an investigation conducted by Szargut (1989), Ayres (2016), Dewulf and Van Langenhove (2006) or Szargut et al. (2002, 2015) have worked in this area. As pointed out by Domínguez and Valero (2013), by considering only chemical exergy, important features of non-fuel minerals are ignored. For instance, the chemical exergy of precious metal gold is 60 kJ/mol, while for aluminum is 796 kJ/mol.

In this context, exergoecology has been proposed for the evaluation of natural resources and one division of this discipline is Physical Geonomics. As defined by Valero (1998), the Physical Geonomics investigates how the exergy concept can be applied to the assessment of non-fuel minerals.

Within the framework of Physical Geonomics, exergy in minerals has mainly two constituents, chemical, and concentration exergies. The total exergy (b_{tl}) which is the minimum amount of exergy required to get the mineral from a reference environment named as Thanatia (Valero and Valero, 2013). The latter represents the conceptualization of a commercial dead planet, in which all fossil fuels have been burned and all minerals have been totally dispersed into the continental crust (Valero et al., 2011). Accordingly, the total exergy (b_{tl}) is determined by adding chemical (b_{chl}) and mineral (b_{cl}) parts into Eq. (1).

$$b_{ti} = b_{chi} + b_{ci} \tag{1}$$

In order to calculate the term b_{ci} , concentrations at the mine (x_m) and the crust of the Earth (x_c) should be considered. The b_{ci} is expressed by Eq. (2).

$$b_{ci} = -RT^{\circ} \left[lnx_i + \frac{(1-x_i)}{x_i} \right] ln(1-x_i)$$
⁽²⁾

In Eq. (2), the expression x_i represents the concentration of the substance *i*, *R* is the gas constant (8.314 J/mol K) and T° is the absolute reference temperature (298.15 K). The minimum energy (Δb_c) that Nature spent to concentrate minerals in a deposit is determined by the subtraction of x_m and x_c , following Eq. (3).

$$\Delta b_c(x_c \to x_m) = b_c(x = x_c) - b_c(x = x_m) \tag{3}$$

Then the exergy replacement costs (B^*) is computed with Eq. (4).

$$B^* = k(x_c) \Delta b(x_c \to x_m) \tag{4}$$

The dimensionless parameter k is the unit exergy cost of a mineral and is calculated as the ratio between the energy invested in the real mining and concentrating process of the mineral, and the minimum theoretical energy that would be required if the whole process were reversible. One key aspect that differentiates ERC from other thermodynamic properties is that ERC contemplates best available technologies for the extraction of non-fuel minerals.

Because of the number of minerals considered in the current study, the ERC values of the 37 non-fuel minerals can be found in Appendix A. In order to highlight the importance of considering the physical quality of non-fuel minerals, the next comparison between ERC values is provided. Gold and silver have ERC values of 553, 250 and 7371 GJ/ton, respectively, while limestone and phosphate rock have values of 3 and 0.4 GJ/ton, respectively. Higher values of ERC indicate a higher quality of minerals and imply a higher loss of mineral wealth when they are extracted. It can be seen that ERC values for minerals that are abundant and easily extracted are lower than those whose concentration in the

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mines is much lower, implying higher energy consumption during the extraction process. A study of mineral exports in LA-20 by destination in 2013 (Palacios et al., 2018) pointed out that conventional material flow analyses of precious metals like gold and silver remain unnotice-able because of their low amounts. However, when considering their physical quality through the ERC concept, they had more weight than lower quality minerals, such as iron and aluminum. Therefore, ERC is a key concept when assessing the loss of mineral wealth in a country or region.

In the case of fuel minerals, such as oil, natural gas, and coal, as they are completely dispersed when they are burned, its ERC is equivalent to their high heating values (HHV). These values have been taken from Valero and Valero (2012).

3.2. Assessment of the loss of mineral wealth

The mineral endowment was first defined by Harris and Agterberg (1981) as the amount of metals in a given region. In this respect, mineral deposits can be seen as a free bonus provided by the Nature. This is because it avoids a lot of mining exergy which would be otherwise spent if minerals were dispersed throughout the crust instead of concentrated in mines. When mineral deposits become depleted, the corresponding free bonus reduces, meaning that in the future, much more energy will have to be put into place in order to obtain the same amount of resources. In the limit, the bonus completely disappears and mining would take place at crustal concentrations. In contrast to fossil fuels, which once burned the resource disappears, non-energy minerals do not disappear, they just become dispersed if not adequately managed. The problem of mineral resources is thus not one of scarcity, but rather of an insufficient provision of cheap energy to extract increasingly diluted commodities (Valero and Valero, 2014).

Hence, this accumulation of minerals, traded later as commodities, means richness for a country or region. Because of the growing need of minerals, they are extensively extracted resulting in what can be defined as the loss of mineral wealth of the producing regions (Gabriel Carmona et al., 2015; Calvo et al., 2015a, 2015b). Exergoecology principles proposed by Valero (1998) were used in this study to have a more robust and complete picture of the loss of mineral wealth in LA-20.

The methodology followed in this paper consists of five stages: 1) data mining collection for non-fuel and fuel minerals, 2) conversion into ERC terms, 3) elaboration of mineral balance in ERC terms, 4) analysis of primary energy sources, and 5) economic analysis. For a better understanding of the methodology, all the stages are represented in Fig. 2.

The first stage consisted of the collection of production data of fuel and non-fuel minerals. For this study, three main fossil fuels (oil, natural gas, coal) and 37 non-fuel mineral commodities were studied: aluminum, antimony, barite, beryllium, bismuth, cadmium, chromium, cobalt, copper, fluorite, gold, graphite, gypsum, iron, lead, limestone, lithium, magnesite, manganese, mercury, molybdenum, nickel, niobium, platinum group metals (PGM), phosphate rock, potash, rare earth elements (REE), salt, selenium, silver, tantalum, tin, titanium, vanadium, wolfram, zinc and zirconium. Data regarding fossil fuel production (oil, coal and natural gas) were provided by the Latin American Organization of Energy (OLADE) (Carrera et al., 2015).

Fuel and non-fuel mineral production, in ERC terms, were taken from a recent publication by Palacios et al. (2018). A summary of the sources of information can be found in Table 1.

To fill gaps in the information and for cross-checking purposes, information of British Geological Survey (2014), U.S. Geological Survey (USGS) (USGS 2014), the Economic Commission for Latin America and the Caribbean (Comisión Económica para América Latina y el Caribe (CEPAL), 2016) and UN International Trade Statistics Database (UN Statistics Division, 2017) was used.

The second and third stage consisted of converting production data



Fig. 2. Methodology used for the assessment of the loss of mineral wealth. The evaluation consisted of five stages where the production of fuel and non-fuel minerals is translated into energy with chemical exergy and the exergy replacement cost (ERC), respectively. Then, it is considered that non-fuel minerals are recovered through an energy source (with an upper and lower price range). Finally, the economic stage is performed by comparing GDP ratios with the recovery prices of minerals.

Table 1

Source of information for mineral production.

Country	Source of information	Country	Source of information
Bolivia Brazil	Delgadillo Camacho et al., 2015 Departamento Nacional de Produção Mineral do Brasil (DNPM), 2015	Argentina Costa Rica Cuba Dominican Republic El Salvador	(USGS, 2014; British Geological Survey, 2014)
Chile	Servicio Nacional de Geología y Minería (SERNAGEOMIN), 2015	Guatemala Honduras Nicaragua	
Colombia	Sistema de Información Minero Colombiano (SIMCO), 2015; Sistema de Información Minero Colombiano (2013)	Panama Paraguay Peru	
Ecuador Mexico	Agencia de Regulación y Control Minero de Ecuador (ARCOM), 2014 Servicio Geológico Mexicano,	Uruguay Venezuela	
	2015		

into exergy terms both for fossil fuel and non-fuel minerals. As stated before, the exergy of fossil fuels is comparable to their high heating values (Valero and Valero, 2012). Concerning non-fuel minerals, their exergy is calculated using ERC (expressed in GJ/t). Therefore, once this conversion was done, a mineral analysis in energy terms (Mtoe) was performed.

The next step consists of assessing what would be the economic
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costs of the "free mineral bonus" lost through extraction, or in other words, to calculate what would be the cost of recovering the extracted minerals once dispersed, back into their initial concentrations in the deposits were they were found. In order to estimate the replacement costs of minerals in monetary units (USD), market prices of primary energy sources in each country were considered (electricity, oil, and coal). In order to have a range of comparison, two prices of primary sources were considered. The lowest price was taken to calculate the lower boundary price (LBP) and the highest, to calculate the upper boundary price (UBP), fourth stage. Prices of primary energy sources were compiled from the database of OLADE (Organización Latinoamericana de Energía (OLADE) 2015). The recovery was calculated with Eq. (5).

$$Recovery = B^* x UBP \text{ or } LBP$$
(5)

Finally, in the fifth stage, an economic analysis was performed. For comparative purposes, GDP values that correspond to the extractive sector and energy prices of each selected country were compiled (Comisión Económica para América Latina y el Caribe (CEPAL), 2016). Then, the ratio between LBP and UBP to the total GDP was obtained for every country to assess the loss of mineral wealth in LA-20 in 2013 and to analyze if the revenues of selling the minerals under the 2013 market conditions did or did not compensate this loss.

Note that when converting energy into monetary units, arbitrariness and volatility is introduced in the analysis. Energy prices often fluctuate because of political and socio-economic factors. The physical analysis, which is robust and universal is therefore valuable in itself. Yet it is worth showing the results in monetary units to bring out in an easier way the order of magnitude of the mineral wealth lost through extraction.

4. Results and discussion

Complete information regarding LA-20 mineral production, exports, and imports in 2013, in mass terms and in ERC terms can be found in the study by Palacios et al. (2018). Based on their information, Table 2 shows the key minerals produced by country.

Even if only 37 non-fuel minerals are considered in this study, LA-20 produced other mineral commodities, such as bentonite, diatomite, dolomite or kaolin. As the vast majorities are consumed domestically, they did not have a considerable impact on mineral trade or on the extractive GDP. Therefore, these minerals did not influence the subsequent economic analysis.

It can be seen that the weight in mass and in ERC terms changed drastically when mineral production is expressed in ERC terms (Table 3) and compared to the mass basis mineral analysis. For instance, the LA-20 production of fossil fuels accounted in mass terms for 57% of the total mineral production (considering both fossil and non-

Table 2

Key	non-fuel	mineral	s proc	luced	by	country	in	20	1:	3
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Country	Key elements produced	Country	Key elements produced
Argentina	Iron, salt, gypsum	Guatemala	Gypsum, salt, magnesite
Bolivia	Zinc, Lead, Tin	Honduras	Salt, zinc, lead
Brazil	Iron, aluminum, salt	Mexico	Iron, salt, gypsum
Chile	Iron, salt, copper	Nicaragua	Gypsum, silver, gold
Colombia	Limestone, iron, salt	Panama	Salt, gold
Costa Rica	Limestone, gold	Paraguay	Iron, gypsum
Cuba	Salt, gypsum, nickel	Peru	Iron, zinc, copper, gold
Dominican	Gypsum, salt,	Uruguay	Limestone, iron, gold
Republic	copper		
Ecuador	Limestone, copper,	Venezuela	Iron, aluminum,
	gold		limestone
El Salvador	Salt		

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Table	
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LA-20 production in E	RC terms for	2013 (U	Jnit: Mtoe).
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Country	Oil	Natural gas	Coal	Non-fuel minerals
Argentina	31.21	33.51	0.05	14.39
Bolivia	3.26	14.82	-	16.75
Brazil	111.64	19.57	5.18	642.08
Chile	0.37	0.67	1.51	84.97
Colombia	53.65	13.09	53.30	2.82
Costa Rica	-	-	-	0.01
Cuba	3.22	0.74	-	1.39
Dominican Republic	-	-	-	15.16
Ecuador	28.01	1.14	-	1.99
El Salvador	0.55	-	-	0.35
Guatemala	-	-	-	0.11
Honduras	-	-	-	1.06
Mexico	139.21	46.64	5.93	44.09
Nicaragua	-	-	-	0.13
Panama	-	-	-	0.04
Paraguay	-	-	-	0.03
Peru	3.46	13.12	0.19	67.42
Uruguay	-	0.00	-	0.14
Venezuela	159.57	19.58	0.75	40.03

fossil fuels minerals), but when this percentage is expressed in exergy terms, it is reduced to 43%.

The non-fuel mineral with the highest weight in the national production in exergy terms was aluminum, with a total production of 559 Mtoe. Iron, which was the first extracted commodity in mass terms, was the second in exergy terms, with a total production of 122 Mtoe. This is because the ERC value of aluminum is more than thirty times higher than the ERC of iron (Valero and Valero, 2014). This observation reveals that ERC unambiguously highlights its importance because it considers mine concentration and scarcity along with other factors.

As it was mentioned in the methodology section, the monetary costs associated with reversing the extractive processes with the usage of local energy sources was also calculated. Market prices of primary energy sources in 2013 for each country in LA-20 were retrieved from the OLADE data base (Carrera et al., 2015) and are shown in Table 4. As can be seen from this table, the differences in energy prices are quite remarkable.

In most countries, the lowest energy price in 2013 corresponded to electricity with an average electricity price of 1690 USD/Mtoe for the

Table 4

Local market princes of primary energy sources used.

		LBP		UBP	
\mathbf{N}°	Country	source	(USD/Mtoe)	source	(USD/Mtoe)
1	Argentina	electricity	3.49×10^2	oil	6.96×10^8
2	Bolivia	electricity	5.81×10^{2}	oil	$5.18 imes 10^8$
3	Brazil	electricity	$1.86 imes 10^3$	oil	$6.79 imes 10^8$
4	Chile	coal	$1.02 imes 10^8$	oil	6.91×10^{8}
5	Colombia	electricity	$2.33 imes 10^3$	oil	$6.79 imes 10^8$
6	Costa Rica	electricity	1.86×10^{3}	oil	7.11×10^{8}
7	Cuba	electricity	$1.16 imes 10^3$	oil	$7.05 imes 10^8$
8	Dominican Republic	electricity	$2.56 imes 10^3$	oil	$1.02 imes 10^8$
9	Ecuador	electricity	$6.98 imes 10^2$	oil	$6.96 imes 10^8$
10	El Salvador	electricity	$3.14 imes 10^3$	oil	$7.05 imes 10^8$
11	Guatemala	electricity	3.61×10^3	oil	7.11×10^{8}
12	Honduras	electricity	$2.33 imes 10^3$	coal	$1.02 imes 10^8$
13	Mexico	electricity	1.41×10^{3}	oil	6.96×10^{8}
14	Nicaragua	electricity	$3.72 imes 10^3$	oil	$6.96 imes 10^8$
15	Panama ^a	electricity	$1.51 imes 10^3$	-	-
16	Paraguay ^a	electricity	5.81×10^2	-	-
17	Peru	electricity	$9.30 imes 10^2$	oil	$6.96 imes 10^8$
18	Uruguay	electricity	$1.86 imes 10^3$	oil	$6.96 imes 10^8$
19	Venezuela	electricity	$2.32 imes 10^2$	oil	$6.80 imes 10^8$
	LA-20	electricity	$1.69 imes 10^3$	oil	$6.85 imes 10^8$

^a only one primary energy source is available.

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industrial sector. The highest energy price corresponded to oil, with an average value of 685 million of USD/Mtoe. In regard to electricity prices, it is worth mentioning that they are subsidized depending on the reference country. As such, in some countries, electricity prices are lower than in others and also lower than compared to global market prices. Many studies are published on the issue of subsidies with pros and cons of subsidies and comparison to international fuel prices (Carlino and Carlino, 2015; Pantanali and Benavides, 2006). However, in some countries, the real amount invested in energy subsidies and its impact on national economies is still unclear. In another study, Di Bella et al. (2015) analyzed the impact of subsidies on fossil fuel and electricity, concluding that it corresponded to an average of1.8% of the total GDP during 2011-2013 in Latin America and the Caribbean. In our study, the issue of subsidies has not been taken into account and reported prices were directly used. The subsidies on energy are thus an additional reason for giving preference to the physical analysis over the monetary one.

The most commonly used and straightforward indicator to measure the revenues of the mining sector is the extractive gross domestic product (GDP). According to statistics reported by the Economic Commission for Latin America and the Caribbean (CEPAL), the extractive GDP, which considers the revenue of the extraction of both fuel and non-fuel minerals, varied between 0.12% and 24.8% in 2016 (Comisión Económica para América Latina y el Caribe (CEPAL), 2016).

Accordingly, using GDP as a comparative element, the loss of mineral wealth for LA-20 in 2013 is shown in Table 5. The production of fuel and non-fuel minerals (in %) was calculated based on the total production in mass terms. The ratios of the extractive GDP, LBP, and UBP to the total GDP were calculated as previously explained (Section 3) in the methodology using data in exergy replacement cost (Mtoe).

Majority of the countries with higher production of fuel minerals had higher differences between the sales and loss of their mineral wealth, as the ratios LBP/GDP_{total} and UBP/GDP_{total} are higher than GDP_{extractive} / GDP_{total}. This is the case, for instance, for Bolivia, Venezuela, Argentina, Mexico and Ecuador, whose share of fuel mineral production in 2013 was higher than 71%. An exception is Guatemala, with a high production of fuel minerals (more than 80%), but its GDP_{extractive/total} was higher than UBP/GDP_{total}.

On the contrary, in countries with higher production of non-fuel minerals (higher than 85%), such as, Chile, Costa Rica, Honduras, Nicaragua, Panama, Paraguay, and Uruguay, the loss of mineral wealth was compensated by the sale of non-fuel minerals, as $GDP_{extractive}/GDP_{total}$ is higher than UBP/GDP_{total} . But that was not the case of Brazil and Dominican Republic, where the income generated by the minerals was lower than the monetary value associated to that loss of mineral capital.

In 2013, LA-20 was the region mainly based on fuel minerals production, with a share of 64% of the total extraction. The average values of LBP/GDP_{total}, UBP/GDP_{total} were 7.44, 18.38, respectively. Additionally, the GDP_{extractive}/GDP_{total} average value for LA-20 was 5.81. Therefore, the recovery of minerals would be between one and three times higher than the economic benefit of the mineral sales if this recovery was carried out with the lowest and highest energy sources, respectively. Therefore, performing a comparison of these indicators (LBP/GDP_{total}, UBP/GDP_{total}) with GDP_{extractive}/GDP_{total} for 2013, shows that the economic revenues of the mineral sales did not compensate the loss of mineral wealth in LA-20.

5. Conclusions

Latin America (LA-20) is a region of great interest due to the production and reserves of important non-fuel minerals that are marketable worldwide. Although previous studies had been performed to measure the impact of mining in Latin American countries at different scales, economic, social, environmental, etc., none of them had quantified the loss of mineral wealth caused by the extraction of minerals. To fill this gap, in this research, we have used the concept of the exergy replacement cost (ERC), based on the Second Law of Thermodynamics, that allows a quantitative evaluation of fuel and non-fuel minerals. The concept considers physical characteristics of minerals, taking into account their scarcity in the crust of the Earth. The ERC together with the methodology herein described was utilized to quantitatively assess the loss of mineral wealth in LA-20 during 2013.

This methodology was used to compare the revenues coming from the sales of minerals, through the indicator $GDP_{extractive} / GDP_{total}$, with the recovery process of the minerals to its initial conditions, using local lowest and highest primary energy sources prices. This approach is represented by two ratios LBP/GDP_{total} and UBP/GDP_{total}, respectively. By comparing these indicators, it is possible to draw conclusions whether the extraction of minerals, and the consequent mineral loss for the territory, was compensated or not by their sales.

A comparison of these values revealed that, in 2013, the economic

Table 5

The loss of mineral wealth in 2013 for LA-20	Э.
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N°	Country	Production Fuel Minerals (%)	Production Non-Fuel Minerals (%)	GDP _{extractive} / GDP _{total} (%)	LBP/ GDP _{total} (%)	UBP/ GDP _{total} (%)
1	Argentina	88.87	11.13	3.20	6.14	8.32
2	Bolivia	97.27	2.73	14.28	22.42	73.30
3	Brazil	30.43	69.57	2.55	3.33	21.42
4	Chile	11.66	88.34	14.34	2.10	13.02
5	Colombia	91.04	8.96	9.18	14.03	14.60
6	Costa Rica	0.00	100.00	0.29	$2.72 imes 10^{-10}$	0.01
7	Cuba	90.72	20.98	0.62	3.44	4.84
8	Dominican Republic	0.00	100.00	2.51	0.01	16.65
9	Ecuador	79.02	20.98	10.41	23.81	25.48
10	El Salvador	0.00	100.00	0.30	$1.45 imes 10^{-6}$	0.33
11	Guatemala	83.25	16.75	1.77	0.85	1.39
12	Honduras	0.00	100.00	0.71	$1.40 imes 10^{-5}$	0.61
13	Mexico	85.68	14.32	6.67	9.27	11.93
14	Nicaragua	0.00	100.00	2.94	$4.68 imes 10^{-6}$	0.88
15	Panama	0.00	100.00	1.60	0.08	-
16	Paraguay	0.00	100.00	0.12	0.09	-
17	Peru	40.17	59.83	10.98	2.83	29.49
18	Uruguay	0.00	100.00	0.34	$5.65 imes 10^{-7}$	0.21
19	Venezuela	91.13	8.87	24.80	41.75	51.96
	Average LA – 20	64.36	35.64	5.81	7.44	18.38

only one primary energy source is available.

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revenues of the sales of minerals was far from equal when compared to the costs of recovering them using the local lowest or higher energy price. Hence, the data shows that the sales of mineral in 2013 did not compensate fairly the loss of mineral wealth in LA-20, indicating a requirement for the shift in the paradigm of assessing fuel and non-fuel minerals, and posing the question of what would be a fairer price of commodities. Although some governments have taken direct action to increase the price of commodities, a new scheme is required for metal prices. The current price of minerals, based on the cost of extraction plus profit, does not provide a sustainable approach to evaluate the loss of mineral patrimony. To overcome this issue, other approaches should be considered. One option could be considering the replacement costs as one of the parameters used to set-up mineral commodity prices. Although the physical value of replacement costs expressed in energy units is valuable in itself, its conversion into monetary with the methodology developed in this paper provides a quantitative assessment. This assessment is helpful for realizing that generally the revenues for the sale of commodities do not compensate the mineral wealth lost through their extraction. This is because currently, mineral prices are not reflective of the fact that future generations will need to spend much more energy to obtain the same amount of resources extracted today. In that sense, ERC becomes a valuable indicator because it objectively shows how much effort was made by the Earth to concentrate minerals. Further research should be oriented in this direction.

This publication is intended to raise awareness among policy makers and local authorities in Latin America about an urgent need on the establishment of a fairer scheme on trading towards more sustainable paths for the production of non-fuel mineral resources in the region.

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Appendix A. Exergy replacement costs of the 37 non-fuel minerals included in the study (Unit: GJ/t per ton of element)

Mineral (Mineral Ore)	ERC (GJ/t)	Mineral (Mineral Ore)	ERC (GJ/t)
Aluminum (Gibbsite)	627	Mercury (Cinnabar)	28 298
Antimony (Stibnite)	474	Melubdonum (Melubdonite)	20,270
Antimony (Subine)	4/4	Nieleel (Comienite)	908
Barite	38	Nickel (Garnierite)	168
Beryllium (Beryl)	253	Niobium (Ferrocolumbite)	4422
Bismuth (Bismuthinite)	489	Platinum Group Metals (PGM)	4491,690
Cadmium (Greenockite)	5898	Phosphate Rock (Apatite)	0.4
Chromium (Chromite)	4.5	Potassium (Sylvite)	665
Cobalt (Linnaeite)	10,872	REE (Bastnaesite)	348
Copper (Chalcopyrite)	292	Sodium (Halite)	44.07
Fluorite	183	Selenium	2235,699
Gold	553,250	Silver (Argentite)	7371
Graphite	20	Tantalum (Tantalite)	482,828
Gypsum	15	Tin (Cassiterite)	426
Iron ore (Hematite)	18	Titanium (Ilmenite)	4.5
Lead (Galena)	37	Vanadium	1055
Lime	2.6	Tungsten (Scheelite)	7430
Lithium (Spodumene)	546	Zinc (Sphalerite)	155
Magnesite	26	Zirconium (Zircon)	654
Manganese (Pyrolusite)	16		

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A.6 Paper VI

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Impact Factor: The international conference ECOS has a great reputation in the field of Thermodynamics and is carried out for more than 30 consecutive years.

Scope: To estimate the behavior of the energy consumption for the production of gold as function of the ore grade by means of a computational model in HSC software.

Contribution to the work:

- To develop a computational model in HSC software for the production of gold.
- To estimate the effect of the ore-grade decline over the energy consumption for the production of gold.
- To compare the result of the model with the corresponding ones reported in the literature.
- To add an input from the mineral-processing perspective to the decline of oregrade over the sustainable production of metals.

Beyond a tonnage perspective for the assessment of mineral resources. Focus on Latin America and the Caribbean

ECOS 2019: Simulation-based approach to study the effect of the ore-grade decline on the production of gold

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Abstract:

With the rush of metal consumption in the last decades, a growing concern has emerged about the decline of ore grades and the consequent increase of energy in the production of metals. When no more rich deposits would be available, metals would be extracted from common rocks. Gold is a precious metal that is widely used in a variety of applications since pieces of jewelry until electronic circuits. To decrease the effects of global warming, it would be necessary to spread the use of renewable energy technologies. This would cause the consumption of more metals, and gold would not be the exception. In this paper, we studied the effect of the ore-grade decline on the production of gold through a computational model developed in HSC software. We used the composition of Thanatia, a state of mineral dispersion into the Earth's crust, as a common rock from which gold would be produced. With our model, it was verified that the specific energy would experience an exponential growth while the ore-grade decreases. Besides, its environmental impact was estimated due to the electricity consumption in the processes. Our approach, with a mineral processing model developed in HSC Sim, assures a rigorous evaluation of the environmental impact associated to the gold production since the whole production process is well known and not assumed or simplified as currently done in most LCA analyses.

Keywords:

Ore-grade Decline, Gold Production, Energy, Environmental, Thanatia

1. Introduction

Gold has been since centuries an icon of royalty and wealth [1]. Due to its extraordinary properties, such as, electrical conductivity, resistance to corrosion and stability that is why it has a vast variety of applications. Gold is used for coinage, in the circuitry of electronic devices, as a component in

alloys to increase the efficiency of solar cells as well as medical applications [2]. Statistics of the World Gold Council [3] shows that in 2017 the primary uses of gold was mostly demanded by the manufacture of jewelry (53%), 39% was used for financial purposes for investment and central banks, and 6% in electronics, **Error! Reference source not found.** (a). In 2017, the total production of gold from mines accounted for 3219 tons. The 64% percent of the gold mine production in the world was mainly dominated by ten countries, **Error! Reference source not found.** (b). The biggest producers were China, Australia, and Russia.



Figure 1. Historical demand for gold by sector (a) and the ten most important producers of a gold mine in 2017 (b). (Source: [3])

Authors like Mudd [4–8], Craig et al. [9], Norgate [10], Calvo et al. [11] have published works in which it is clear the ore grade in deposits in the last years have declined. In a paper by Mudd [4] in 2007, he studied the behavior of the ore grade over time in mines in Brazil, Australia, South Africa, Canada, and the United States. A clear tendency in the decline of the ore grade was observed. As an example, in Australia in 1859 the average ore grade was 37 g/t and in 2005 was 2 g/t. Cox and Singer reported in 1992, an average gold content of 0.22 g/t for different gold deposits [12]. While the ore grade decreases over time, the energy for metal processing increases. In 1991, the average energy consumption of two gold mines was 172 GJ/kg of gold, while in 2006, for twenty-two mines investigated was 187 GJ/kg of gold [4].

The shift towards more renewable energy technologies to decarbonize the society will cause more consumption of metals [13–15]. In research about material restrictions for renewable energy technologies, Valero et al. [16] stated that to cut the dependency on fossil fuels will produce a more profound dependence on non-fuel minerals. In the limit, where no more mineral deposits would be available, commons rocks would be used as a source for the production of metals. They proposed an ideal state of mineral dispersion into the Earth's crust coined as Thanatia. The latter represents a state of mineral distribution from which metals can be produced [1].

Although the extraction of metals from common rocks is feasible, it would imply the use of the use of more energy as mentioned by Skinner in 1976 [17]. Authors like Harmsen et al. [18], Bardi [19], Norgate and Jahanshahi [10] supported this statement on the necessary increase of specific energy for the extraction of metals from low-grade deposits. Based on LCA analysis carried out in SimaPro and mathematical equations, Norgate and Haque [20] and Rankin [21], respectively, also showed an exponential growth in the energy required for the production of metals when the ore grade decreases. In 2002, Steen and Borg estimated the production of metals from common rocks sustainably [22]. They reported increments of one and two orders of magnitude for the production cost of metal concentrates, such as copper, cadmium, manganese, etc.

In this paper, we develop a model in HSC Chemistry software version 9.7.1.0 [23] to study the behavior of the specific energy required to produce gold by varying the ore-grade. For this study, we consider that the ore grade will go from an average representative ore-grade to a concentration of

gold found in common rocks. Thanatia's composition is used as gold-ore for this research. Also, by assuming that the ore will be placed in different locations, we estimate some environmental impacts with GaBi software, version 8.7.0.18 and database 8007 [24]. The purpose of this work is to add more information to look for more sustainable mechanisms for the production of metals. Furthermore, we would like to encourage a more in-depth analysis of the production processes of metals for a proper evaluation of the environmental impacts.

2. Thanatia

Valero at CIRCE proposed Thanatia as a state to estimate the "free bonus" given by Mother Nature to have minerals concentrated in deposits [1,25]. Thanatia, which comes from the Greek "thánatos" means death, represents an ideal state in which minerals are entirely dispersed into the Earth's crust. Thanatia is made up of 324 species, 292 minerals and 32 diadochic elements [1,26]. A complete description of the substances in Thanatia can be found in [1]. The composition of Thanatia will be used for the production of gold in our model. Gold in Thanatia is found mostly in nativ1.21E-07 wt-%) and tellurides, such as calaverite (2.46E-08 wt-%) and sylvanite (3.12E-08 wt-%) [1].

3. Organization of paper

The routes for metal production depends upon the type of ore. Therefore, according to the composition of Thanatia, an extensive literature review was necessary. Generally, gold can be obtained as it is found as native from or tellurides [1]. For both types, the comminution process is essential. In this process, the ore is reduced in size through crushers and mill until an appropriate size in which the metal contained in the ore can be liberated [27,28]. The specific energy in comminution can be calculated by applying is Bond's equation [27,29] Equation (1):

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

where W is the specific energy consumption of the mill (kWh/t), Wi is the work index measured in a laboratory mill (kWh/t), P80 and F80 are 80% the product and feed passing sizes (μ m), respectively. EFx in the product of the Rowland efficiency factors which depend on the mill, size, type of grinding circuit, etc. [27,29–32]. The theoretical power draw by the mill (kW) is determined by W x T, where T is the throughput tonnage (t/h) [27]. A typical particle size after the comminution process is usually below 75 µm [33–35].

Fundamentals of gold production have been reviewed by Marsden and House [33], Yannopoulos [36]. The appropriate route for gold processing of the native gold, because of its high density, is through gravity concentration. Therefore, studies by Carrasco [37], and Valdivieso et al. [38] were analyzed. For the extraction of gold from the tellurides entails processes of flotation and pyrometallurgical treatment (roasting). On this regard, literature by Elis and Deschênes [39], Zhang et al. [40], and flowsheets of telluride processing plants, such as Emperor mines in Fiji [33] were examined. The recovery of gold from native and tellurides was made with solvent extraction trough cyanide leaching with a conventional process of carbon in pulp (CIP). Then, electrowinning was considered for the recovery of gold from the leaching solution. Studies conducted by Sen [41], Muir et al. [42], Beyuo and Abaka-Wood [43], Brandon et al. [44] and Adams [45] were revised.

4. Set-up of the model

The computational model in HSC Chemistry-version 9.7.1 software [23] was developed based on the study of different flowsheets, especially for tellurides ores, and technical papers [33,38–40]. The

experience of the research group at the Helmholtz Institute Freiberg for Resource Technology and the Research Centre for Energy Resources and Consumption (CIRCE) was decisive on this task. Thanatia was considered for the chemical composition of the ore from which gold is extracted. As the starting point, it was taken its original concentration of 1.44-03 g/t Au as reported in [1]. Then, by reducing the number of other minerals, especially quartz, an average representative value of 2.72 g/t Au was considered for the simulation.

In a recent publication by the research group, Thanatia's composition was used to estimate the effort made by Mother Nature to have minerals concentrated in mines. In this paper, we use a similar layout and methodological approach. A simplified flow chart of the comminution, concentration, and refining processes for the set-up of the model is shown in Figure 2.



Figure 2. Simplified flowchart to produce gold in cathodes by changing the ore.

Due to the considerable number of assumptions to simulate the production of gold from Thanatia, only main ones are summarized in these papers.

For ore-handling, the consumption of fuel for transporting the open pit mine to the facility plant was assumed 0.6 L/ton of rock as suggested in [11], where the tonnage prevails over the distance. Due to the dispersed state of minerals in Thanatia, it was treated as a complex ore. Therefore, the input ore in the model was assumed 6000 tons per hour. The concentration process consists of comminution (crushing, grinding, and re-grinding), gravity concentration and flotation. The specific energy during comminution was calculated with Equation (1). The 80% passing size of the feed (F80), and the product (P80) for every crusher and mill were obtained directly from the HSC model. As previously explained in Section 3, the work index has a direct influence on the specific energy. Since Thanatia is a complex-ideal ore, and a single value for its hardness cannot be readily determined, in this work as well as in Paper Gold 1, it was considered a range of values for the work index (Wi) from 3 to 42 kWh/t [46]. The fact that of not taking into account a single value for Wi constitutes a difference with Valeros'approach [1,47] to estimate the specific energy.

Because of the high density of gold, only gravity concentration is necessary for the native gold stream [27,37,38]. Manufacture's data about gravity concentrators were reviewed [48] about the consumption of energy. In case of the gold associated with the tellurides, a re-grinding is required to

liberate as much as gold as possible from tellurides. Then, flotation consists of circuits of roughers, scavengers and a cleaner which assure that gold is concentrated enough before roasting. The latter is a pyrometallurgical process in which gold contained by tellurides is liberated. In a publication about the estimation of some environmental impacts of gold production, Norgate and Haque [20] reported some figures for the specific consumption of energy. From this paper [20], it was assumed consumption of natural gas was 0.35 GJ/t Au for roasting, 1.4kWh/t ore during leaching and 3100 kWh/t Au for electrowinning. The specific energy per ton of gold was estimated through the flow rate in the model and the respective ore grade.

5. Results and analysis

Based on the assumption explained in the previous section, the model was appropriately set-up, and the simulation campaign was performed. As an example of the simulation, in Figure 3 is seen the crushing and grinding circuits in the comminution process with 2.72 g/t Au as ore grade.



Figure 3. Screen capture of the simulation for the comminution process in HSC software.

As an example, results of the simulation and further data processing to obtain the specific energy to produce gold from the composition of Thanatia with 2.72 g/t-Au for ore grade, a representative work index (Wi) of 15 kWh/t and assuming an 80% passing (P80) size at the end of comminution is shown in Table 1.

Table 1. Results for Wi=15 kWh/t and P80 final size of 75 µm for an ore grade of 2.72 g/t-Au.

Process	Specific Energy (GJ/t-Au)
Ore-handling	8.53E-03
Concentration	2.39E+04
Roasting	3.50E-01
Leaching	7.68E+03
Cyanidation	1.85E+03
Electrowinning	9.57E+03
TOTAL	4.20E+04

As seen in the previous table (Table 1), 57% of the total energy to produce gold from Thanatia corresponds to the concentration process (comminution, gravity conc., and flotation). To examine the energy consumption of these processes, the power draw and specific energy are shown in Table 2.

5 - 5	1 5 6 5	0
Stage	Power Demand (MW)	Specifc Energy (kWh/t-ore)
Comminution	102	17.0
Gravity concentration	4	0.7
Flotation	2	0.4
TOTAL	108	18.0

Table 2. Power draw and specific energy for comminution, gravity concentration and flotation for Wi=15 kWh/t and P80 final size of 75 μ m for an ore grade of 2.72 g/t-Au.

In the table above (Table 2) more than 90% of the energy is consumed by the comminution process (crushing and grinding). Therefore as a way to validate the result from the model in HSC and more calculation, the specific energy during this process is compared with values reported in the literature. Chapman and Roberts [49] and Ballantyne et al. [50] in their researches published some representative figures for the specific energy in the comminution process in general and processing of gold, respectively. By doing the appropriate conversion of 17.0 kWh/t into the same units as reported by Chapman and Roberts [49] (61 MJ/t) and Ballantyne et al. [50] (194 kWh/oz-Au), it is in the same range of magnitude with the figures reported by the authors. Therefore, we take the results of our model are logical and valid. These will be presented and analyzed in the next sections.

5.1. Specific energy

In Figure 4 is shown the specific energy for the production of gold from Thanatia as a complex ore. In the figure, the arrow indicates the direction in which time increases. The next processes were considered: ore-handling, concentration (comminution and gravity conc.), roasting, leaching, cyanidation, and electrowinning. Figure 4 has been plotted by changing the ore grade (from 1.44-03 g/t Au to 2.72 g/t Au) and by a range of the work indexes and different final particle size (P80).



Figure 4. Specific energy for the production of gold with Thanatia's composition by changing the ore grade, work index (Wi) and final size in comminution (P80).

As it was expected, the higher values of the specific energy are higher when the work index (Wi) and the final size (P80) increase. An exponential growth exits, the specific energy consumption increases when the ore-grade of the deposit decreases. Also, when the particle size decreases, the specific energy for processing increases. That is why the band of specific energy is wider for P80 of 10 μ m rather than 75 μ m, and the former overlaps the latter.

The model in HSC allows the use of a complex composition of minerals in low concentration, as they exist in Thanatia and it was possible to incorporate changes in ore grade. That is why our model in HSC is a more robust way to determine what was previously done by mathematical procedure done by Rankin [21] and with SimaPro by Norgate and Haque [20].

5.2. Some environmental impacts

The life cycle assessment (LCA) is a methodology to evaluate the effects on the environment of a product by measuring the impacts of the corresponding fabrication process [51]. LCA's principles have been applied to assess the environmental effects of the production of gold for a general location by Norgate and Haque [20] and China by Chen et al. [52]. None of these studies have gone deeper in the variables that intervene directly on the production process, for instance, the effect of the final size in comminution. *I*n this work, through the direct export-import link between HSC and GaBi, we will evaluate the environmental impacts of the production of gold from ore with Thanatia composition.

The assessment of impacts is mainly associated with electricity during comminution because it accounts for the highest energy consumption during the production processes. The LCA tool in HSC software allows doing the life cycle inventory (LCI), which is a stage before the LCA, easily by the production process under study. The tool enables to export an Ecospold file that is ready to be imported in GaBi. We followed this procedure, and we assumed that the ore deposit with Thanatia composition would be placed in one representative country in five continents and we interlinked the electricity mix of every country with the process imported from HSC. As an example, Figure 5 shows the connection of the introduced production process from HSC with electricity mix to evaluate some environmental impacts with GaBi.



Figure 5. Screen capture of GaBi to assess some environmental impacts of the production process imported from HSC.

We used GaBi software, version 8.7.0.18 and database 8007 [24]. The environmental impact categories investigated were air pollution trough global warming potential (GWP), acidification potential (AP) and photochemical ozone creation potential (POCP) and for water pollution eutrophication potential (EP). Figure 6 shows the previous impact categories for an ore grade of 2.72 g/t Au, work index (Wi) of 15 kWh/t and assuming an 80% passing (P80) size at the end of comminution of 75 μ m.

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Figure 6. Main environmental impact categories in different locations for 2.72 g/t Au, work index 15 kWh/t and P80 at the end of comminution of 75 μ m.

The largest GWP occurs in South Africa followed by China. Then, one order of magnitude lower is the GWP for the United States and, the European Union and finally Brazil. These differences depend mainly on the composition of the electricity mix. According to statistics of the International Energy Agency (IEA) in 2016, 90% and 68% of the primary electricity production came from coal in South Africa and China, respectively. On the other hand, approximately 33% and 31% of the electricity was produced by burning natural gas and coal in the United States. For the European Union, 23% of the electricity was generated by coal firing power plants. Hydroelectricity meant approximately 76% of the total electricity produced in Brazil [53]. As we can see, comminution represents the most extensive energy consumer process in the production of gold from Thanatia. Thus the composition of the electricity mix will have a direct influence on the number of pollutants released to the environment.

6. Conclusions

The high consumption of metals in the last years has caused that rich metal deposits have been already exploited. At the edge, when no more attractive deposits would exit, metals would be produced from common rocks. In this work, we undertook the effect of the decline of ore grade on the production of gold. For this endeavor, we developed a computational model in HSC Chemistry, which is specialized software for mineral processing and chemical reactions for the production of metals. Then, with the model, a gradual decrease in the concentration of free-gold and other gold-bearing minerals, trends of the specific energy were studied. The ore grades varied from an average representative value of 2.72 g/t Au to the concentration that gold would have in common rocks. Thanatia, an ideal state of mineral dispersion was taken as the common rock from which will be produced. The concentration of gold in Thanatia is three orders of magnitude lower than the current values, 1.44-03 g/t Au.

The results of the model show that comminution is the highest energy consuming process. The specific energy was compared to the respective ones reported in the literature, and they are in the same range of values; hence the results of the model are rational and reliable. Our model confirmed the trend of exponential growth on the specific energy consumption because of the decline of the grade studied by mathematical equations and LCA analyses until now. The advantage of having a model in HSC will allow the assessment of ores with different mineral compositions and ore grades in gold mines. On contrast to LCA analyses, which consider the metal production process like a "black box."

On the contrary, the model in HSC, the effect of a variable on the overall production process and its impact on the environment can be better estimated. The model can be used to forecast the impact of

the ore grade decline in mines. Also, pathways to reduce energy consumption towards sustainable production of metals can also be studied with the interlinked connection between HSC and GaBi software.

While the consumption of metals is expected to increase in the coming years, tools like HSC along with other existing ones can be used in the search for more sustainable routes for metal production.

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