TESIS DE LA UNIVERSIDAD
DE ZARAGOZA

2014

55

Rosa Adriana Domínguez Vega

Exergy Cost Assessment in Global Mining

Departamento

Instituto Universitario de Investigación Mixto
CIRCE

Director/es

Valero Capilla, Antonio
Valero Delgado, Alicia

http://zaguan.unizar.es/collection/Tesis

ISSN 2254-7606

Prensas de la Universidad
Universidad Zaragoza

Universidad Zaragoza
1542

Tesis Doctoral

EXERGY COST ASSESSMENT IN GLOBAL MINING

Autor

Rosa Adriana Domínguez Vega

Director/es

Valero Capilla, Antonio
Valero Delgado, Alicia

UNIVERSIDAD DE ZARAGOZA

Instituto Universitario de Investigación Mixto CIRCE

2014

Repositorio de la Universidad de Zaragoza – Zaguan http://zaguan.unizar.es

Exergy Cost Assessment in Global Mining

By Rosa Adriana Domínguez Vega

PhD Dissertation

Directed by:

Dr. Antonio Valero Capilla
Dr. Alicia Valero Delgado

Zaragoza, 2014

Acknowledgements

I want to express my gratitude to CONACYT (Consejo Nacional de Ciencia y Tecnología) Mexico for the financial support during the development of this dissertation.

I want to thank Profr. Antonio Valero and Dra. Alicia Valero for the opportunity to work with them and for their guidance and valuable comments during these years, which made possible the development of this thesis. I would like to thank Prof. Wojciech Stanek from the Institute of Thermal Technology in the Silesian University of Technology, who was always willing to help me during my 3-month stay in his Institute.

I want to thank my colleagues and the administrative staff of CIRCE, of the Mechanical Engineering Department, and of the University of Zaragoza for the friendly work environment during these years.

Finally, I want to thank my parents for their unconditional support.

Abstract

Economic, social and technological development of current society is strongly linked to the extraction of mineral resources. A society which is constantly growing consumes these resources fast and almost unlimited. The continual increase of worldwide demand of mineral resources is especially enhanced by the economic growth of China and other Asian countries, which require large amounts of raw materials in the construction, infrastructure and manufacture sectors. The depletion of non-renewable natural resources is the consequence of this progress and is the greatest challenge that the mining industry has to face. Consequently, future availability of mineral resources is increasingly gaining importance in the strategic government planning.

It is well known that once the minerals have been extracted, several processes which consume large amounts of energy are needed in order to produce useful commodities. The energy consumption in mineral extraction and processing depends mainly on the minerals quality and composition. As a consequence of the depletion of mineral deposits, the energy requirements and environmental burden are constantly increasing due to a general reduction of global ore grades. Accordingly, more materials need to be processed to obtain an equivalent amount of metal. In this regard, a critical issue that mineral industry needs to overcome is the energy availability required for mineral extraction and processing.

Therefore, it is of imperative importance to analyze and understand the processes involved in the mining industry so as to determine potential improvements while accounting for the depletion factor of raw materials. The first activity can be carried out via a thermoeconomic approach. Thermoeconomics has been traditionally used for the optimization of thermal power plants using exergy as the unit of measure. In this PhD, the thermoeconomic analysis is adapted and modified to cover the complexities of mining and metallurgical processes, where raw materials in addition to energy flows come into play. That said, if the scarcity factor of mineral resources wants to be taken into account in the analysis, an additional variable needs to be included. This is done through the exergoecological approach proposed by Valero et al. (2003). Conceptually, the Exergoecological method allows for an evaluation of mineral resources by means of the Exergy Replacement Cost, which is the exergy required to return to the initial state of concentration and composition found in mines, the minerals that have been totally dispersed throughout the crust once their useful lives have come to an end. Accordingly, the aim of this PhD is to adapt and apply thermoeconomic methodologies so as to perform an absolute Life Cycle Assessment (LCA) of mineral resources: a conventional one from the cradle to the entry gate (production of the refined raw material) and an additional one from the grave to the cradle, thereby accounting for the depletion factor of minerals.

In order to perform an exergy analysis of mining and metallurgical processes, a set of objectives were defined. The first specific objective of this PhD thesis was to accomplish a detailed study of technologies and associated energy consumptions in the mining and metallurgical industry. A second objective was to analyze the influence of technological learning and declin-

ing ore grades on the availability of world non-fuel mineral resources, to become acquainted if technological breakthroughs that have occurred can preclude the rising energy demand in the mining industry. With the results obtained in the first and second activities, an important improvement in the exergoecological methodology was presented: exergy replacement costs which had been traditionally assessed in a static way, could be modified taking into account the long-term decline in ore grades. A further improvement carried out in this PhD was to solve the allocation problem among products, by-products and wastes commonly appearing in the mining and metallurgical industry. Accordingly, a new allocation procedure to be used in the Thermoecological analysis applied to mining and metallurgical processes has been proposed based on the newly obtained exergy replacement costs. The fifth objective of this PhD was to merge the Thermoeconomic analysis with the Thermoecological Cost methodology developed by the ITC group in the Silesian University of Technology, so as to combine the strength of both approaches for the analysis of the mineral's industry. Finally, each of the objectives described above were applied to different case studies.

Resumen

El desarrollo económico, social y tecnológico de la sociedad actual está fuertemente ligado a la extracción de recursos minerales. Una sociedad en constante crecimiento que consume estos recursos rápida e ilimitadamente. El continuo incremento de la demanda mundial de recursos minerales se debe en gran medida al crecimiento económico de China y otros países asiáticos, que demandan una gran cantidad de materias primas en los sectores de la construcción, la infraestrucuta y la manufactura. El agotamiento de los recursos naturales no renovables es la consecuencia de este progreso y constituye el mayor reto al que se enfrentará la industria minera. De ahí que la disponibilidad futura de los recursos minerales está adquiriendo importancia en los planes estratégicos de los gobiernos.

Una vez que los minerales han sido extraídos, una serie de procesos que consumen grandes cantiades de energía son necesarios para producir materias primas utilizables. El requerimiento energético de la extracción de minerales y en su posterior procesamiento depende principalmente de la calidad y composición del mineral. Considerando la disminución en la ley mineral a nivel global, los consumos energéticos y los impactos ambientales se han venido incrementando continuamente. Adicionalmente, es necesario procesar más material para obtener una cantidad equivalente de metal. En este sentido, uno de los factores críticos que la industria minera tendrá que afrontar será la disponibilidad de energía para la extracción y el procesamiento de los minerales.

Por lo anterior, es de suma importancia analizar y entender los procesos de la industria minera para determinar las posibles mejoras cuando se tiene en cuenta el factor de escasez de las materias primas. La primera actividad puede realizarse a través de un enfoque termoeconómico. La Termoeconomía ha sido utilizada tradicionalmente para la optimización de plantas termoeléctricas haciendo uso de la exergía como unidad de medida. En esta tesis doctoral, el análisis termoeconómico es adaptado y modificado, teniendo en cuenta la complejidad de los procesos mineros y metalúrgicos, en los cuales se presentan flujos de materias primas y energía. Cuando se considera el factor de escasez de los recursos minerales en este tipo de análisis, es necesario incluir una variable adicional. Esto se lleva a cabo a través del enfoque Exergoecológico propuesto por Valero et al. (2003). Conceptualmente, el metódo Exergoecológico permite realizar una evaluación de los recursos minerales utilizando los costos exergéticos de reposición, los cuales representan la exergía requerida para restituir los minerales que han sido totalmente dispersados en la corteza terrestre una vez que su vida útil ha terminado, al estado inicial de composición y concentración en el que se encuentran en las minas. De ahí que esta tesis tiene como objetivo principal adaptar y aplicar metodologías termoeconómicas que permitan realizar un Análisis de Ciclo de Vida absoluto de los recursos minerales: un análisis convencional de la "cuna" a la puerta de entrada (producción de las materias primas refinadas) y un análisis adicional de la "tumba" a la "cuna", en el cual se cuantifique el factor de escasez de los minerales.

El análisis exergético de los recursos minerales y los procesos metalúrgicos de la industira de la minería realizados en esta tesis, requirió el establecimiento de una serie de objetivos. El primero de ellos fue realizar un estudio detallado de las tecnologías y los consumos energéticos asociados a la indutria minera y metalúrgica. Un segundo objetivo fue analizar la influencia del aprendizaje tecnológico y la disminución de la ley mineral en la disponibilidad de los recursos minerales, con el objetivo de conocer si la adquisición de experiencia a través del tiempo, ha sido capaz de evitar el aumento en la demanda de energía que presentan los procesos extractivos y de metalurgía. Los resultados obtenidos de las dos actividades anteriores, permitieron una importante mejora del metódo Exergoecológico: los costos exergéticos de reposición que tradicionalmente habían sido evaluados de manera estática, pudieron ser actualizados considerando la tendencia del decremento de la ley mineral. Una mejora adicional presentada en esta tesis fue resolver el problema de asiganción de costos entre productos, subproductos y residuos que comunmente aparecen en la industria minera y metalúrgica. Considerando los nuevos costos exergéticos de reposición obtenidos, se propuso un nuevo procedimiento de asiganción de costos que será utilizado en el análisis termoeconómico aplicado a los procesos mineros y metalúrgicos. Otro objetivo the esta tesis, consitió en la integración del análisis termoeconómico realizado a través del Costo Termoecológico desarrollado por el grupo del ITC de la Silesian University of Technology, para combinar las ventajas de ambos enfoques para el análisis de la industria minera. Finalmente, cada objetivo descrito anteriormente fue aplicado a diferentes casos de estudio.

Contents

Chapter 1

Overview of mineral resources and the mining industry

The aim of this starting chapter is to provide an overview of mineral resources and the mining industry. Since this PhD is focused on the assessment of global mining, an overview of world mineral supply and market price evolution is performed. Additionally issues like international reporting, criticality of raw materials, sustainable development in the mining industry and life cycle assessment of abiotic resource depletion are reviewed.

1.1 Minerals as resources

Resources are valued for their function in society, whether economic, cultural or physical. Society is highly dependent on minerals and metals. For instance, minerals are valued because they can generate wealth with which goods and services can be purchased. Additionally, they can be used to produce metals which are essential to maintain the standard of living of actual society e.g. transport, construction, infrastructure, health, leisure, defence, etc. According to Sohn (2006), the demand for minerals and metals is related with the society patterns and levels of consumption of goods and services produced in the economy and the evolving mix of raw materials used in each product or service. Equally, Giurco et al. (2010) believe that people's daily lives is linked directly or indirectly to the availability of mineral resources, mineral production and consumption demand which in turn determine the value that society implicitly or explicitly confer to these resources. Figure 1.1 shows the minerals and metals used everywhere by actual society.

Mining activities begin with exploration and evaluation of an area of interest. If the exploration and evaluation is successful, a mine can be developed, and commercial mining production can commence. Bradley (2007) claims that minerals are not simply collected, gathered or mined (e.g. extracted and separated) in the sense of obtaining ready-made supply. Minerals are created and produced, using highly complex, capital-intensive processes that transform matter into economic goods. In fact, the profitability will be affected by several economic, technical, social and geopolitical issues.

Hence, a mineral deposit is a concentration of a mineral of sufficient size and grade that might, under the most favorable of circumstances, be considered to have economic potential. Once the mineral deposit has been explored and is known to be of sufficient size, grade, and

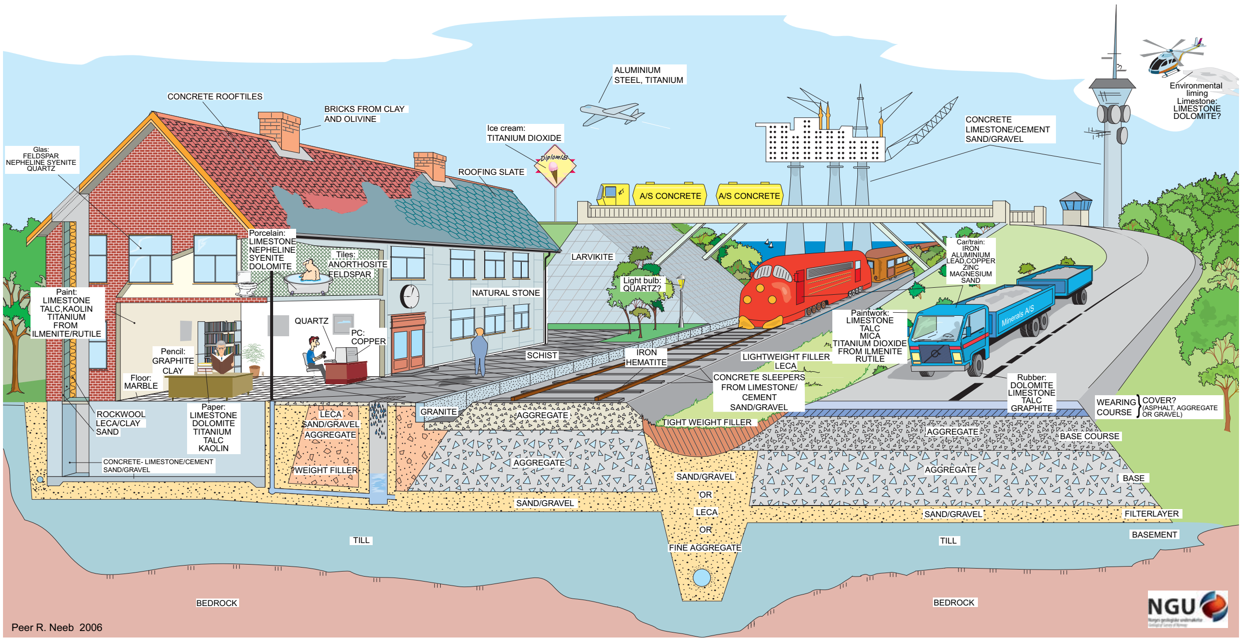


Figure 1.1: Everyday's uses of minerals and metals. NGU (2008).

accessibility to be producible to yield a profit, it becomes an ore deposit. According to Cox & Singer (1992) a mineral deposit model is the systematically arranged information describing the essential attributes (properties) of a class of mineral deposits.

The globalization of the mining industry makes imperative the developing of international standards for reporting mineral reserves, mineral resources and exploration results in order to underpin the mining industry and its capability to supply the worldwide increasing demand of mineral resources. The mining industry depends on financial investments, hence it is important to define a common terminology in order to enable investors to understand the risk involved in estimating mineral resources.

Weatherstone (2008) accomplished an overview of the international standards for reporting of mineral resources and reserves, claiming that CRIRSCO (Committee for Mineral Reserves International Reporting Standards) was established in 1994 to assess mineral resources taking into account; mining, metallurgical, economic, marketing, legal, environmental, social and governmental issues. According to the CRIRSCO, the Joint Ore Reserves Committee (JORC) defines *mineral resource* as a concentration or occurrence of material of intrinsic economic interest in such form, quality and quantity that there are reasonable prospects for eventual economic extraction. Mineral resources are subdivided, in order of increasing geological confidence, into *inferred*, *indicated* and *measured* categories. An *ore reserve* is the economically minable part of a measured or indicated mineral resource. Ore reserves are subdivided in order to increasing confidence into *probable ore reserves* and *proved ore reserves*.

The *U. S. Geological Survey* (USGS) use meanwhile the categories *reserve* and *reserve base*, which are similar to JORC's ore reserves and mineral resources definitions, respectively. The mineral resource classification is shown in Fig. 1.2. Reserves are part of the reserve base which could be economically extracted or produced at the time of determination. *Marginal Reserves* is that part of the reserve base which, at the time of determination, which presents economic uncertainty. *Subeconomic Resources* is the part of identified resources that does not meet the economic criteria of reserves and marginal reserves. *Undiscovered Resources* can be classified as hypothetical or speculative resources.

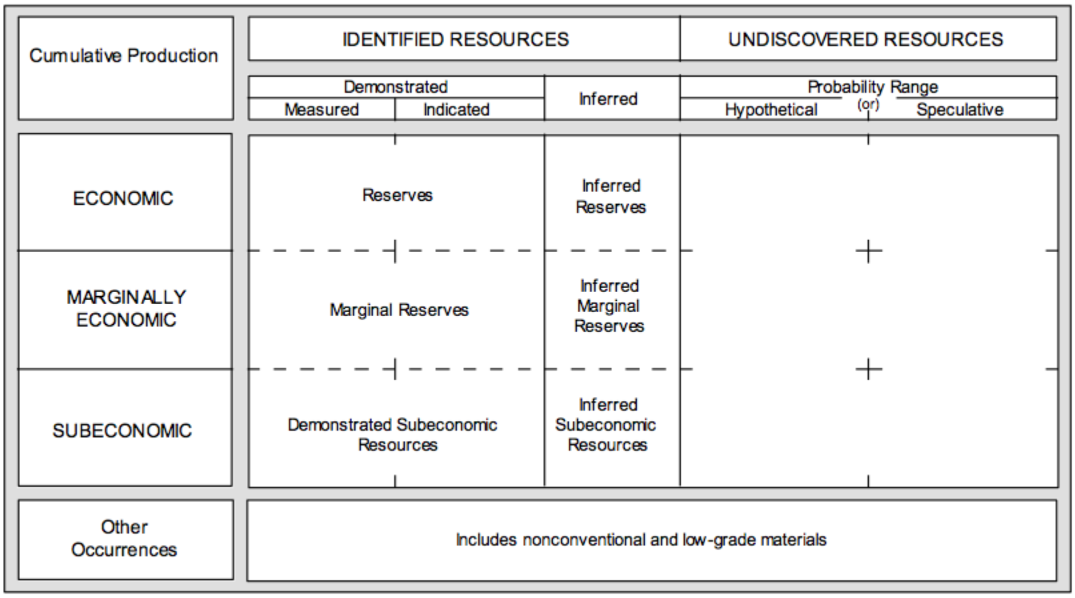


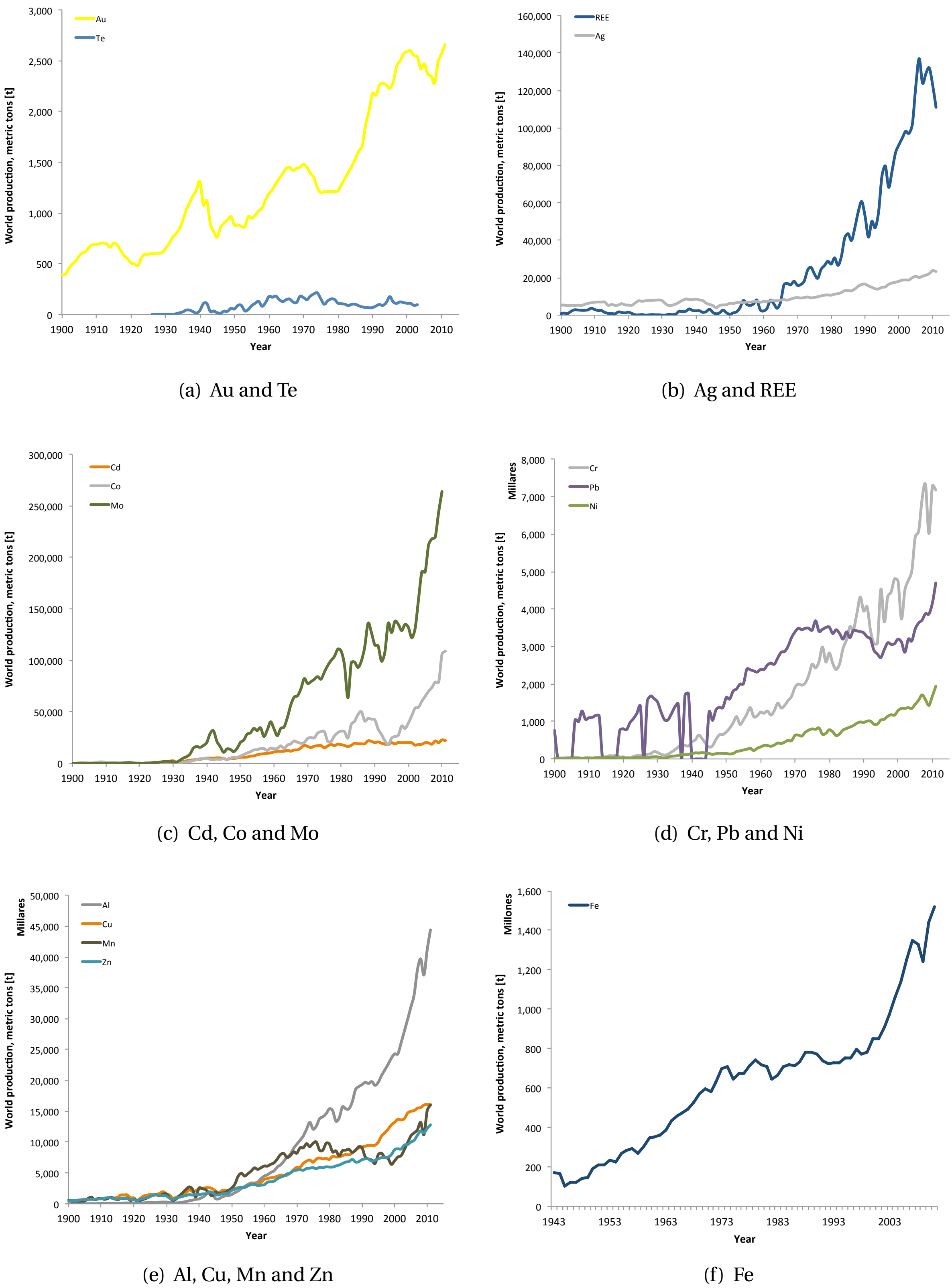
Figure 1.2: Mineral Resource Classification (USGS, 1980).

Additionally to land mineral deposits, the existence of deep-ocean minerals deposits has been known for more than a century. However, surveys devoted to understanding their genesis, distribution and resource potential began more recently, like those performed by Hein et al. (2013), Massari & Ruberti (2013). The minerals located in these marine deposits are crucial for an assortment of high-tech, green-tech and energy applications. For instance, the rare earth elements are used in plenty of new electronic and advanced components: such as fuel cells, mobile phones, displays, hi-capacity batteries, permanent magnets for wind power generation, green energy devices, etc. Although exploration contracts to develop deep-ocean mineral deposits have been signed in countries such as: China, France, Germany, India, Japan, Korea and Russia, technical challenges as well as environmental considerations need to be overcome.

1.2 Overview of world mineral supply

This section presents a general review of production and prices of metals. In this regard, the distribution of global supply and demand of mineral resources has changed significantly in recent years.

Humphreys (2013) believes that a new mercantilism is reshaping the world metal supply. The major countries consuming metals used to be also the major countries producing them, hence their interest to promote mine development to provide low cost raw materials. However, over the past fifty years the production of commodities of consuming countries has declined, and other countries like China have emerged over a very short time as the largest producer in the world, using their low cost capital and innovative metallurgical technologies. Now, producing countries are more interested on how to maximise the benefit of metal extraction to their economies rather than on how to supply cheap raw materials. Consequently, recent high metal prices have led to increase the number of countries which are looking to metals production in order to promote their development.



(a) Au and Te

(b) Ag and REE

(c) Cd, Co and Mo

(d) Cr, Pb and Ni

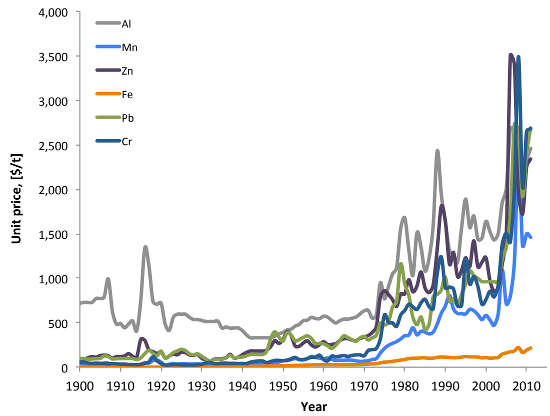
(e) Al, Cu, Mn and Zn

(f) Fe

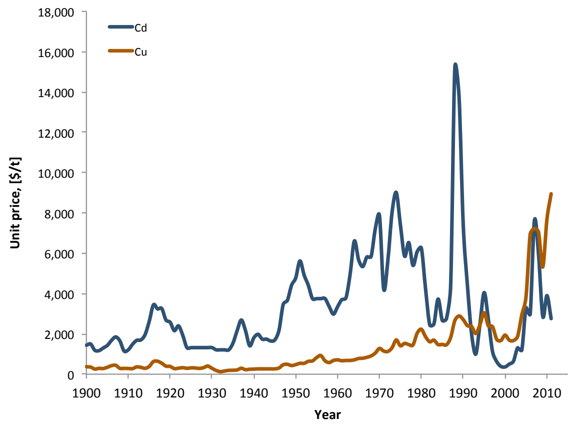
Figure 1.3: World production of metals. Data from *U. S. Geological Survey* (USGS).

According to Ghosh & Hem (1984), the commercial production of metals depends on factors such as: accessibility of ore deposits, richness of ore deposits, nature of extraction and refining process for the metal, physical and chemical properties of the metal as well as the demand for the metal. These factors depend on economics. A metal becomes a common one if it is readily available and easily produced with low processing cost and if it allows development of attractive properties.

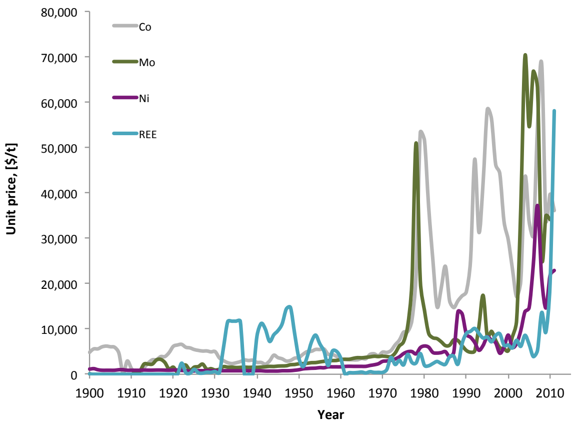
The world production of the metals analyzed in this thesis, is presented in Fig. 1.3. It can be seen that iron ores as steel is by far the most widely produced metal. This is due to the fact that iron ores are available in abundance in easily accessible deposits, the processing of iron ores is relatively simple and economical and because alloys of iron have a wide range of useful properties. The nonferrous metals which are produced in large quantities include metals such as aluminium, copper, manganese and zinc. In lesser amounts, metals such as lead, nickel, cadmium, cobalt and molybdenum, are produced. Finally, precious metals such as silver and gold, are produced in minor quantities as well as rare earth metals or less common metals such as tellurium. Nevertheless, the general trend of all metals is an abrupt increase (exponential-like) in their worldwide production.



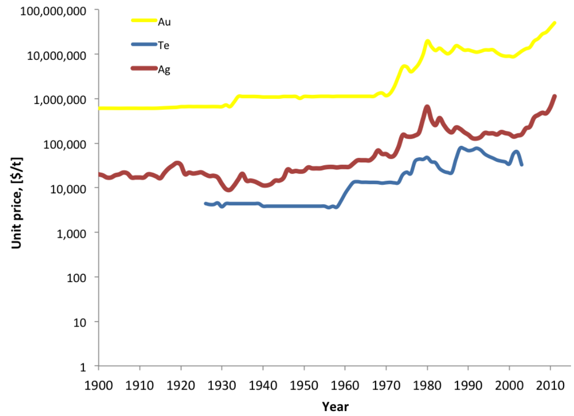
(a) Fe,Mn,Pb,Al,Zn and Cr



(b) Cd and Cu



(c) Ni,REE,Mo and Co



(d) Te,Ag and Au

Figure 1.4: Unit price of metals [$/t]. Data from *U. S. Geological Survey* (USGS).

The high demand of metals and their consequent depletion has an immediate effect on market prices. The unit price of internationally traded metals analyzed in this thesis, is presented in Fig. 1.4. It can be observed that iron ores as steel has the lowest price. The opposite case is that of gold, which is by far the most expensive of all metals analyzed in this thesis. In general Fig. 1.4 shows that metals price volatility increased in the 1980s, reaching record highs in recent times. This fact is driven by the strong demand from emerging economies, such as China and India. The magnitude of price fluctuations has increased drastically and in many cases caused commodity prices to multiply within only few years (e.g. lead or REE).

According to Kriechbaumer et al. (2014), metal prices are the result of complex market dynamics and stochastic economic processes. Labys et al. (1999) state that metal price depend on macroeconomic variables such as industrial production, consumer prices, interest rates, stock prices, and exchange rates. Humphreys (2013) based on Goldman Sachs report *The Revenge of the Old 'Political' Economy* [1] published in 2008, argues that mineral prices increase because companies are making investments in the most accessible deposits instead of those with highest quality. The latter leads higher cost and lower efficiency. In the opinion of Humphreys, the world faces not so much a resource problem but an investment problem.

1.2.1 Critical raw materials

One of the most important issues influencing the use of raw materials in the future is technological change. The high-tech metals (e.g. antimony, cobalt, lithium, tantalum, tungsten and molybdenum) are indispensable to new environmentally friendly products. For instance, electric cars require lithium and neodymium, car catalysis platinum, solar panels require indium, gallium, selenium and tellurium, energy efficient high-speed trains require cobalt and samarium, and new fuel-efficient aircraft needs rhenium alloys. Appendix A shows in Table A.4 the main uses as well as the main driving emerging technologies for the several materials including those considered critical raw materials.

A mineral is said to be critical depending on a number of factors such as such as geopolitical and depletion issues. Achzet & Helbig (2013) give and overview about differences and similarities of 15 criticality assessments for metallic raw materials performed by several working groups around the world from 2006 until 2011, concluding that there is a lack of consensus about which indicators give reliable information for raw material supply risk and how these indicators should be aggregated. The indicators identified by Achzet & Helbig (2013) for evaluation of supply risk include: country concentration, country risk, depletion time, by-product dependency, company concentration in mining corporations, demand growth, recycling/recycling potential, substitutability, import dependence, commodity prices, exploration degree, production costs in extraction, stock keeping, market balance, mine/refinery capacity, future market capacity, investment in mining, climate change vulnerability, temporary scarcity, risk of strategic use and abundance in earth's crust.

Other survey is the report performed by the ad-hoc Working Group (2010), which identify a list of critical raw materials for the European Union in regards to the economic importance and supply risk. The survey analyzes 41 metals, concluding that there are 14 critical raw materials for the EU: antimony, beryllium, cobalt, fluorspar, gallium, germanium, graphite, indium, magnesium, niobium, PGMs, REE, tantalum and tungsten, as depicted in Fig. 1.5. It is important to highlight that geological availability was not considered for determining criticality of raw mate-

[1] The Goldman Sachs Group, Inc. is a global investment banking, securities and investment management firm. http://www.goldmansachs.com

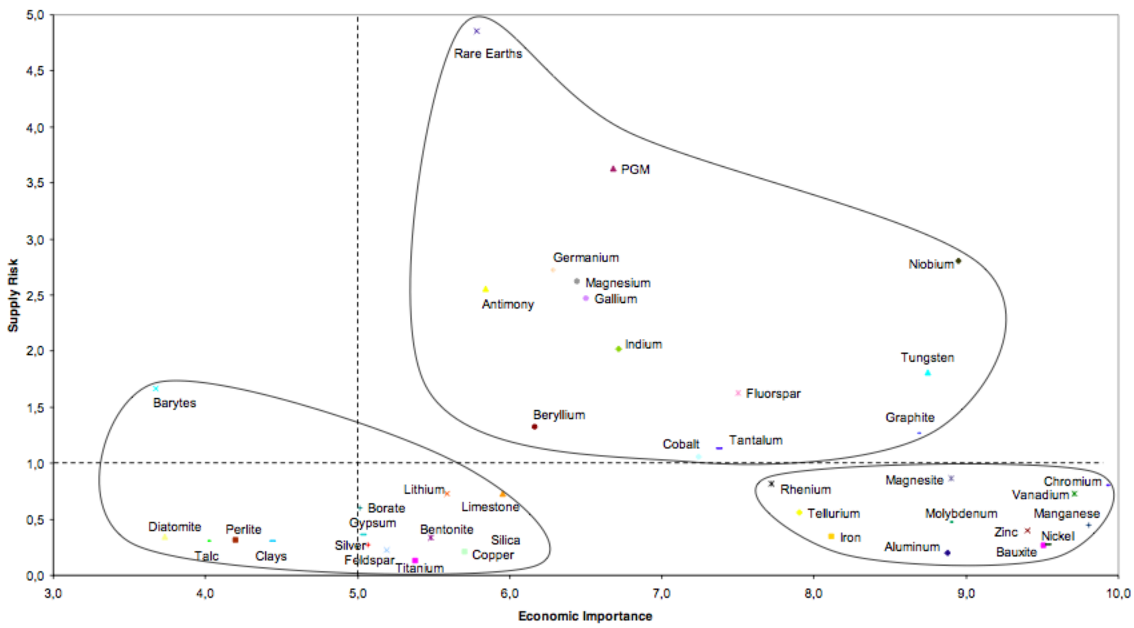


Figure 1.5: Critical raw materials for the European Union. The ad-hoc Working Group (2010).

rials because global reserves are not considered as a reliable indicator of long term availability. Instead, according to the aforementioned study, geopolitical and economic changes are issues that impact greatly on the supply and demand of raw materials.

It has to be highlighted that slight changes of the parameters of the supply risk metric of materials positioned in the sub-clusters of Fig. 1.5 may lead to a reclassification of these materials as "critical". The supply risk includes issues such as: political and economic stability of the producing countries, the level of concentration of production, the potential to substitute and the recycling rate. The supply risk is attributed mainly to the fact that countries like China, Russia, the Democratic Republic of Congo and Brazil control the worldwide production, as Fig. 1.6 shows. This production concentration, generally is heightened by low sustainability and low recycling rates.

According to Achzet & Helbig (2013) the aim of criticality assessment methods is to analyze driving factors, which makes a raw material critical from an economic, ecological, social or even ethical perspective. The criticality assessment methods constitute a starting point for a better understanding of raw material supply and demand. In regards to demand and supply of metals there is currently only intransparent and limited data available. It becomes therefore urgent to elaborate comprehensive databases of all raw material supply chain levels from the mining, to the manufacturing of products and the end of life phase with dissipation and recycling.

1.2.2 The role of recycling

Lee (1998) defines resource depletion as a resource which has been consumed and discarded and can no longer be utilized by human beings. Lee considers that some of the factors that affect resource depletion are:

- Reserves: The more reserve the resource has, the less tendency for depletion it will have.

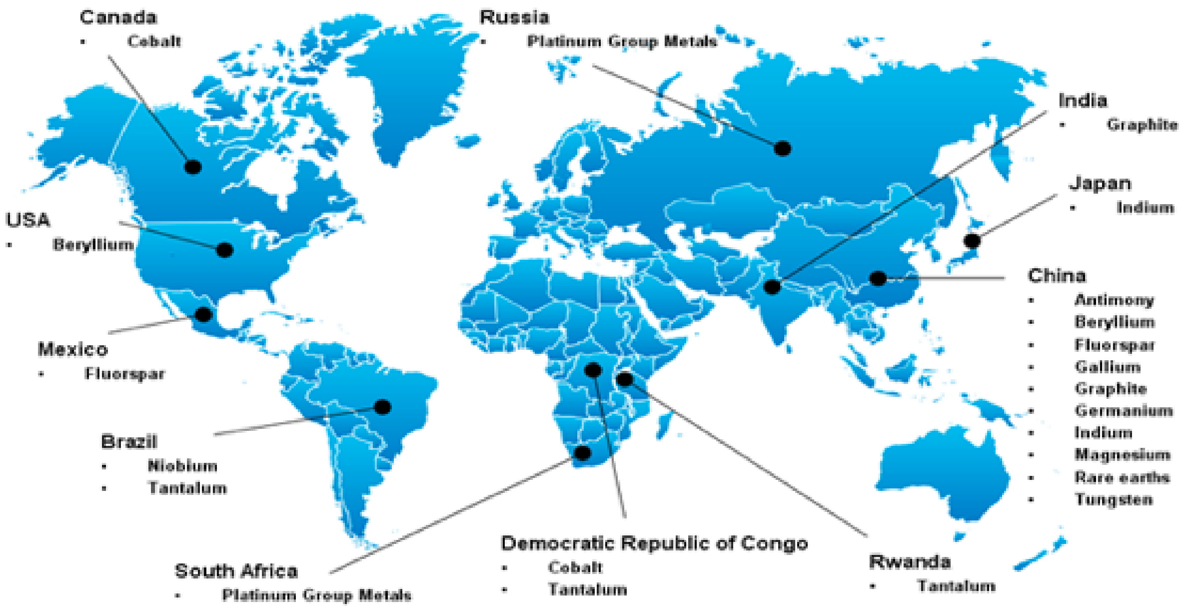


Figure 1.6: Production concentration of critical raw materials for the European Union. The ad-hoc Working Group (2010).

- Consumption rate: For those resources which have equal reserves, the greater the consumption rate, the more serious the depletion.
- Natural replenishment rate: If the consumption rates of renewable resources are smaller than their replenishment rates, then these resources should have no depletion problems. For non-renewable resources, the natural replenishment rate is so low that it can be neglected.
- Recycling rate: Resources can be recycled from discarded products and be re-manufactured into new products for human use. Hence, the recycling of a discarded resource can reduce its consumption rate, a high recycling rate can considerably diminish the resource depletion.
- Resource substitution: If a particular resource can be easily and economically substituted by other resources, its depletion may be reduced.
- Resource distribution: Most of the resources are not distributed equally over earth. Hence, local resource depletion problems depend on the local resource distribution characteristics.
- Resource reliability: The reliability of imported resources that some countries need to import from other countries to support their own development influence the local depletion.

Of the aforementioned factors, recycling plays a major role. In order to counteract the worldwide demand for primary mineral resources, it is imperative to recycle materials more widely and more effectively. Consequently, once the scarcity of "virgin" material becomes acute and should commodity prices rise, the recovery of secondary resources from technospheric stocks, popularly referred to as *urban mining* (Brunner & Rechberger 2004) may become a realistic option. Indeed, this possibility is gaining increasing attention and has been addressed as a suitable and necessary alternative by the UNEP International Resource Panel (Graedel et al. 2010) or the Swedish Environmental Protection Agency (SEPA 2012). Accordingly, in the future, metals will be supplied from a combination of primary metal produced from newly mined ores and recycled metals. Brobech (1996) and Bravard et al. (1972) claim that recycling must play an important role in the life cycle of metals production and should involve issues like education, research, proposals and targets. Furthermore, recycling operations requires technological, economic and environmental proficiency.

Most metals are recyclable, either easily (e.g. aluminium) or with deliberate programs (e.g. lead, platinum). According to Giurco et al. (2010), the overall stock of recyclable materials is rising, but the availability of various metals for recycling differs widely. In this regard, legislation and product management system like the end of life vehicle legislation often lead to improved recycling rates.

Efficient recycling of products as well as all kinds of production residues at various points in the life cycle of a product, reduces significantly the demand of raw materials. Furthermore, in several situations recycling leads to energy savings and reduction of climate change impacts. For instance, to obtain steel or aluminium from scrap, already requires less energy than from primary raw material. However, depending on how concentrated or dispersed the metal is and the transport required, recycling may not always have lower energy requirements.

The higher the import dependence on an individual metal, the more important recycling becomes, particularly if substitution possibilities are limited. The ad-hoc Working Group (2010) listed a set of actions to improve the efficient recycling of raw materials. The latter includes the design of products using materials that can be recycled, selecting materials that contain a high percentage of recycled content, reducing the number of different materials within an assembly, marking parts for simple material identification, using compatible materials within an assembly, selecting materials that do not need to be separated for recycling, making products easy to disassemble, identifying discarded products with critical raw material for proper collection instead of stockpiling them in households or discarding them into landfill or incineration, improving overall organisation, logistics and efficiency of recycling chains, preventing illegal exports of discarded products containing critical raw materials and increasing transparency in flow and promoting research on system optimisation and recycling of products and substances.

That said, according to Wellmer & Becker-Platen (2002), a recycling rate of 100% is impossible to achieve because depending on the application, a very pure metal could be required. Reaching the quality of primary raw materials, would entail higher energy requirements and environmental impacts. Heighten recycling together with material efficiency improvements will play important roles, but for the foreseeable future it is likely that new primary raw materials will continue to be required. Moreover, access to and extraction of primary raw materials will always be needed, due to market growth or new applications. Even if there is a total recycling the breach between the time of product manufacturing and product end of life phase needs to be overcome. Finally, recycling is determined by economic issues such as the ratio of the prices for recycled and primary raw material.

1.2.3 Environmental and social implications in the mining industry

As aforementioned, recycling still constitutes (with the exception of a few metals) a minor practice. Consequently, traditional mining will constitute in the short to medium term the main mineral supplier with not insignificant consequences to the environment. Indeed, mining is one of the activities with the greatest environmental impact from a cradle to grave perspective. It is a fact that the worldwide increase in production, use and disposal of minerals and metals has caused harmful environmental impacts, from global warming to local pollution affecting land, air and water. Ayres (2008) states that minerals extracted from the earth and utilized for economic purposes are not literally "consumed" because they become waste residuals that do not disappear and may cause environmental damage. Giurco et al. (2010) claim that these impacts will likely become unsustainable in the medium to long-term.

The climate change has brought green house gas emission constraints, which are an effort to internalise major global environmental costs. In the mining industry, fossil fuels are the main source of energy. Accordingly, mechanisms like carbon trading, is likely to cause increased cost for mining production. Other environmental cost at local level include mine site closure and storing of waste rock. In the US and Europe, stricter environmental regulations and greater difficulty obtaining mining permits has made open cut mining economically unattractive. Toxic emissions from mining are harmful to communities and the natural environment. Besides, mine wastes such as the tailings and waste rock remaining after completion of a project, is a challenge for the mining industry due to given declining ore grades and deeper mines.

Technology plays a key role in addressing the environmental impacts. For instance, implementing scrubber systems to capture sulfur dioxide emissions from smelters and converting this to sulphuric acid, implementing tall stacks from smelters to ensure adequate dispersion of atmospheric pollutants, methane gas extraction systems prior to coal mining and sulphidic mine waste and acid and metalliferous drainage. However, Giurco et al. (2010) assert that new technologies not always led to lower environmental costs. Hence, it is a challenge for future technologies.

A way to counteract environmental but also social problems associated with the mining industry is with sustainable development practices. Indeed, several studies like those performed by Cleveland & Ruth (1997), Shields (1998), Wellmer & Becker-Platen (2002), suggest that sustainable development is currently one of the most complex and challenging issues of the mining industry, because it involves the preservation, rational use and enhancement of natural resources.

As is well known, the World Commission on Environment and Development WCED (1987) performed the report "Our Common Future", where long-term environmental strategies for achieving sustainable development were proposed. In this report, the Commission highlighted that "Humanity has the ability to make development sustainable to ensure that it meets the needs of the present without compromising the ability of future generations to meet their own needs". The latter is a widespread definition of sustainable development. Although a more specific mining sustainable development definition could be: "sustainability means the design, construction, operation and closure of mines in a manner that respects and responds to the social, environmental and economic needs of the present generations and anticipates those of future generations in the communities and countries where it works" according with gold mining company Placer Dome (now Barrick Company). Nappi & Poulin (1998) assert that the major sustainability issue for metals is the influence on environmental and social conditions. Similarly, Yellishetty et al. (2011) claim that social, environmental and economic objectives of sustainability must be met over the long-term. Accordingly, the main drivers for sustainability management include: economic management from wise energy use, fulfillment of societal expectations, improvement of communication and transparency, maximize social benefits, adherence to international best practice, industry leadership and improvement business performance.

In this respect, Giurco & Cooper (2012) have proposed the *Mineral Resources Landscape* which is a practical tool to conceptualize minerals sustainability through five frameworks: ecological, technological, economic, social and governance domains, which interact and determine behavior of extraction and use of minerals within a system view.

The role that sustainability is playing in the mining industry has been studied in a number of surveys. For instance, Kumah (2006), Mudd (2007*b*,*c*) have studied gold, Yellishetty et al. (2011) have analyzed steel and copper. Other studies, conducted by Ayres (2008), Ayres & Ayres (2002), Nappi & Poulin (1998), Prior et al. (2012), Santos & Zaratan (1997), Shields (1998), Wellmer & Becker-Platen (2002) have analyzed the sustainability from a global perspective, coming to the conclusion that a set of indicators need to be defined to ensure economic, environmental and social limits to achieve sustainable development objectives. Worrall et al. (2009) proposed 72 sustainable development indicators for the mining sector, including environmental, socio-political and economic criteria.

Sustainability can be also considered in terms of endowing future generations with sufficient capital stock to ensure their well-being, achieved through a relationship between resource prices and economic welfare. There are several surveys performed by Svedberg & Tilton (2006), Tilton (2003) and Yaksic (2009) that address sustainability through an economic point of view. Martin & Skinner (1998) for instance, carried out a survey in the Czech Republic, and demonstrated that adjusting resources prices through a revenue neutral shift in taxes can move an economy closer to an efficient use of resources, and improve society's welfare[2].

Norgate & Haque (2010) prompt that extended producer responsibility and stewardship programs are an effective way to involve producers and/or distributors with commercial goods at the post-consumer stage, in order to optimise the efficient use of metal resources and stocks while at the same time minimising their environmental impacts. In the same way, in the opinion of Giurco et al. (2010) mining companies respond to social impacts by putting in practice, concepts such as:

- Corporate Social Responsibility (CSR) outline the responsibility of corporations to maximise the positive and minimise the negative social or environmental impacts associates with their mining operations.
- Social License to Operate (SLO) encourage companies to maintain their operations in a way that does not contradict the values and attitudes of the community members living in proximity to the mine's operations.

Environmental and social criticism, as well as changing public perceptions regarding the sustainability of mining practices is modifying the way mining companies operate and interact with the community.

[2]However, the sustainability of metal supplies can be overcome from a physical perspective. The physical approach involves the concept of limits of mineral ores. Even if mineral depletion from a geological point of view would not be reached, it is important that sustainability indexes includes geological information to assess mineral availability as is proposed in this PhD.

1.3 The fixed stock and opportunity cost paradigm

As was seen in the previous sections, the mining industry is currently undergoing challenges such as commodity price fluctuation, energy demand rise, increment in water and cyanide consumption, cost increase, declining ore grades or increasing pollution and waste materials released. Arguably, the greatest challenge to be faced is the depletion of non-renewable natural resources, as it is this issue what entails economic, environment and social disruptions and not the way around Skinner (1986), Szargut (2008), Szargut & Stanek (2012), Szargut et al. (2002), Valero, Valero & Domínguez (2011), Valero, Valero & Martínez (2010). In this respect, there is a debate about the long-run availability of mineral commodities since Meadows et al. (1972) asserted in their book *Limits to Growth* that unrestrained consumption and economic growth was prompting a surplus in the carrying capacity of the Earth. More recently, in their book *Limits to Growth: The 30-Year Update*, Meadows et al. (2004) reinforced their message about how economic and population growth interacts with finite resource supplies.

According to Tilton (2001, 2003), the debate about mineral depletion reflects two perspectives. On the one hand, there are the pessimists who fear mineral depletion as well as the environmental and social external costs associated with the production and use of mineral commodities. On the other hand, there are the optimists, who see no risk because they believe that as cost and prices go up new technologies will be developed, and more recycling and conservation measures that reduce production cost and consumption will come up. Accordingly, there is a discourse about the way to assess the long-run availability of mineral resources mainly because there are two models to assess mineral depletion. One based on a physical perspective, known as the fixed stock paradigm. An other one based on an economic perspective, known as the opportunity cost paradigm. Besides the unpredictability in regards to future developments in mineral supply and demand, as well as the shortage of widely accepted methods for assessing the total social costs of producing and using mineral products.

The fixed stock paradigm is based on the fact that the earth is finite and therefore mineral resources must also be finite. Gordon et al. (2007) found that discovery of new resources of copper ore has not kept pace with the amount of ore extracted to supply the increase in the copper demand. If this situation continues, it will imply eventual scarcity. Notwithstanding, Tilton (2003) highlights some shortcomings of this approach. For instance, the recyclable nature of minerals that makes possible to reuse them, substitution between alternative resources, the immensity of the fixed stock of many mineral commodities, and the eventually eliminating demand, due to the fact that before the last amount of a particular mineral is extracted from the earth's crust, cost would rise to the point where they are no longer affordable.

In this respect, Harmsen et al. (2013) asserts that mineral availability is related to accessibility, which in turn is tightly connected with energy consumption. All processes such as mining, land-recovering, transport, crushing and grinding, smelting, refining, etc. require significant amounts of energy. Furthermore, Eckelman (2010) claims that these energy requirements will continue to increase as average ore grades decrease and more rock needs to be processed for an equivalent amount of metal.

The opportunity cost paradigm assesses resource availability by what society has to give up in order to produce another unit of a mineral commodity. Tilton & Lagos (2007) are convinced that this approach gives a better interpretation of resource depletion and availability, through the price and the opportunity cost of using the resource. Svedberg & Tilton (2006) do not discard that economic depletion may occur (because mineral commodities become too expensive to use) but suggest that new technology will cut down the cost and prices of mineral commodities.

However, decreasing ore grades entails an increasing in the amount of ore mined and energy intensity, bringing on additional environmental and social cost that have been largely neglected in mineral costs. Nonetheless, Gordon et al. (2007) believe that economic analysis applied to the assessment of metal sustainability is most useful to determine materials substitution and recycling rates, rather than scarcity.

According to Tilton (1996, 2003, 2010), mineral depletion will depend on the race between the cost-increasing effects of depletion and the cost-reducing effects of new technology and innovations. Gordon et al. (2007) assert meanwhile that assessing the long-run availability of minerals will depend on several factors such as: potential constraints on traditional mining resulting from the availability of energy sources, water limitations, climate change, legal restrictions, environmental protection, social disruption, international trade, recycling and reuse, substitution, growth in demand and technology change.

Otherwise, authors like West (2011) highlight that decreasing ore grades is much more a manifestation of improving extractive technologies than of depletion of high grade deposits. However, as estimates of resources vary greatly, there is no way to know whether mineral commodities will become more or less available in the future. In this respect, Yaksic (2009) claims that shortages of mineral commodities can arise for a variety of different reasons like wars, embargoes, cartels and other market manipulations, natural disasters, accidents, cyclical booms in global demand, inadequate investment in new mines and processing facilities and resource depletion. Other surveys, like the one developed by the ad-hoc Working Group (2010) suggest that geological availability is not considered as a problem for determining scarcity of natural resources, inasmuch as factors like changes in the geopolitical-economics framework are of major importance. These changes have an effect on the supply and demand of natural resources, which in turn depends on the growth of developing economies and new emerging technologies.

Although the debate will continue, the challenge is to develop methods that allow to obtain reliable information able to support or refute these paradigms, as well as suitable indicators to assess mineral availability. In this regard, the Exergoecology approach proposed by Valero & Valero (2010*a*) could shed some light on the debate. It should be noted that the Exergoecology approach and consequently this thesis is based on the physical fact that the world is finite in size, meaning that the intensive use of natural resources used to satisfy human activities, is gradually exhausting the planet and its stock, as depicted in studies carried out for different commodities like: copper (Valero et al. 2008), gold (Mudd 2007*b*), nickel (Mudd 2010, Norgate & Haque 2010) and iron (Costa et al. 2001, Michaelis et al. 1998).

One of the most used methods to evaluate mineral resource depletion and the performing of mining and metallurgical operations is through the well known “Life cycle Assessment” (LCA). The next section makes a critical review of this methodology so as to identify its strengths and weaknesses on this topic and to propose ways to improve it.

1.4 LCA for abiotic resource depletion assessment

An adequate management of resources requires appropriate evaluation techniques, allowing the quantifcation of the associated impacts. In this context, the Life Cycle Assessment (LCA) is gaining prominence for the evaluation of mining activities . The LCA methodology assesses the environmental impacts associated with a product, process or service throughout its life by inventorying material resources, energy inputs and environmental issues, through a cradle to grave approach. Two main international standards, ISO 14040 and ISO 14044 describe the required and recommended elements of LCAs. The ISO standards identify four phases for conducting a LCA: 1) Goal and Scope; 2) Life Cycle Inventory (LCI); 3) Life Cycle Impact Assessment (LCIA) and 4) Life Cycle Interpretation.

The product life cycle is commonly divided into the following stages (EPA 2003):

- cradle to entry gate (raw material extraction and refining)
- entry gate to exit gate (product manufacture)
- exit gate to grave (product use, recycling and disposal)

Life cycle assessment (LCA) is a promising tool in the pursuit of sustainable mining. The latter has two major issues, first the depletion of mineral resources and second the direct environmental effects of mining. As a consequence, the use of life cycle assessments to mining and processing minerals has increased in the last years. For instance, LCA has been applied to different countries in the mining sector such as in Mexico (Suppen et al. 2006), in Hungary (Durucan et al. 2006) or in China (Xiao et al. 2003). However, a great number of life cycle assessments of metal production process do not consider the mining and processing stages in any detail, largely due to lack of publicly available data, according to Norgate & Haque (2010). Hence, LCA generally consider both, mining and processing minerals as one stage in the metal life cycle.

An additional problem with classic LCA is the life cycle impact assessment. LCA assess the contribution of an input or output flows through different characterisation weighting factors which are the contribution per unit of input or output flows for different impact categories. Accordingly, the total contribution to the impact category is the sum of each one. The characterisation values for the mineral and energy resources categories and their impact, is usually evaluated through the Eco-indicator 99. This indicator is based on current concentrations of ore within the earth's crust. The variation in these concentrations during an established period of time, expresses the impacts on the mineral resources category in terms of surplus energy. This indicator takes into account the energy used for mining, the ore grade of presently mined ores and the ore grade of future mined ore grades. Strauss et al. (2006) state that this indicator values the concentrations of an ore much more than the scarcity.

However, there are other indicators used for assessing abiotic resource depletion. According to Steen (2006), the existing methods for characterisation and weighting of abiotic resources appear to be based on four types of problem definitions. First, considering that mining cost will be a limiting factor. Second, assuming that collecting metals or other substances from low-grade sources is mainly an issue of energy. Third, inferring that scarcity is a major threat. And fourth, deeming that environmental impacts from mining and processing of mineral resources are the main problem.

Besides, several authors such as Steen (2006), Stewart & Weidema (2005) and Yellishetty et al. (2009) assert that there are four types of indicators for abiotic resource depletion in LCA:

Type 1. Energy or mass This assessment method consist in the summation of energy and materials on energy and mass basis, focusing on current consumption but without consider the ore grade.

Type 2. Relation of use to deposits This methodology considers not only the current consumption but also the reserve deposits for becoming aware of abundance or scarcity.

Type 3. Future consequences of resource extractions This assessment method consist in the aggregation of energy impacts based on future scenarios.

Type 4. Exergy consumption or entropy production This methodology lies in the aggregation of exergy and/or entropy impacts.

In Type 1 methodology, the consumption rates for different abiotic resources are already aggregated during characterization into one summarizing indicator. The use of abiotic resources is therefore neglected. Type 1 methodology suggest that all abiotic resources are exchangeable and equally important with respect to their mass or energy content. In this respect, Brentrup et al. (2002) proposed to asses the consumption of abiotic resources into separate impact subcategories and integrating them into one summarizing indicator called the Resource Depletion Index. Steen (2006) believe that if different substances are added up to obtain a category indicator, the total value will depend on how many substances are included and how they were grouped.

The Type 2 methodology has an additional problem due to the fact that available reserve deposits are defined in the context of economic availability considering the technologies available to exploit them as well as their accessibility (geographically and politically), hence as technologies advance and permit to process ores of lower grades, the reserve base grows. Hence, the major deficiency in Type 1 and 2 methodologies has been their lacking ability to adequately reflect the loss in functionality related to their use, as well as their emphases on resource extraction as opposed to an emphasis on product use and disposal, as the human activity responsible for resource depletion.

All the factors mentioned above consider that reserves are not static. Type 3 and 4 point out future consequences. The Type 3 methodology based on the future consequences of resource extractions consider that extracting high concentration resources today will force future generations to extract lower concentration resources leading to an increased impact on environment and economy. Weidema (2000), assert that the main problem involved in valuing resources depletion is that the effect or damage occurs in the future. Therefore, the assessment depends on the assumptions on how this future looks like. In this sense, there is a distinction between three types of future affects caused by present resource use: 1) future increase in the energy requirement for extraction and preparation of those resources, which are presently available as stocks of high quality, 2) future decrease in human consumption opportunities, as a result of genetic resources (biodiversity) and 3) future decrease in human consumption opportunities, as a result of reaching an ultimate resource limit which is not energy but is land. This author believes that arable land will be the first resource to become limiting.

The proposal of Finnveden & Ostland (1997) meanwhile could be categorized into Type 4 methodologies. Finnveden & Ostland (1997) and McDonough & Braungart (2002) state that the inputs to the technical system studied in LCA should be traced back to extraction of raw materials from the earth. For instance, the electricity or metallic copper should not be an input, but instead the primary energy sources extracted from the environment used to produce the electricity or the copper ore found in nature are appropriate inputs to a system described in LCA. In this respect, Finnveden & Ostland (1997) suggest that the characterisation weighting factor for abiotic deposits can be represented by the chemical exergies of ores, calculated for system boundaries compatible with the LCA methodology. Hence, the exergy consumption may be used as a characterisation parameter. Finnveden & Ostland (1997), Cornelissen & Hirs (2002) and Dewulf & Van Langenhove (2002, 2005) have applied the exergy analysis into the Life Cycle Assessment methodology. The exergy instead of energy, is preferred due to its capability to account the quality of the energy and the chemical exergy of non-energetic raw materials. Finnveden & Ostland (1997) have used the exergy in the LCA as a measure of the depletion and use of energy and material resources. These authors believe that the useful energy (exergy) is the ultimate limiting resource because it has an associated energy cost that will be limiting to some extent when it becomes too high. The use of exergy methods in order to accomplish analysis in the mining industry that helps attaining sustainable development is widely supported in Dincer (2002), Rosen (2002), Rosen & Dincer (2001), Rosen et al. (2008) because it allows to evaluate efficiency, improve and reduce inefficiencies and identify environmental and economics impacts. The detractors of Type 4 methodologies point out that they involve some conceptual problems because entropy and exergy are considered as very abstract indicators for loss of functionality, which makes it questionable whether they can be generally accepted as representative for the very specific situations that apply to each type or resource. In this regard, Stewart & Weidema (2005) deem that the definition of an entropy baseline on which quantification could be based is debatable.

Accordingly, Stewart & Weidema (2005), claim that the information required to quantify the effects of resources depletion should include the functionality/quality, the ultimate quality limit and the backup technologies. There is not an agreement on the quantification of energy consumption by backup technologies for the depletion of abiotic resources. However, there is a general consensus about the energy requirement for backup technologies which are:

- The *lower limit* for the energy requirement (the least amount of effort).
- The *upper limit* for the energy requirement is the energy requirement of existing technology to convert the resources not directly reusable (extracted and processed) to a initial conditions of the resource mined from ores.

The Exergoecological approach used in this PhD provides an integrated view of the above methodologies, with a strong thermodynamic basis. The aim is to keep the strengths of the previous approaches and try to solve some unresolved issues so far encountered for the assessment of abiotic resource depletion. Accordingly, a thermodynamic approach to perform an absolute LCA of metal mining and production was been proposed by Valero & Valero (2012). To evaluate the depletion of non-fuel minerals, the aforementioned method quantifies the exergy costs required to replace the extracted minerals with current available technologies, from a completely degraded state. This is performed through the inclusion of the "Exergy Replacement Cost". In this way, an absolute LCA (see Fig. 1.7) can be performed by including a new stage in the analysis, namely:

- grave to cradle (concentration process by nature)

In this way, both, the lower and upper limit for the energy requirement mentioned by Stewart & Weidema (2005) are fulfilled in the proposed absolute LCA approach. The first limit is set through using exergy as the unit of measure (minimum thermodynamic value used to obtain the mineral) and the second one is the real energy of the process through the so called exergy replacement costs. The use of exergy assures reliability and objectivity to the results. In this respect, it shares the same advantages and disadvantages of Type 4 methodologies. However, the problem with the baseline is solved, as it uses a coherent degraded Earth as the starting point of the calculations. The details of the methodology will be explained in chapter 4.

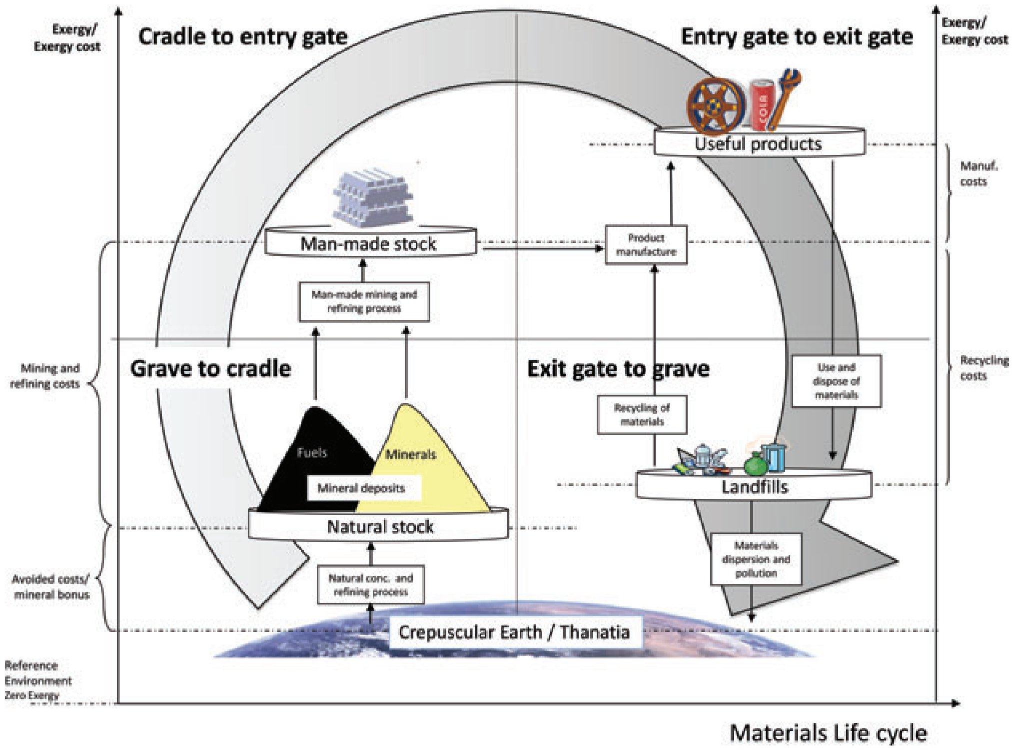


Figure 1.7: Life cycle assessment from grave to grave. Valero & Valero (2012).

1.5 Summary

Mineral resources are finite, therefore they will eventually be depleted by ongoing extraction. In this chapter, a general outlook of the mineral situation (world production and price of metals) in the actual society as well as the factors which influence the availability of minerals resources and the environmental consequences of mineral extraction were analyzed.

Undoubtedly, sustainable development is one of the most complex and challenging issues because it involves the preservation, rational use and enhancement of natural resources. At the same time social, environmental and economic objectives of sustainability must be fulfilled over the long-term.

Resource depletion depends on several factors such as: availability of energy sources, water limitations, climate change, legal restrictions, environmental protection, social disruption, international trade, recycling and reuse, substitution, growth in demand and technology change. In this respect, the life cycle assessment is a promising tool in the assessment of mining and processing minerals. The chapter ended with a critical analysis of current LCA approaches for the evaluation of abiotic resource depletion. A new methodology for addressing a good number for open issues in conventional LCA was proposed, based on the exergoecological approach. Such methodology involves the inclusion of a new stage in the LCA methodology, namely the grave to cradle stage, thereby accounting for the depletion degree of minerals. Consequently, an absolute LCA can be performed: from the cradle to the grave and back again to the cradle.

In the next chapter, the first stage of LCA: cradle to entry gate (raw material extraction and refining) is analyzed, as the first step for an absolute life cycle assessment.

Chapter 2

Metal Resources and Energy

Mining industry provides essential raw materials like coal, metals, minerals, sand, and gravel to the manufacturing and construction industries. There is a wide variety of metallurgical processes in mining industry, which depends on the metal extracted, the ore grade, mining conditions, available technology, economic issues, etcetera. The aim of this chapter is to describe the main physical processes applied in mining and metallurgical industry, in order to describe the metal processing and energy consumption of each commodity analyzed and applied in different case studies in this thesis. The analysis of these processes constitutes the first stage of LCA: cradle to entry gate (raw material extraction and refining).

In this chapter, an introduction of the main physical processes applied in mineral processing and extractive metallurgy is presented. The information presented in this section was taken from several sources: Ghosh & Hem (1984), Gupta & Mukherjee (1990), Rosenqvist (1983), Wils (2006). Afterwards, the metal processing and energy requirements of selected metals analyzed in this thesis are given. Energy requirements data for metal processing varies greatly, and increase substantially due to different factors such as: lower ore grades, deeper mines, complex ores and more mine wastes.

2.1 Mineral processing and extractive metallurgy

Production of metals from natural ores is mainly a separation process. The separation processes can be classified into two stages.*Concentration* which is the separation of the compound containing the desired metal from other constituents. This stage includes the mining and beneficiation processes.*Extraction and Refining* which is the separation of the desired metal from other constituents of the metallic compound and further purification of the metal.

There are two basic mining techniques: underground and open-pit mining. The method selected depends on a variety of factors, including the nature and location of the deposit, and the size, depth and grade of the deposit. The most common method is the open-pit mining, due to the lower energy consumption. Underground mining requires more energy than surface mining due to greater requirements for hauling, ventilation, water pumping, and other operations. The mining process can be divided into two general stages, each involving several operations. The first stage is extraction, which includes activities such as blasting and drilling in order to remove material from the mine. The second stage is materials handling, which involves the transportation of ore and waste away from the mine to the mill or disposal area. A brief description of the operations used in mining follows.

Drilling is the act or process of making a cylindrical hole with a tool for the purpose of exploration, blasting preparation, or tunneling.

Blasting uses explosives to aid in the extraction or removal of mined material by fracturing rock and ore by the energy released during the blast.

Digging is to excavate, make a passage into or through, or remove by taking away material from the earth. The goal of digging is to extract as much valuable material as possible and reduce the amount of unwanted materials. Digging equipment includes hydraulic shovels, cable shovels, continuous mining machines, longwall mining machines, and drag lines.

Ventilation is the process of bringing fresh air to the underground mine workings while removing stale and/or contaminated air from the mine and also for cooling work areas in deep underground mines.

Dewatering is the process of pumping water from the mine workings.

Mineral processing (or Beneficiation) follows mining and consists of several operations required to prepare and classify ores before the valuable constituents can be separated or concentrated for its further use or treatment. In order to separate the minerals from gangue (the waste minerals), it is necessary to crush and grind the rock to liberate valuable minerals. This process of size reduction is called *comminution*. Apart from regulating the size of the ore, it is a process of physically separating the grains of valuable minerals from the gangue minerals, to produce an enriched portion, or concentrate, containing most of the valuable minerals, and a discard, or tailing, containing predominantly the gangue material.

There are two fundamental operations in mineral processing: *liberation* (the release of the valuable minerals from their waste gangue minerals, by means of comminution) and *concentration* (separation of these values from gangue). According to Wils (2006), grinding is the greatest energy consumer, accounting for up to 50% of a concentrator's energy consumption. The main physical methods which are used to concentrate ores are:

- *Sorting* is the separation based on optical and other properties.
- *Gravity concentration* is the separation based on differences in density.
- *Froth flotation* is the separation utilising the different surface properties of the minerals.
- *Magnetic separation* is the separation dependent on magnetic properties.
- *High-tension separation* is the separation dependent on electrical conductivity properties.

Extractive metallurgy deals with extraction of metals from their ores. Mining and extraction processes consists of some individual sequential steps. For instance, electrolysis is applied to aluminium, zinc, copper and many other metals. Smelting is performed for extraction of iron or lead. The steps can be physical operations like comminution, filtration, casting, distillation, etc., or chemical operations such as leaching, smelting, etc.

The extractive metallurgy classified the methods of extraction and refining into: *pyrometallurgy* which is performed at high temperatures, *hydrometallurgy* which is carried out in aqueous media at or around environment temperature and *electrometallurgy* which employs electrolysis for separation at high or environment temperature.

2.1.1 Pyrometallurgy

Pyrometallurgical methods of metal production are usually cheaper and suited for large scale productions. There are several processes used in pyrometallurgy such as:

Calcination is the thermal treatment of an ore to provoke its decomposition as well as the elimination of volatile products (generally carbon dioxide and/or water).

Roasting usually involves heating of ores below the fusion point in excess of air. It produces a chemical conversion and makes the raw materials more suitable for subsequent reduction. Some roasting operations includes: oxidizing, volatilizing and chloridizing.

Oxidizing roasting: this operation is performed to burn sulphur from sulphides with conversion of sulphides in whole or in part into oxides. For example

$$PbS(s) + \frac{3}{2}O_2(g) = PbO(s) + SO_2(g) \tag{2.1}$$

Under certain conditions, oxidizing roasting may involve other reactions, leading to formation of sulphates or even the release of the metal itself in elemental form.

Volatilizing roasting: this is carried out to eliminate volatile oxides such as As_2O_3, Sb_2O_3 and ZnO.

Chloridizing roasting: this is done to convert certain metal compounds to chlorides from which the metal may be subsequently obtained by reduction. The reaction is of the type

$$2NaCl(s) + PbS(s) + 2O_2(g) = Na_2SO4(s) + PbCl_2(l) \tag{2.2}$$

Smelting is a process for the reduction of a metal oxide to metal, carbon is by far the most common reducing agent because of its easy availability and low cost.

2.1.2 Hydrometallurgy

Hydrometallurgical processes have the objective of isolate and win metals by the use of water or aqueous solutions. It involves a large sort of processes such as cyanidation for treating gold and silver ores, and the Bayer process for the production of alumina. There are several operations used in hydrometallurgy such as:

Leaching is a process used to recover metals from ores by dissolving the metal into a solution in contact with the crushed ore. There are different types of leaching, such as: high temperature acid or alkaline leaching, cyanide leaching of gold and bioleaching of sulfide minerals.

Precipitation of Impurities is a chemical process in which a dissolved substance separates from solution as a fine suspension of solid particles. Also called crystallisation when the solids formed are crystals.

Solvent Extraction (SX) is a process to separate dissolved metals (e.g. uranium, copper, nickel, cobalt, etc.) from impurities or between them. A solution of a metal leached from an ore is mixed with an organic solvent containing specific extractant chemicals. The aqueous and organic phases form an emulsion in which the extractant chemicals in the organic solvent bind to the metal ions and pull the metal into the organic phase. The mixture is left to settle so that the organic and aqueous phases separate. The organic phase containing the concentrated, purified metal is removed. The metal ions are then transferred from the solvent back into an aqueous solution from which they can be recovered in high purity.

Adsorption and Ion Exchange is the accumulation or concentration of a substance on a surface. In physical adsorption, molecules are attracted to a surface by intermolecular forces of attraction. In chemical adsorption, molecules, atoms or ions are attached to a surface by chemical bonds.

2.1.3 Electrometallurgy

Electrometallurgy is the application of electrolysis to the winning and refining of metals. Electrometallurgy is usually the last stage in metal production after corresponding pyro or hydrometallurgical operations. As stated by Rosenqvist (1983), electrowinning is important for the very reactive light metals aluminum and magnesium, which are almost always produced by electrolysis of fused salts. Furthermore, electrorefining is fundamental for the recovery of valuable impurities, such as silver and gold from copper.

Electrowinning recovers a metal (such as copper, zinc or nickel) from a solution containing the metal ions. An electrowinning production cell is an electrochemical cell with an applied electric current in which metal ions deposit the metal on the cathode.

Electrorefining is the electrolytic purification of the crude metal produced by pyrometallurgical operations. The basic metal is dissolved from a positive electrode and further, it is reduced on the cathode where the final product is highly pure metal.

2.2 Metal Processing and Energy Requirements

In this section, a brief description of the main uses, physical, chemical and geological characteristics, producing countries and the extractive and production processes as well as the energy requirements of 17 metals used throughout the development of this thesis are presented. Additional information about uses of these and other metal are presented in Appendix A. A summarize table of the energy consumption of each metal is presented, the E_{mining} represents the empirical energy data for mining and concentration processes, whilst the E_{refining} accounts the additional energy required to obtain the metal in an average refining grade through the smelting and refining processes.

2.2.1 Aluminum

Aluminium is an important commodity for modern manufacturing, used in construction and automobile production. It is a lightweight, high-strength, corrosion-resistant metal with high electrical and thermal conductivity, and it is easy to recycle. Primary aluminum is produced globally by mining bauxite ore, refining the ore to alumina, and finally, smelting alumina to produce aluminum. More than 95% of the bauxite today is gained from open mines. Secondary aluminum is produced by sorting, melting and treating recycled aluminum scrap (Classen et al. 2007). The major producers are Australia, Guinea, Jamaica and Brazil.

The total energy for the production of alumina from bauxite ore in the ground includes the following main processes: mining, crushing, griding, clarification, filtering and calcination.

A simplified overview of the processes is given in Fig. 2.1, followed by a brief description of the production processes. In chapter 6, section 6.3.2 additional information about aluminium production is presented.

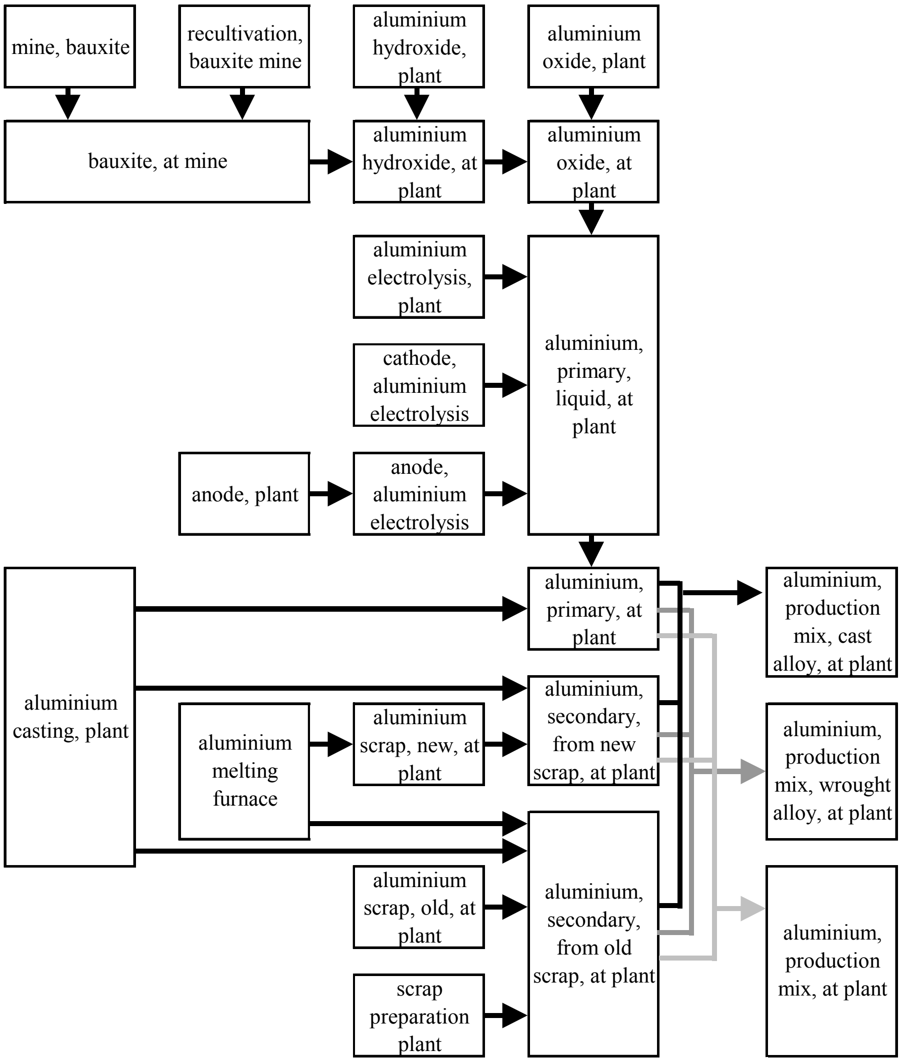


Figure 2.1: Simplified overview of the processes for the aluminium production. Classen et al. (2007).

According to Classen et al. (2007), the ore is won in stripes using hydraulic excavators and / or belt loaders. Drilling and blasting is only needed in some mines with exceptionally hard bauxite. The bauxite is transported to the mobile grinder and possibly to a dryer from where it is shipped to the aluminium oxide extraction plant. 98% of the world wide production of aluminium hydroxide and aluminium oxide is based on the Bayer-Process, whilst 98% of the industrial production of aluminium is done by electrolysis of aluminium oxide (Hall- Heroult process). This process requires a big amount of electricity.

As stated by Boustead & Hancock (1979), the concentrating energy requirement in USA summarizes 30.52 GJ/t, additionally it has a high energy use about 283.11 GJ/t for the refining process. The aluminum industry produces ingots of pure aluminum (greater than 99%). Whilst, Yoshiki & Toguri (1993) assert that if mining and ore preparation (crushing, washing or wet screening, and drying) are considered as the concentrating process, the energy consumption is 36.63 GJ/t while 127.38 GJ/t is the energy demanded in the refining process (smelting). Taking into account that for the production of 1 tonne of alumina, which produces about 0.53 tonnes of aluminum, is required approximately 2 tonnes of bauxite, the energy required in this concentrating process is 37.37 GJ/t whilst the refining process requires 53 GJ/t for the best operated anode cells to 61 GJ/t for some traditional cells, on the report of IPPC (2009*a*).

When aluminum is produced from bauxite, Classen et al. (2007) state that the energy required for both concentrating and refining processes is 78.7 GJ/t. If the production of alumina from bauxite ore is done through the Bayer process, Chapman & Roberts (1983) affirm that the energy requirement is about 50 GJ/t of aluminum correspond to the energy consumption for the concentrating process and 228 GJ/t are used in the concentrating process to produce aluminum by the electrolysis of alumina in the Hall cell (Hall-Heroult process is a very electricity-intensive).

Ayres et al. (2002) state that the energy consumption per tonne of aluminum in the refining process through 1997 was 53.43 GJ/t, in 2002 it was 48.922 GJ/t and during 2005 it was reported as 40.075 GJ/t. These data shows a decrease which is partly due to the closure of some older smelters, according to EAA (2006). Either the amount of 175 GJ/t for this process was reported. The most efficient smelters operate with an energy consumption of about 46.8 GJ/t. Margolis (1997) argues that the average energy consumption of aluminum reduction will continue to decrease as old and obsolete smelters are shut down, existing smelters are retrofitted and modernized, and new cells lines with moderns technology are built. This technology renewal is slow, especially due to the high investment costs of new capacity. Otherwise, is not expected substantial energy savings from the Hall-Heroult electrolytic process.

The most accurately data for the aluminum production process involves an energy requirement for the concentration process of gibbsite from the ground as 37.77 GJ/t, reported in IPPC (2009*a*), while the energy consumption in the refining process of gibbsite to obtain pure aluminum is 55.692 GJ/t. Table 2.1 summarize the energy consumption in mining and refining of aluminium, according to the aforementioned process used to obtain it.

Table 2.1: Energy consumption in the aluminium production. Values expressed in GJ/ton of Al.

	E_{mining}	E_{refining}	E_{total}
Boustead & Hancock (1979)	30.52	283.11	313.63
Chapman & Roberts (1983)	50	228	278
Yoshiki & Toguri (1993)	36.63	127.38	164.01
EAA (2006)		40.07–53.43	
Classen et al. (2007)			78.7
IPPC (2009*a*)	37.37	53	90.37

On the report of DOE (2007), it is asserted that the aluminum industry has large opportunities to further reduce its energy intensity, because is constantly evaluating, adopting, and improving furnace technologies and practices. This provides not only energy and environmental benefits, but also cost savings. According to Margolis (1997), the average energy consumption of aluminium reduction will continue to decrease as old and obsolete smelters are shut down, existing smelters are retrofitted and modernized, and new cells lines with moderns technology are built. This technology renewal is slow, especially due to the high investment costs of new capacity. Otherwise, is not expected substantial energy savings from the Hall-Heroult electrolytic process.

2.2.2 Cadmium

Cadmium applications has shifted away from the market areas of pigments, stabilisers and coatings to Ni-Cd batteries which have extensive applications in the railroad and aircraft industry, cellular telephones and portable computers (Classen et al. 2007). Cadmium is a very scarce element (0.1 – 0.2 ppm in the earth's crust) (Ayres & Ayres 1996). It is a by-product of zinc extraction. Nowadays, approximately 80% of world cadmium production was derived from mining, smelting, and refining of zinc, and the remaining 20% came from copper and lead smelting and the recycling of cadmium products USGS (2011*a*). According to Ayres & Ayres (1996), Japan was the biggest producer of refined metal, followed by Russia, Belgium and USA.

The most common production process for cadmium production is the electrolysis from processed cadmium sludge from hydrometallurgical zinc operations. This operation includes three stages; precipitation, oxidation and electrolysis. If cadmium is removed with copper by reduction with zinc dust during the hydrometallurgical zinc refining, the metallic sludge constitutes the most important source for cadmium refining process, Classen et al. (2007) report an energy consumption of 4.5 GJ/t .

Otherwise, assuming the concentrating process as a chemical leaching, the energy consumption will be 103.5 GJ/t, according to Kihlstedt (1975). While, Botero (2000) reports the refining energy requirement as 6.48 GJ/t. Table 2.2 summarize the energy consumption in mining and refining of cadmium, according to the aforementioned process used to obtain it.

Table 2.2: Energy consumption in the cadmium production. Values expressed in GJ/ton of Cd.

	E_{mining}	E_{refining}	E_{total}
Kihlstedt (1975)	103.5		
Botero (2000)		6.48	
Classen et al. (2007)		4.5	

2.2.3 Chromium

Chromium is one of the modern industry's essential element and important raw material for the production of stainless steel, and this is the major form in which chromium is recycled. It has a wide range of uses in metals, chemicals, and refractories. Chromium is obtained from chromite ore. Chromite enhances thermal shock and slag resistance, volume stability, strength and is used mainly in the ferrous and non-ferrous industry, cement industry and glass manufacturing. Ayres & Ayres (1996) assert that chromium (along with cobalt) is the archetypical 'strategic metal' because of its importance in corrosion and heat resistant alloys, especially in the so-called 'superalloys' used in aerospace technology. The major chromite ore and concentrates producing countries are South Africa, India and Kazakhstan, representing 70% of 2008 world production as a whole. South Africa and Zimbabwe hold about 90% of the world's chromite reserves and resources, according to Murthy et al. (2011).

Chromium metal is a metallurgical industry product. It is produced by one of two processes: electrolysis or aluminothermic reduction (Classen et al. 2007), as shown in Fig. 2.2. The metallurgical route involves smelting in an electric furnace to yield ferro-chromium. Chromium is considered to be made by alumiothermic process (75%) and electrolysis (25%).

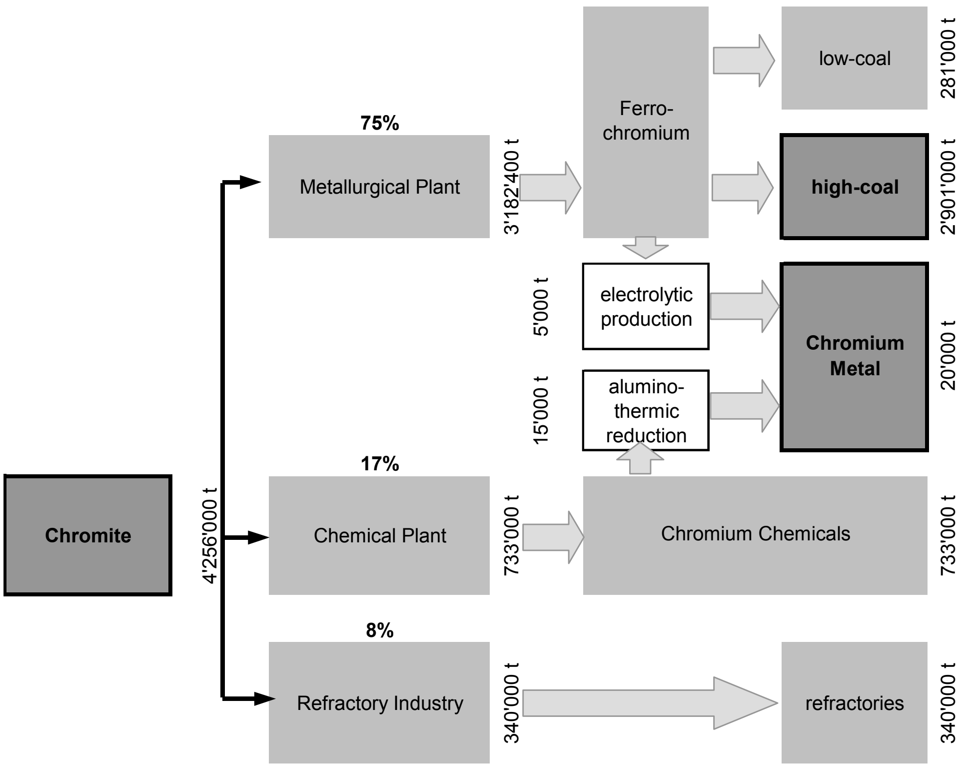


Figure 2.2: Scheme of the main processes in the chromium production. Classen et al. (2007).

According to Boustead & Hancock (1979), the energy requirement for producing chromium was 0.33 GJ/t. Chapman & Roberts (1983) report the energy requirement for mining and concentrating ore to produce chromium as 3.11 GJ/t, whilst the smelting and refining processes is 129.84 GJ/t . Classen et al. (2007) state that the energy needed for the production of metallic chromium is 0.29 GJ/t during the concentrating by aluminothermic process and 0.025 GJ/t for the refining step. The consumption of energy for the production of chrome is 0.5 GJ/t, on the report of IPPC (2009*a*). Table 2.3 summarize the energy consumption in mining and refining of chromium, according to the aforementioned process used to obtain it.

Table 2.3: Energy consumption in the chromium production. Values expressed in GJ/ton of Cr.

	E_{mining}	E_{refining}	E_{total}
Boustead & Hancock (1979)			0.33
Chapman & Roberts (1983)	3.11		
Classen et al. (2007)	0.29		0.025
IPPC (2009*a*)			0.5

2.2.4 Cobalt

Cobalt is a crucial element in many technological applications. The largest end-use of cobalt is for high-temperature resistant ‘superalloys’ in jet engines. Cobalt is mainly produced as a by-product and recovery of other abundant metals such as copper, platinum or nickel. Ayres & Ayres (1996) states the cobalt is undoubtedly a ‘strategic’ mineral, given the small number of producers and the importance of its uses. According to Harper et al. (2012), the three principal cobalt-using countries are China, Japan, and the United States, together account for approximately 65% of cobalt end use products. The ad-hoc Working Group (2010) state that Chinese competition regarding primary production and limited options for substitution, cause cobalt to be considered critical material for EU.

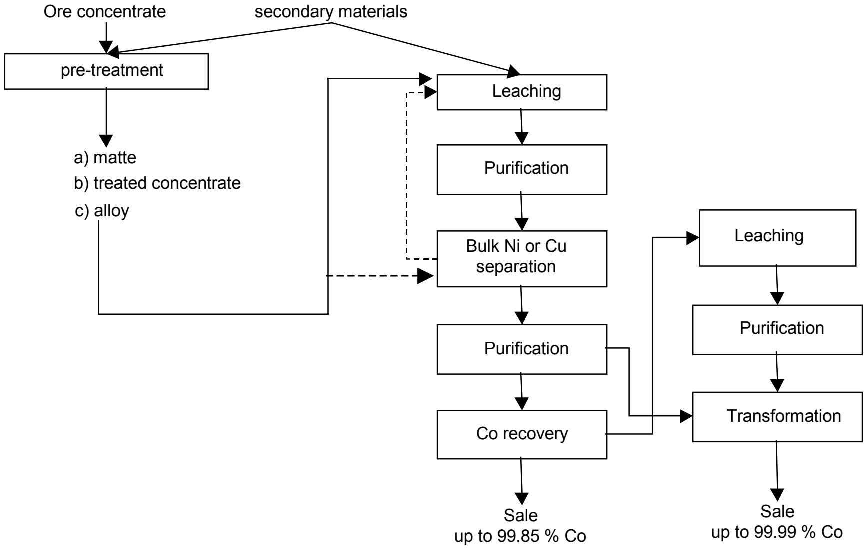


Figure 2.3: Generic flow sheet showing possible process steps for cobalt production. IPPC (2009*a*).

Cobalt can be produced during the recovery of nickel after separation by solvent extraction (SX). Cobalt can be electro-won, recovered by hydrogen reduction or precipitated for further refining using atmospheric and oxygen pressure leaching. Figure 2.3 shows a generic route of possible process steps for cobalt production.

Cobalt can be extracted from spend liquor of cooper mine, therefore the energy for mining and concentrating ore is disregarded. Chapman & Roberts (1983) report that the smelting and refining processes require 129 GJ/t. Botero (2000) indicates that the energy needed for mining and concentrating cobalt from sulphide ore is 193 GJ/t. Table 2.4 summarize the energy consumption in mining and refining of cobalt.

Table 2.4: Energy consumption in the cobalt production. Values expressed in GJ/ton of Co.

	E_{mining}	E_{refining}	E_{total}
Chapman & Roberts (1983)		129	
Botero (2000)	193		

2.2.5 Copper

Copper is used as pure metal and as alloying element with other metal and steels. Its utility is based on its physical and chemical properties, like electrical and thermal conductivity, ductility, workability and corrosion resistance. Then, the main use of copper is in wiring, plumbing and telecommunications. The by-products of copper are zinc, lead, molybdenum, cobalt, arsenic, selenium, tellurium and silver. Copper ores are low in grade and most copper in mined from large open pit mines requiring large amounts of materials processing. Ayres & Ayres (1996) assert that copper mining involves more materials displacement than any mining activity except coal mining and uranium mining. The main producing countries are United States, Australia, Canada, Chile and China (USGS 2011*a*).

There are many different process possibilities to obtain the metal, it will depend on the ore composition as well as the local costs of energy supply, nonetheless basically two different types can be distinguished: hydrometallurgical and the pyrometallurgical process with a share of 90.6 % and 9.4 % of the world-wide copper produced in 2004. Pyrometallurgical process includes mainly three stages: (1) ore mining and beneficiation, (2) smelting and reduction and (3) final refining, while the hydrometallurgical process skips the beneficiation step, instead a leaching step is done which is followed by electro-winning. Classen et al. (2007) report that the ore is mined mainly in open cut operations rising to 70 % in open pit, then 30 % is mined in underground. Figure 2.4 depicts the primary copper production route.

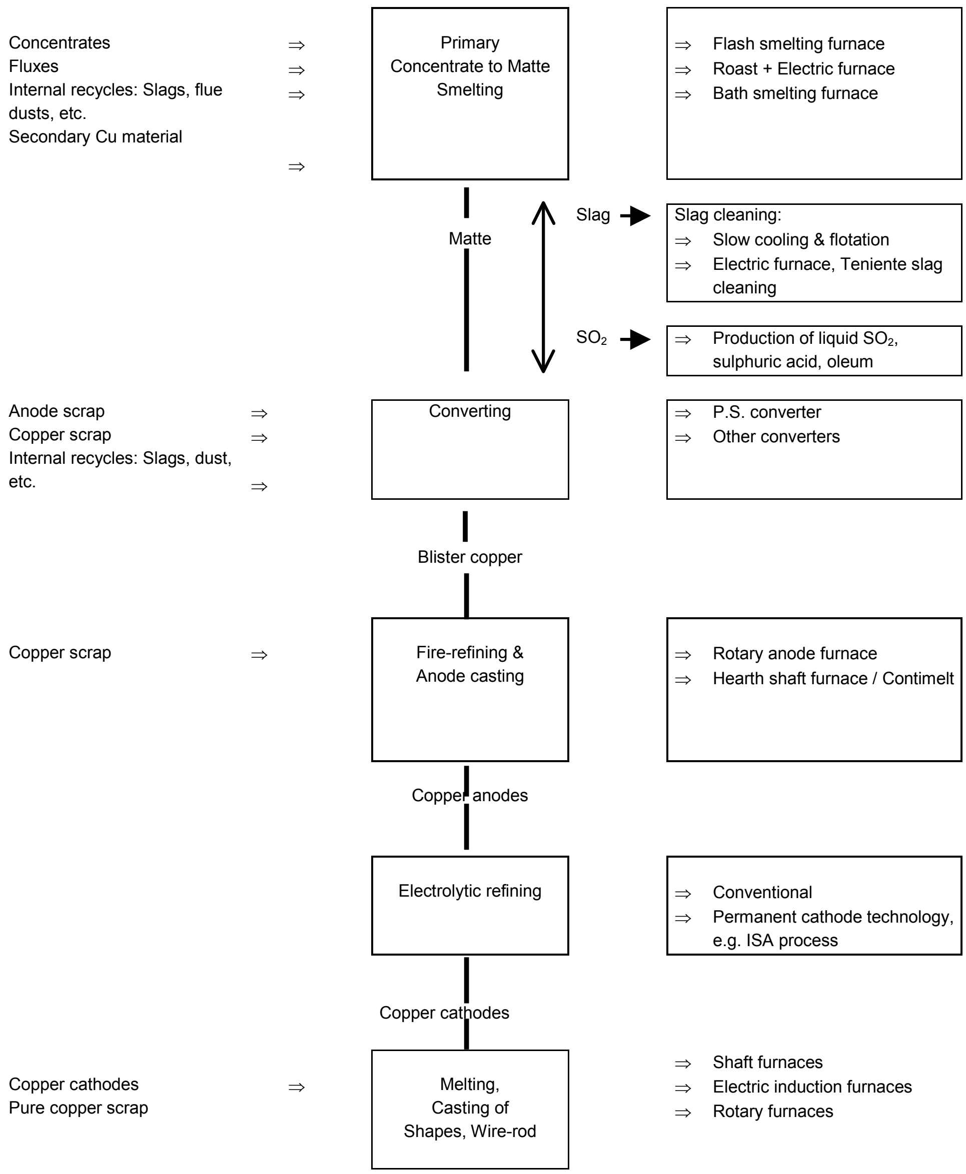


Figure 2.4: Primary copper production route. IPPC (2009*a*).

Copper is mining from currently mined ores averages around 0.8 percent in grade globally, thence the energy consumption in OECD countries for copper production from typical ore is 60 GJ/t. In an open pit and low-grade copper mine (0.5 %) in the form or chalcopyrite, Kihlstedt (1975) reports the energy needed for concentrating as 42.84 GJ/t. The low grade of copper ore (0.5 to 2 %) makes mining and ore preparation quite energy intensive compared to the other metals industries, thence Yoshiki & Toguri (1993) report the energy consumption during these processes is 62.7 GJ/t, while the refining process requires 95.47 GJ/t.

According to Boustead & Hancock (1979), the gross energy requirement to produce copper from ore by the hydrometallurgical route is 73.75 GJ/t whilst the primary smelting and refining processes need 54.25 GJ/t. Classen et al. (2007) argue that in pyrometallurgical processes the average consumption in the concentration stage is 7.59 GJ/t, while the smelting and refining process have a energy consumption of 12.5 GJ/t. The hydrometallurgical process based on the solvent extraction-electro-wining has energy requirement of 46.8 GJ/t and it is used mainly for oxide ores, also the sulphide ores can be recovered by this technique but they have to be roasted prior to leaching. During copper production the energy used in the electrolytic process is the most significant, 17 GJ/t on average are required for concentrating while 1.26 GJ/t is the energy consumed by the electrorefining stage using copper concentrate, as reported on IPPC (2009*a*).

Chapman & Roberts (1983) assert that considering the best practice in the copper mining, the total energy required to mine and concentrate copper is 66.7 GJ/t taking into account that the ore grade ranges about 0.6 %, but if is consider that it is 1 % the energy requirement decrease to 40 GJ/t, for the smelting and refining processes the energy requirement is 47 GJ/t. Ayres et al. (2002) outline that the energy required for copper production where energy-saving technologies has been introduced give the weighted average for mining and concentration as 32 GJ/t and only 15 GJ/t for smelting in the case of the lowest grade ores currently mined.

Applying a Life Cycle Assessment (LCA) methodology in order to calculate the gross energy requirement in the production process, and considering a generation efficiency of 50 % due to the utilization of thermoelectric and hydroelectric power plants, Norgate et al. (2007) calculate the energy requirement for the hydrometallurgical route as 128 GJ/t, whilst the pyrometallurgical route accounted an energy consumption of 66 GJ/t, including both process concentrating and refining.

Finally, considering that the recent energy efficiency improvements are in the smelter and not in the mining and concentration step, is considered that the actual energy consumption by pyrometallurgical process for the concentration stage is 32 GJ/t and for refining is 28 GJ/t. Alvarado et al. (1999) state that there is a consensus that further energy savings are both technically and economically feasible and can be achieved. Table 2.5 summarize the energy consumption in mining and refining of copper, according to the aforementioned process used to obtain it. The reasons for the large discrepancies between energy requirements are the improvements of current technologies and introduction of new processes.

2.2.6 Gold

Gold is used mainly for jewelry, electronics, bar hoarding and official coins. One of the peculiarities of gold is that it can be recycled easily from jewellery, then gold is a renewable resource with no degradation in quality. Gold is commonly found native in Nature.

According to USGS (2011*a*), the world gold production during 2010 was produced in the following countries: China (13.8%), Australia (10.2%), USA (9.2%), South Africa (7.6%), Rus-

Table 2.5: Energy consumption in the copper production. Values expressed in GJ/ton of Cu.

	E_{mining}	E_{refining}	E_{total}
Kihlstedt (1975)	42.84		
Boustead & Hancock (1979)	73.75	54.25	128
Chapman & Roberts (1983)	66.7	47	113.7
Yoshiki & Toguri (1993)	62.7	95.47	158.17
Ayres et al. (2002)	32	15	47
Classen et al. (2007)	7.59	12.5	20.09
IPPC (2009*a*)	17	1.26	18.26

sia (7.6%), Peru (6.8%), Indonesia (4.8%), Ghana (4%), Canada (3.6%), Uzbekistan (3.6%), Brazil (2.6%), Papua New Guinea (2.4%), Mexico (2.4%), Chile (1.6%) and other countries (19.7%). The major reserves are located in Australia (14.4%), South Africa (11.84%), Russia (9.86%) and Chile (6.71%). Reserves data are dynamic because they may be reduced as ores are mined and/or the extraction feasibility decreases, or more commonly, they may continue to increase as further deposits (known or recently discovered) are developed, or currently exploited deposits are more completely explored and/or new technology or economic variables enhance their economic feasibility. Hence, reserves data are a major issue because they betray where the largest resources are, allowing us to be aware of the countries that must improve its mining methods in order to extract in the best possible way.

The world official bullion reserves in 2009 were estimated by the USGS (2011*b*) at 30,700 t, while the estimated production in 2009 was 2,450 t. Kelly & Matos (2011) claim that the rising trends in world production and consumer price are driven by the continuous growing demand of commodities needed to satisfy the consumption levels of the actual society. In this regard, Yellishetty et al. (2011) state that world production of gold has been increasing almost continuously since 1950 because of economic conditions that have lead unit values fluctuations, mining growth/decline cycles and market volatility.

A survey performed by Valero & Valero (2010*b*) depicts that gold is one of the most depleted commodities with a depletion degree of 75% with respect to 1900 reserve base values. According to Shafiee & Topal (2010), the depletion time or proportion of mine production to reserves shows that, on average, world gold reserves will diminish in less than 40 years.

The production process of gold from auriferous ores begins with exploration and discovering a deposit. There are two kinds of mine configuration, open pit (the ore can be mined in four generic steps: drilling, blasting, loading and hauling) and underground (in which in addition to the operations mentioned before, a tunnel needs to be dug into the Earth). The kind of processing that follows the ore production process depends on the grade and type of ore, e.g. higher ore grades are taken to a mill where the ore is converted to a fine slurry of powder. However, lower ore grades are taken to leach pads, in which an oxidization process is applied before being sent to the leaching tank. Subsequently, three steps are followed: stripping, electro-winning and smelting. At this point the gold is in form of dorè bars with a 60% and 95% content of gold. The final step of gold mining is the refining process where the ore is converted into pure gold. Figure 2.5 shows the general route to produce gold and other precious metals, like silver and PGM's.

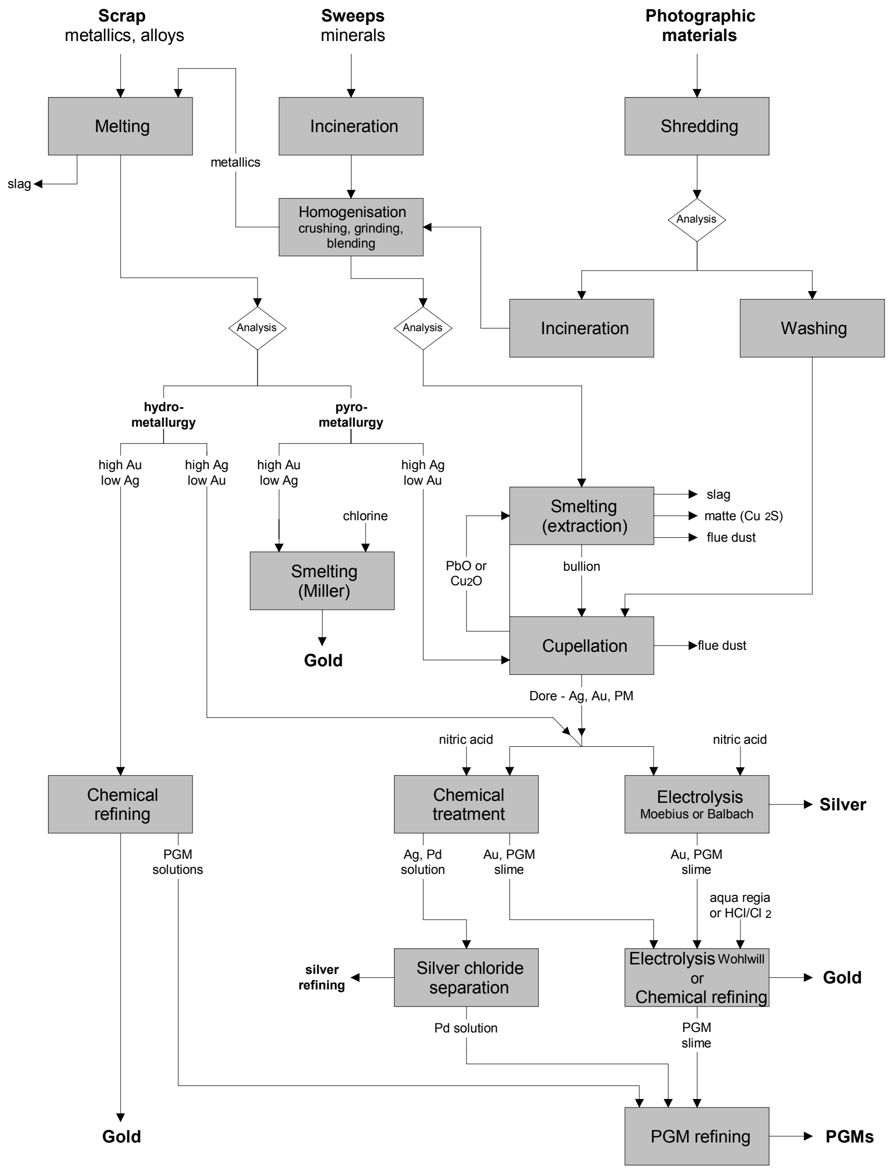


Figure 2.5: General flow-sheet for precious metal recovery. IPPC (2009*a*).

Gold records multiple peaks in production due to technological transitions that have occurred in the industry. Besides, there have been a number of gold booms due to several factors, first the discoveries of greatest new mines in the mid-1800s, second the foremost increase in the real price of gold during the 1980's and finally the development and widespread adoption of the carbon in pulp (CIP) process technology which allows to process low-grade ores in an economical way. Willett (2002) states that the advantage of mining gold is that there is practically no market entrance barrier for gold, due to the fact that any quantity of gold, even very small amounts from small-scale mining can be sold.

Gold production is one of the processes with the greatest energy requirements in the mining industry. Energy consumption is dependent on several factors such as the recovery process and the kinds of mining operations analyzed in this chapter. For instance, energy consumed in open pit (OP) mining usually is greater than the energy required in underground (UG) mining because ore grades in open pit mines are smaller than those presented in underground mines. For open pit mines the average energy requirement is 170,000 GJ/t whilst for underground mining is 127,000 GJ/t of gold produced. The energy required to separate the gold from the mine increases abruptly when the concentration of the ore in a deposit approaches zero.

The process extraction in open mining consist of three general steps: mining, processing and refining. First, the ore is mined through four processes drilling, blasting, loading and hauling, second the ore processing can be done through milling, oxidization and leaching, stripping, electro-winning and smelting, it will depend of the specific characteristics of the types of ore and the third step is the conversion into pure gold through a further processing.

Classen et al. (2007) perform a survey of global gold mining, then main results are described. The energy requirements will depend of the process used, e.g. data from 2000 to 2006 in Papua New Guinea indicates that the concentration energy requirement is 17,389.83 GJ/t for open pit mines using cyanide leach and carbon in pulp (CIP) or pressure oxidation processes, while for refining is required 8.05 GJ/t by electrolysis. In Chile, information from 2002 shows that the concentration process for an open pit mine consists of primary crushing, a pre-crushing circuit, grinding, leaching, filtering and washing, also it has a dry tailings disposal system because of site-specific environmental conditions, the refining is realized by electrolysis, finally the requirements are 192,642.14 GJ/t and 86.8 GJ/t for both concentration and refining processes, respectively. Reports from 2002 to 2005, indicates that Yanacocha a gold mine in Peru, considered one of the most important in the world has a energy consumption of 11,778.64 GJ/t for concentration and 6.6 GJ/t for refining processes. During 2002 Canadian data of three mines of which two are underground and produce only gold, report that the ore from the mine is recovered by gravity concentration, milling (primary and secondary crushing, rod/ball mill grinding), cyanidation techniques and carbon in pulp process followed by electrowinning and refining, the total amount of energy required is 81,264.71 GJ/t for the concentration process and 5.88 GJ/t for refining. Gold production in USA includes open pit and underground mines, through different processes in average the energy consumptions for concentration and refining processes are 35,213.11 GJ/t and 5.88 GJ/t, respectively. An underground mine in South Africa reported during 2006 the total requirements for both concentration and refining 42,293.71 GJ/t and 5.89 GJ/t, respectively, the methods used for mining are 50 % conventional (drilled, blasted and scraped or washed) and 50 % mechanized drift and fill trackless (drilled, blasted and loaded with scoop trams to internal ore passes), the unrefined gold bullion bars containing between 60 % and 95 % gold. Australia has open pit and underground mines, in 2005 they report an average consumption of 22,013.94 GJ/t for the concentration process and 5.87 GJ/t for refining. The open pit mines from Tanzania reported a energy consumption of 5.87 GJ/t for refining process during 2005. Mudd (2007*b*) assert that global trends in gold mining shows a total energy consumption of 143,000 GJ/t as average data between 1991 and 2006. In 1976 the U.S. Bureau of Mines reported that the amount of energy required to produce gold from all primary sources was about 62,247.95 GJ/t, as report on ITP (2002).

2.2.7 Iron

The most important use of iron ore is as the primary input to steel making. The end-using sectors of steel are automobile and construction. The latter is of great importance in developing countries, especially when they are industrialising. Iron is the 4^{th} most common element in the outer earth crust. The economically most important iron minerals are hematite and magnetite. Most of the iron ore today is gained from open mines. The thickness of the recoverable ore deposit usually is in the range of 100 meters. Iron ore is mined mainly in China, Brazil and in Australia. Nearly all iron ore is reduced to iron in blast furnaces, it is usually known as pig iron or "hot metal" if is liquid. In general, blast furnace burden contains lump ore, sinter and pellets, therefore the gross energy consumption include the energy used in the sinter, pellet and coke oven plant plus the energy required in blast furnace, oxygen furnace or electric arc furnaces. Figure 2.6 displays a rough overview of the cradle to gate process of the cast iron and steel production.

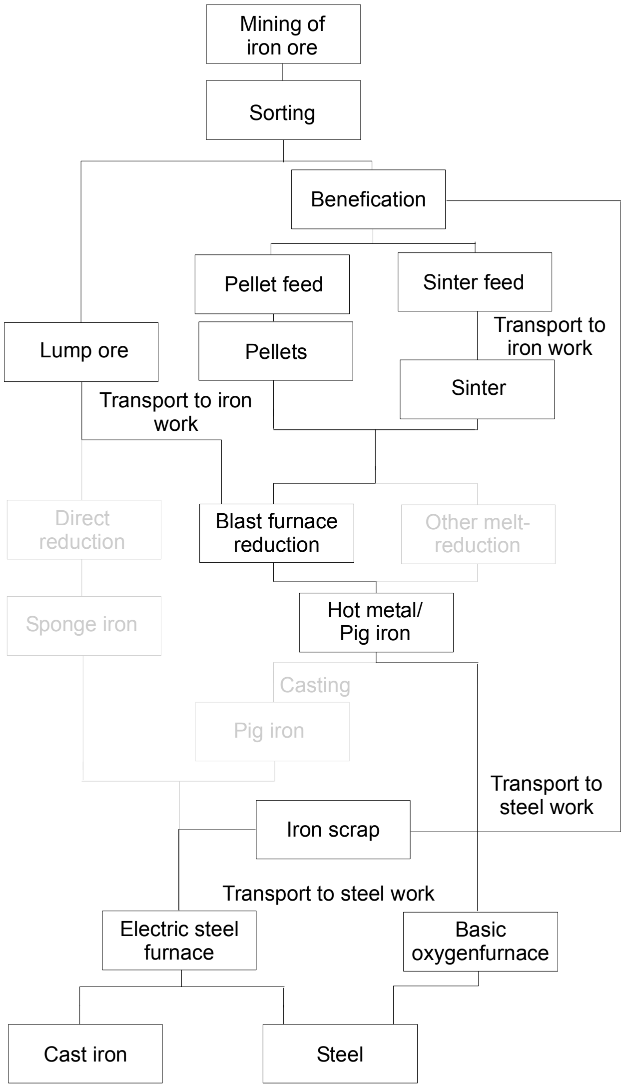


Figure 2.6: Overview of cast iron and steel production Classen et al. (2007).

The process of concentrating iron ore from ore in the ground requires 1.11 GJ/t and the refining process has an average consumption of 24.67 GJ/t based on the fuel energy to operate a blast furnace, according to Boustead & Hancock (1979). Whilst, Botero (2000) reports the total energy requirements for the concentrating process as 1 GJ/t and a high energy use around 28 GJ/t is required for the refining in the blast furnace, considering a concentration upper than 92 %.Classen et al. (2007) state that the energy utilized in the overall mining process is 28.8 GJ/t including electricity and fuels utilized in the sinter, coke and pellet plants as well as in the blast furnace. Sohn (2006) states that technological change in steel making has produced 20-25% increase in efficiency. The energy accounting for all the process is 20 GJ/t, as reported on IPPC (2009*b*). Table 2.6 summarize the energy consumption in mining and refining of iron.

Table 2.6: Energy consumption in the iron production. Values expressed in GJ/ton of Fe.

	E_{mining}	E_{refining}	E_{total}
Boustead & Hancock (1979)	1.11	24.67	25.78
Classen et al. (2007)			28.8
IPPC (2009*b*)			20

2.2.8 Lead

The main applications of lead are batteries and pigments. The main lead mineral is galena, although it occurs frequently with zinc, copper, arsenic, tin, antimony, silver, gold and bismuth. Mixed lead-zinc ore deposits are the most important. Argentiferous lead and lead-zinc ores, which frequently appear together, are found in almost all silver-producing countries. According to Classen et al. (2007), per tonne of lead mined, 2.3 kg of silver is jointly extracted and refined. United States, Australia, Canada, China and India are the nations with the biggest share of lead mine production.

Lead bullion may contain varying amounts of copper, silver, bismuth, antimony, arsenic and tin. There are two methods of refining crude lead: electrolytic refining and pyrometallurgical refining, as depicted in Fig. 2.7.

Kihlstedt (1975) reports that in the production of lead from a low-grade ore mined on underground mine, the energy consumptions for concentrating and refining processes were 4.95 GJ/t y 7.56 GJ/t respectively, the concentrating process involves mining, comminution, flotation, tailings disposal, filtration and drying. According to Boustead & Hancock (1979), the production of lead from ore in the ground requires during the concentrating process 11.34 GJ/t. The sinter production and blast furnace operation for the refining process consumes 17.31 GJ/t. Whilst Chapman & Roberts (1983) report the energy requirement for mining and concentrating ore to produce lead is 9.5 GJ/t, whilst the smelting and refining processes require 18.9 GJ/t .

There are two basic pyrometallurgical processes available for the production of lead from sulphide concentrates: sinter oxidation/blast furnace reduction route or direct smelting reduction process. Modelling the smelting process as a combination of both processes Classen et al. (2007) state that the energy consumption for this stage is 2.535 GJ/t, 44 % through the older inter oxidation/blast furnace processes and 56 % by the new direct smelting process (QSL, Kivcet). The energy requirement for the sintering/smelting process using a special design blast furnace named the Imperial Smelting Furnace (ISF) is 1.4 GJ/t, whilst there are several processes for direct smelting such as Smelt/Ausmelt furnaces (ISA), Kaldo (TBRC) and QSL integrated process have an average consumption of 1.35 GJ/t, according to data reported on IPPC (2009*a*). Table 2.1 summarize the energy consumption in mining and refining of lead, according to the aforementioned process used to obtain it.

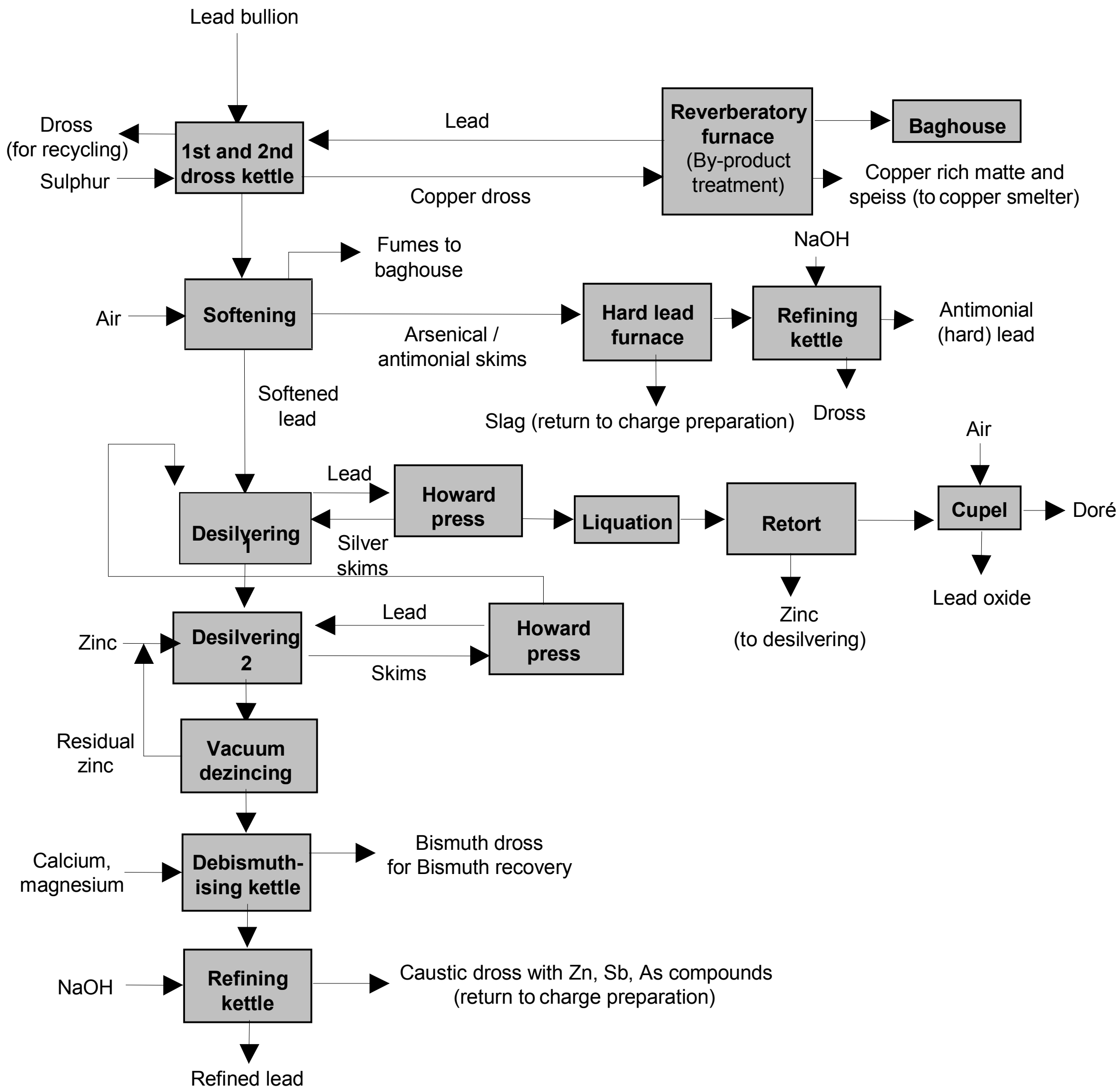


Figure 2.7: Diagram of lead refining processes IPPC (2009*a*).

Table 2.7: Energy consumption in the lead production. Values expressed in GJ/ton of Pb.

	E_{mining}	$E_{refining}$	E_{total}
Kihlstedt (1975)	4.95	7.56	12.51
Boustead & Hancock (1979)	11.34	17.31	28.65
Chapman & Roberts (1983)	9.5	18.9	28.4
Classen et al. (2007)		2.535	
IPPC (2009*a*)		1.4	

2.2.9 Manganese

Manganese metal is hard and very brittle, and its primary uses in a metallic form are as alloying, desulphurising, and deoxidising agent for steel, cast iron, and non-ferrous metals, steel is the main form in which manganese is recycled. Whilst, manganese compounds are used in chemical industry and battery manufacture. Nowadays, about 17% of the magnesium supply is produced by recycling of magnesium wastes. The main producing countries of manganese are: Australia, Brazil, China, Gabon and India.

Manganese ore are generally mined in open pits. After mining, the beneficiation step follows with operations such as crushing, gravity concentration, converting, calcining or reducing and sintering. Then, the production of pure manganese metal can be performed through two main options, electrolysis of aqueous manganese salts (this process involves milling, reduction, calcination, leaching, filtration, precipitation and electrolysis) or electrothermal decomposition of manganese ores (this multistage process includes several smelted stages). Figure 2.8 depicts a summary of manganese products and their process routes.

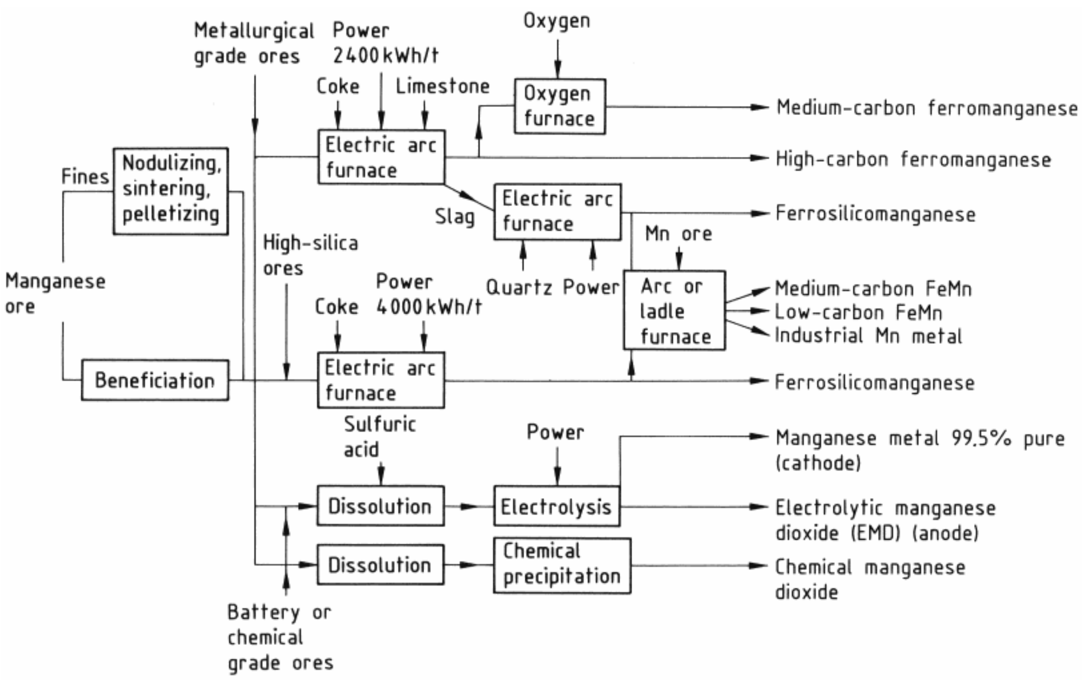


Figure 2.8: Manganese products and their process routes Classen et al. (2007).

Chapman & Roberts (1983) report that the energy requirement for mining and concentrating ore to produce manganese is 1.83 GJ/t, whilst the smelting and refining processes requires around 116.93 GJ/t using either electric arc or blast furnace. Whilst, Boustead & Hancock (1979) report the energy for electrowining of manganese from leach liquor as 148.67 GJ/t. According to Botero (2000), the energy consumptions for concentrating and refining processes are 15.5 GJ/t and 41.4 GJ/t, respectively . Whilst, Classen et al. (2007) report the energy requirement for the production of manganese during the concentration process as 16.5 GJ/t, whilst the refining process consumes 23.22 GJ/t. Table 2.8 summarize the energy consumption in mining and refining of manganese.

Table 2.8: Energy consumption in the manganese production. Values expressed in GJ/ton of Mn.

	E_{mining}	E_{refining}	E_{total}
Boustead & Hancock (1979)		148.67	
Chapman & Roberts (1983)	1.83	116.93	118.76
Classen et al. (2007)	16.5	23.22	39.72

2.2.10 Molybdenum

Molybdenum in its pure stage is a lustrous grey metal that can be used for a wide range of industrial applications. It is mainly used as an alloying element in steel, cast iron, and superalloys to increase hardenability, strength, toughness, and corrosion resistance. About the half of the world-wide produced molybdenum originates as co-product from the copper industry. Molybdenum is obtained commercially almost exclusively from molybdenite, which is either mined and concentrated as the primary product of the mine during the ore processing from a copper mine. Molybdenite concentrate is converted to technical-grade molybdenum trioxide by a roasting operation. The energy requirement for mining and concentrating ore to produce molybdenum is 136 GJ/t, whilst the smelting and refining processes require 12 GJ/t, in accordance to Chapman & Roberts (1983). The consumption of energy for the smelting and refining of molybdenum in an electron beam furnace reported on IPPC (2009*a*) is 18 GJ/t. Table 2.9 summarize the energy consumption in mining and refining of molybdenum.

Table 2.9: Energy consumption in the molybdenum production. Values expressed in GJ/ton of Mo.

	E_{mining}	E_{refining}	E_{total}
Chapman & Roberts (1983)	136	12	148
IPPC (2009*a*)		18	

2.2.11 Nickel

The importance of nickel comes from its capability, when alloyed with other elements, to increase strength, toughness and corrosion resistance of metal over a large temperature range. It thus plays a key role in technology (aerospace, marine, electronics, etc.) and construction applications. Nickel is crucial to the iron and steel industry, predominately stainless steel production and nickel alloying.

Global nickel production has increased from 10,000 tonnes in 1900 to 2.1 million tonnes in 2012. More than 60% of the world nickel production during 2011 (1,800,000 ton) was produced mainly in the following five countries: Russia (15.6%), Indonesia (12.8%), Philippines (12.8%), Canada (11.1%), and Australia (10%). The largest reserves (80,000,000 tonnes of nickel) are located in Australia (30%), New Caledonia (15%), Brazil (11%), Russia (7.5%) and Cuba (6.9%), according to data reported by the USGS (2011*b*). It is expected that its demand will rise along with the increasing consumption trends of China, India and other emerging countries. To satisfy this demand, it is likely that most of future nickel will have to come from laterites. Therefore, assessment of energy and greenhouse emission cost for different routes of Ni production is an imperative task that has received close attention in surveys performed by Eckelman (2010), Mudd (2010), Norgate & Haque (2010). In this thesis, the analysis is performed using exergy in Section 5.2.4.

Nickel is found and produced from two types of ores; oxidic (laterite and saprolite) and sulphidic ores. Due to their complex metallurgy, there is a wide range of extraction, concentration and refining processes required. Whilst the nickel content of sulphide ores can be concentrated using economical techniques, laterite processing has a tendency to be more cost-intensive (because of the extensive and complex treatment required to extract nickel), even though mining costs are lower than those for sulphide ores.

Approximately 60% of nickel is mined from sulphide deposits and 40% from oxide deposits, although paradoxically approximately 60% of nickel resources are found in laterites and the remaining 40% is contained in sulphides, according to USGS (2011*b*). The reason behind this relates to the complexity of processing nickel laterites compared to sulphides with the refining of the former implying a substantial amount of energy. Besides, the continuous decline in sulphide ore grades along with the increasing cost of underground mining, will mean that future supply of nickel will come from oxide ores, which are relatively uniform in grade and can be surface mined. Then, nickel derived from laterites will need to increase significantly in the future in order to satisfy the growing demand. During nickel production from sulphides, there are important by-products obtained such as: copper, cobalt, gold, iron and PGM (Platinum Group Metals). Cobalt, chromium and iron are the main by-products meanwhile, associated with nickel production from laterites.

In recent years, the idea of using new leaching technologies instead of pyrometallurgical routes has been raised. Nevertheless, Mäkinen & Taskinen (2008) state that almost 90% of the world's nickel production capacity is still based on pyrometallurgical processes.

According to Eckelman (2010), the smelting and refining steps consume most of the primary energy, whilst mining and concentrating account for only 7-35%, depending exactly on the nickel product as well as the source. Notwithstanding, the energy required for nickel ore mining, milling and beneficiation will continue to increase as average ore grades decrease and more materials need to be processed in order to acquire the same amount of metal.

Table 2.10 shows the energy consumption associated with the mining and refining processes of nickel production from laterites and sulphides according to different studies.

Table 2.10: Energy consumption in the nickel production. Values expressed in GJ/ton of Ni.

	Sulphides			Laterites		
	E_{mining}	$E_{refining}$	E_{total}	E_{mining}	$E_{refining}$	E_{total}
Boustead & Hancock (1979)			232.23			696.71
Chapman & Roberts (1983)	67	150	217	6.3	570	576.3
Classen et al. (2007)	20.19	84.88	105.07			
Norgate et al. (2007)		114	228			388
IPPC (2009*a*)		18.5	45			
Mudd (2010)	39.46	100.2	139.66		572	

The lower energy values presented by the European Commission, in its document Integrated Pollution Prevention and Control – IPPC (2009*a*), derive from the fact that nickel production comes from sulphide ores containing 4 to 15% nickel, which is a relatively high ore grade compared with those of the other references published in Table 2.10. Furthermore, energy values from an international database such as those presented in Classen et al. (2007) are based on diverse sources and are not only from one particular mine or country, hence the range.

2.2.12 Nickel laterites

Laterite ores are generally found with iron oxide or silica compounds and are difficult to upgrade it to a concentrate. Laterite ore concentrations are rarely high, typically having a maximum nickel content of 3% was reported on IPPC (2009*a*). The general route of producing nickel from laterite ores consists of five linked operations: ore mining, drying, roasting, melting and refining, as shown in Fig. 2.9.

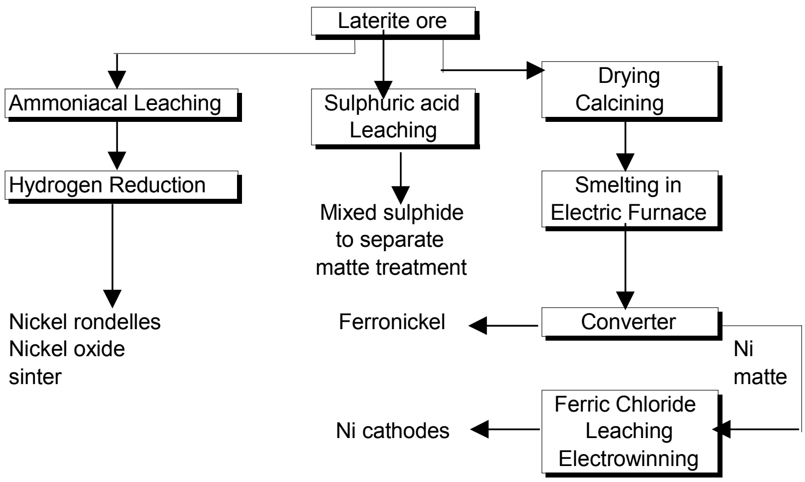


Figure 2.9: Generic flow sheet for the production of nickel from laterite ores IPPC (2009*a*).

A brief process description follows.

Laterite ores mining: Laterite ores are formed near the surface, consequently, laterite mines are mostly open cut. The energy required to concentrate the ore from the mine is very small compared to the energy required to refine it.

Drying and Roasting: Since laterite ores are found in tropical climates dotted around the equator, a high moisture content is present. Hence, it is necessary to remove it by drying or calcining. Before smelting, the ore is usually roasted in a rotatory kiln electric furnace, which is a pyro-processing equipment used to acquire high temperatures in ores in a continuous process. These two stages and the next one, are those which require the highest energy input as natural gas, carbon and electricity, respectively.

Smelting: An electric furnace is usually used for smelting. Nickel matte is obtained following the addition of sulphur so that the nickel oxide is converted to a nickel sulphide matte. Subsequently, it can be treated with the same processing methods as the matte produced from sulphide ores.

Refining: There are several processes in the refining of nickel depending on the final products obtained. For instance, ferronickel is gained from converting processes (oxidation of the iron that is still in the matte through a Peirce-Smith converter by injecting air or oxygen into the molten bath); nickel cathodes are derived from leaching; metallic nickel can be produced by electro-winning; and metal powders can be obtained via hydrogen reduction.

In this step, an improved technique used is the pressure leaching of laterites, where conditions such as pressure, temperature and other parameters are set in accordance with the ore properties or desired products in order to achieve the best possible metallurgical conditions. The resultant solution is purified either by modern solvent extraction methods or by traditional precipitation methods. By-products such as cobalt, iron and other minerals are also obtained.

2.2.13 Nickel sulphides

Sulphide ores are typically derived from volcanic or hydrothermal processes with a typical nickel content ranging from 0.4 to 2%, according to Classen et al. (2007). Nickel production from sulphide ores involves either underground (95%) or open cut mining (5%). The processes to produce nickel from sulphide ores include several steps: ore mining, beneficiation, drying, roasting, smelting, converting, sulphuric acid, leaching, reduction, electrolysis, purification of leachate and carbonyl. Figure 2.10 gives an overview of the process options.

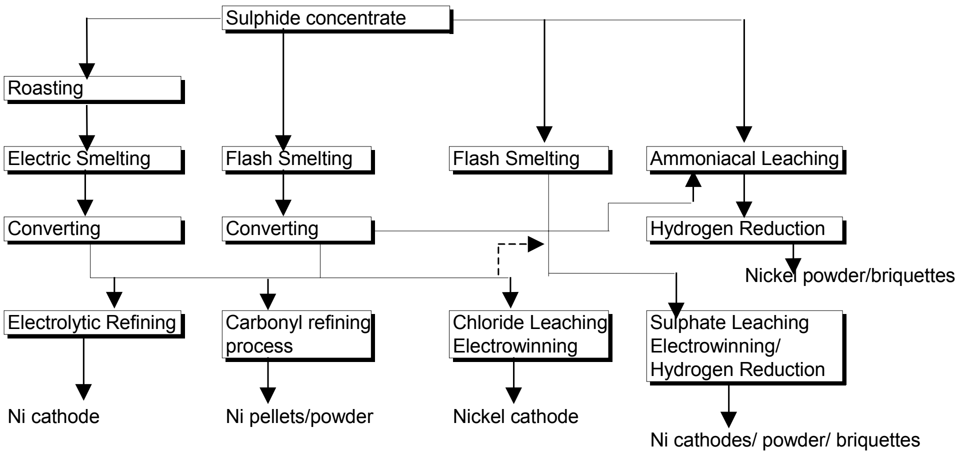


Figure 2.10: Generic flow sheet for the production of nickel from sulphide concentrates IPPC (2009*a*).

There are assorted processes used to produce nickel and the differences depend on factors such as the grade or the concentrate and the presence of other metals in the material mined. The options for nickel production from sulphide concentrates are classified in Table 2.11. A short description of each process involved in sulphide mining and refining is presented next.

Table 2.11: Processes for nickel production from sulphide ores.

Option	Processes
A	Mining and beneficiation, drying and roasting, smelting, converting and electrolysis.
B	Mining and beneficiation, drying and roasting, smelting, converting and carbonyl.
C	Mining and beneficiation, drying and roasting, smelting, converting and leaching.
D	Mining and beneficiation, smelting, converting and carbonyl.
E	Mining and beneficiation, smelting, converting and electrolysis.
F	Mining and beneficiation, smelting, converting and leaching.
G	Mining and beneficiation, smelting, converting, leaching and hydrogen reduction.
H	Mining and beneficiation, smelting and leaching.
I	Mining and beneficiation, smelting and electrolysis.
J	Mining and beneficiation, leaching and hydrogen reduction.

Sulphide ores mining and beneficiation: Sulphide ores are normally found hundreds of metres below the surface, therefore, they require an underground mining infrastructure. However, the major advantage of sulphide ores is that they can be concentrated easily by flotation, a method which upgrades the Ni content to some 7-25 %. In this process, the ore is mixed with special reagents and agitated by mechanical and pneumatic means.

Drying and Roasting: This step is needed to carry out the smelting process which requires dry sulphide ore containing less than 1% moisture. Smelting processes require a roasting step to reduce sulphur content and volatiles. According to Norgate & Haque (2010), an opportunity to improve this step is the use of the emerging bath smelting technology for ferronickel production instead of the rotatory kiln/electric furnace process.

Smelting: The smelting process is often achieved in a conventional flash smelting furnace or in an Outokumpu flash furnace (DON process), which is characterized by its low energy consumption. In the DON process, high grade nickel matte of low iron content is produced in the flash smelting furnace directly without subsequent converting.

Converting: Nickel is recovered into a sulphide matte containing 35-70% Ni, Co, Cu and precious metals. The matte still contains iron and sulphur that are oxidized in a Pierce-Smith converter to sulphur dioxide and iron oxide by injecting air or oxygen into the molten bath.

Refining: The mattes produced by the smelting process must go through a multi-stage process in order to: recover and refine the metal content, reject iron and ultimately recover copper, cobalt and precious metals. Matte can be treated by pyrometallurgical methods but hydrometallurgical processes are more widely used.

Leaching: Matte can be leached under different processes as a function of the substance used. For instance, nickel leach with chloride solution using chlorine gas, as an oxidant, allows the acquisition of copper, cobalt, lead and manganese as co-products. Another option is atmospheric leaching in a sulphate base whereby copper and cobalt are obtained as by-products.

A further process is ammonia pressure leaching which uses air as an oxidant; this process is followed by hydrogen reduction to produce metallic nickel powder and eventually copper and cobalt. Ferric chloride leaching is an additional method where nickel is electro-won. This process has by-products like iron, cobalt, chrome, aluminum and lead.

Lately, a new technology for Ni production is being used, namely that of heap leaching including biological activation. Although it is mainly applied in laterites, recent projects have been developed for sulphide ores. Mudd (2010) claims that heap leaching has an appreciably low capital cost but still there is dubiety regarding ore chemistry and leaching dynamics.

Reduction: Hydrogen pressure reduction produces metallic nickel powder and briquettes.

Electrolysis: Nickel is placed onto pure nickel cathodes from sulphate or chloride solutions in electrolytic cells.

Carbonyl: Nickel carbonyl is formed by the reaction of metal with carbon monoxide at low temperature and pressure.

2.2.14 Rare Earth Elements

Rare earth elements are integrated by a group of seventeen chemically similar elements; lanthanide, yttrium and scandium series. There is a classification for light, medium and heavy elements, as shown in Table 2.12. This classification is important in order to determine the suitable separation process.

Table 2.12: Rare Earth Elements Classification. Koltun & Tharumarajah (2008)

Type	Element	Symbol
Light	Lanthanum	La
	Cerium	Ce
	Praseodymium	Pr
	Neodymium	Nd
	Promethium	Pm
Medium	Samarium	Sm
	Europium	Eu
	Gadolinium	Gd
Heavy	Terbium	Tb
	Dysprosium	Dy
	Holmium	Ho
	Erbium	Er
	Thulium	Tm
	Ytterbium	Y
	Lutetium	Lu
	Yttrium	Y
	Scandium	Sc

Rare earth resources are inequable distributed in the world. Minerals such as bastnasite and monazite, have been recovered for commercial production. Bastnasite deposits are found in China and United States, whilst monazite deposits are in Australia, Brazil, China, India, etc., hence China produce more than 90 % of REE. China is applying export restrictions. Massari & Ruberti (2013) declare that this fact has greatly increased the REEs prices, causing tension and uncertainty among the world hi-tech markets. Then, new mine projects are underway in other countries.

Rare earths can be used like a mixture or with various levels of purity, depending on the technical application (phosphors, high refractive glass, lasers, permanent magnets, capacitors, memory systems, magneto-optical recording, oxygen sensors, temperature resistant mater, high temperature superconductivity, decolourising, polishing, deoxidising, pyrophoric properties, alloys, oil refining and catalytic converters). As new products and new applications are devised, the demand will increase and it is possible the exhaustion of the resources in near future.

On the other hand, recovery processes have been developed but none of them is currently commercially viable. In regards to substitution, the ad-hoc Working Group (2010) asserts that a lot of applications for rare earth are available but the problem lies on loss of performance.

The mineral monazite is a source of mostly light RE elements and contains considerable amount of radioactive elements (thorium and uranium) and phosphorus. Koltun & Tharumarajah (2008) state that overall production processes of REE can be separated into three stages, as depicted in Fig. 2.11 and described briefly below.

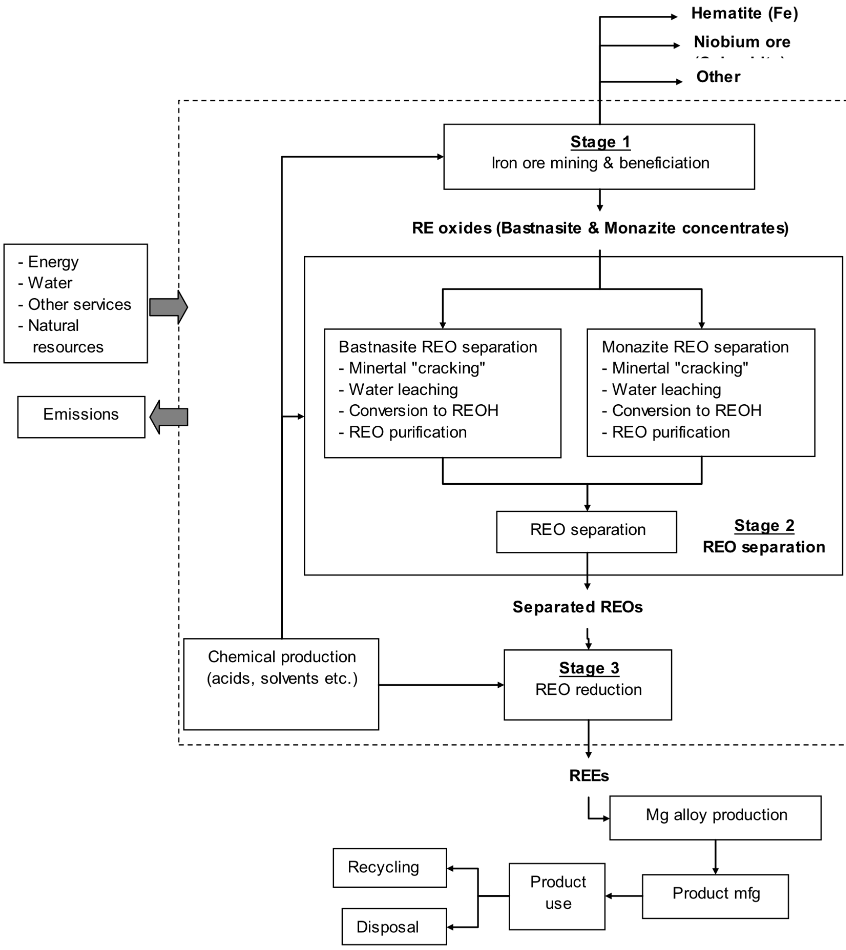


Figure 2.11: The "cradle to gate" LCA boundary for the production of separated mix of REO Koltun & Tharumarajah (2008).

Mining and beneficiation: rare earth minerals are mined as by-products from mining of other ore types, such as iron ore. Bastnasite and monazite are two of the major sources of rare earth elements. The ore is mined in open-pit mines where ore is processed to extract ore up to the point of delivery of ore concentrates. Beneficiation separates bastnasite and monazite generally using gravity separation, magnetic separation and flotation.

Separation of REOs: rare earth oxides contained in the ore concentrates of bastnasite and monazite are separated through a cracking process. This stage involves a progressive separation of light, medium and heavy REOs. The main processes for extraction and separation of REO from bastnasite are precipitation, solvent extraction (S/X) and ion exchange.

The hydrometallurgical route to separates REO from bastnasite includes: 1) pre-leaching; 2) calcination; 3) caustic conversion and drying/oxidation; 4) hydrochloric acid leaching and removal impurities; 5) separation of light REO form medium and heavy REO (Nd/Sm separation); and 6) separation of medium REO from heavy REO by solvent extraction and precipitation and further S/X for individual REO. The hydrometallurgical process used in extracting RE oxides from monazite involves: 1) autoclave leaching; 2) radioactive elements removal; 3) cerium extraction; 4) light RE extraction from medium and heavy REO; 5) stripping for further separation of medium REO from heavy REO; 6) precipitation and re-extraction for precise separation of light, medium and heavy REO.

Reduction of REEs: rare earth elements are separated from their respective grouped REOs. A solvent extraction process is used for recovery of individual RE oxides from light (La, Pr, Nd), medium (Sm, Eu, Gd) and heavy REE mixture.

The reduction of the rare earth elements has been carried out by fused salt electrolysis for light REE (La-Nd), whilst medium and heavy REE are produced by metallothermic reduction. Table 2.13 depicts the consumption of electricity (considering an efficiency of 40%) and heat for six rare earth elements, accounted by Koltun & Tharumarajah (2008).

Table 2.13: Energy consumption for production of 1 kg of rare earth metals. Data modified from Koltun & Tharumarajah (2008).

REE	Energy consumption (MJ/kg REE)	
	Oxide production	Metal production
Lanthanum	296.75	53.45
Cerium	523.05	56.1
Praseodymium	296.275	55
Neodymium	591.7	53
Gadolinium	3607.25	43.05
Yttrium	1198.25	47.6

2.2.15 Silver

Silver is used, today, primarily for its chemical and electronic properties. Silver is a relatively rare metal. According to Ayres & Ayres (1996), it constitutes about 0.2 parts per million, by weight, of the earth's crust. Plenty of gold mines produce silver because the extraction of silver ore is carried out mainly as by-product from lead/zinc, copper and gold deposits. The major producing countries of silver are Mexico, China, Peru, Australia and Russia.

The survey performed by Classen et al. (2007) shows that the amount of silver extracted during 2000-2006 from mines in Papua New Guinea are almost equal than gold as well as the energy consumption for concentrating and refining process which are 17,100 GJ/t and 7.92 GJ/t, respectively. Throughout 2002 an open pit mine in Chile produces mainly silver consuming 5,142.86 GJ/t in the concentration process and 2.32 GJ/t in the refinement.The open pit Yanacocha mine in Peru produces silver in less quantity than gold, hence the consumptions with regards to concentration and refining process are 33,057.22 GJ/t and 18.54 GJ/t, which are higher than those for gold production. The ITP (2002) reports that in 1976 the Bureau of Mines estimates that 2,743 GJ/t were required to produce silver. The energy consumption for both concentrating and refining processes was reported as 1,582 GJ/t by Kellogg (1977).

2.2.16 Tellurium

A recent application of tellurium is for the thin film solar cells, although it has common applications such as thermoelectric devices and as an steel alloy. Tellurium is a relatively rare element. It is commonly extracted as a by-product of processing copper, lead, gold, and bismuth ores. The tellurium content in the copper varies considerably, according to Classen et al. (2007) an average 7 g refined tellurium is produced per tonne copper that is extracted. Tellurium is produced mainly in the United States, Canada, Peru and Japan.

The metallic impurities form anode slime of copper, is the main source for the production of tellurium. The slime contains tellurium, beside various metals like Bi, Sb, Se, Pb, Au, Ag, As or Ni. Therefore, the separation process is usually done for all metals at one place. The tellurium is separated from the slime as copper-telluride-cementate, through the following process: (i) dissolving of copper-cementate with sulphuric acid, (ii) electrolysis of tellurium from the solution and (iii) purification of cathode-tellurium with melting, as shown in Fig. 2.12.

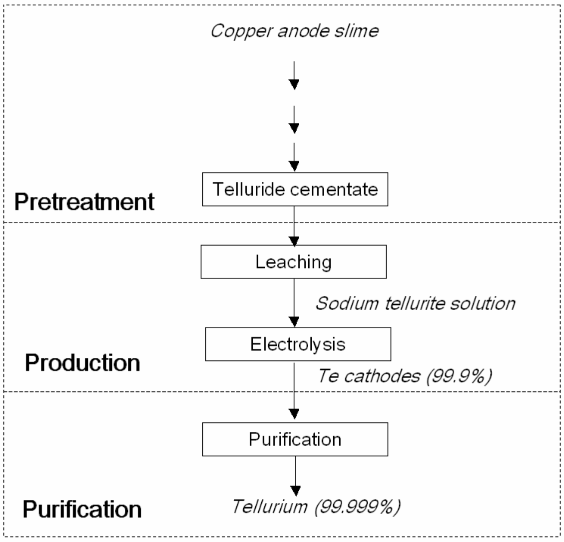


Figure 2.12: Production process of tellurium IPPC (2009*a*).

Dissolving cementate and electrolysis: the cementate of copper-telluride is treated with sulphuric acid. The next step is the electrolysis of the solution to extract the tellurium at the cathode.

Purification: high purity tellurium is produced by electrolytic purification and subsequent melting and atomization or by vacuum-distillation.

2.2.17 Zinc

Zinc is an important industrial metal which is extensively used both in metallic and chemical forms. It has useful electrochemical properties, forms useful alloys (e.g. with copper and tin) and makes a good protective coating for iron or steel. Zinc is one of the main nonferrous metals, which are largely produced and largely consumed in the world. It is produced in many countries such as Australia, Canada, China, Kazakhstan, Mexico and Peru. The most important zinc mineral is sphalerite. There are two routes to produce zinc, hydrometallurgical process that accounts almost 80 % of total zinc production and pyrometallurgical process that produces the remaining 20 %, according to Xiao et al. (2003) (Fig. 2.13). About 70 % of zinc is won from a sulphidic ore and is mined mostly underground.

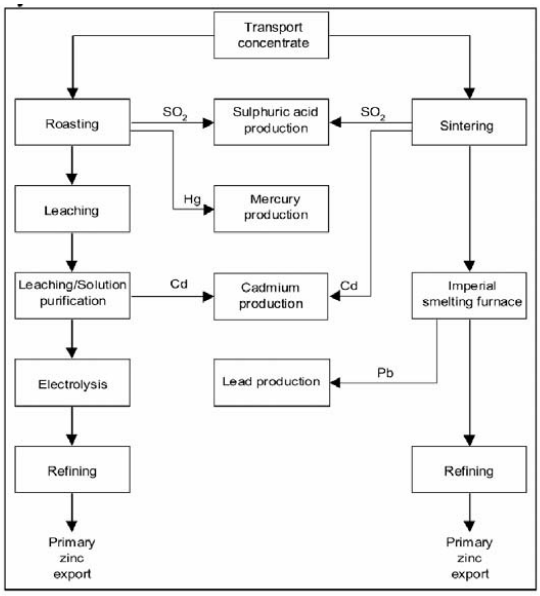


Figure 2.13: General scheme of zinc production Classen et al. (2007).

Zinc and lead are extracted together from sulphidic ores and are mined largely underground. The ore is transferred to the beneficiation step where processes such as gravity concentration, flotation and neutralisation, are performed. Zinc can be produced by pyrometallurgical or hydrometallurgical methods. The pyrometallurgical route uses the Imperial Smelting Furnace (ISF) for zinc/lead concentrates followed by a refining stage to separate zinc from cadmium, lead, copper, arsenic, antimony and iron. The hydrometallurgical route is used for zinc sulphide. The first step is the roasting process to produce zinc oxide, followed by several leaching stages to obtain zinc, which does not requires a further refining. The electrolysis process is the hydrometallurgical route used to produce zinc from primary raw material, the energy consumption during this refining stage reported by the IPPC (2009*a*) is 14.76 GJ/t.

According to Classen et al. (2007), smelting of zinc is a multi-output process that delivers three co-products: zinc, cadmium sludge from zinc electrolysis and indium from leaching. Undoubtedly, zinc extraction is the major source for raw material. However an allocation factor for three products zinc, indium and cadmium has to be determined. Since cadmium is considered as a contaminant that has to be isolated from the main product anyway, the cadmium containing sludge is regarded as burden free. For every tonne of zinc extracted 1.5 kg of cadmium is refined. For Indium, there is a ratio of 45 g refined Indium per tonne extracted zinc.

According to Boustead & Hancock (1979), the energy requirement by the electrothermic method to obtain zinc from ore is 69.8 GJ/t, including overall process. Whilst, Chapman & Roberts (1983) assert that the energy requirement for mining and concentrating ore to produce zinc is 11.7 GJ/t, the smelting and refining processes requires 63.3 GJ/t by electrothermic or 49.6 GJ/t by electrolytic means.

The energy consumed in the open pit mining of zinc (for an ore grade of about 5 %) and ore preparation is 4.464 GJ/t, which is relatively low compared with the high energy consumption of 63.21 GJ/t for the refining process through electrothermic operations. Yoshiki & Toguri (1993) argue that less energy-intensive methods of zinc production include electrolytic route, reductive flash smelting and the Plasmazinc process. The gross energy needed to produce special high-grade zinc reported by Dove & Boustead (1998) is 51.05 GJ/t, this energy includes the consumption of all ancillary operations, tracking all operations back to the extraction of raw materials from the ground. According to Ayres et al. (2002), the International Zinc Association has concluded that the total energy in fuels and electricity required to produce a tonne of concentrate is 7.6 GJ/t, while 50 GJ/t is required to produce refined zinc.

According to Classen et al. (2007), the mining process has an energy requirement of 0.62 GJ/t and once obtained the primary raw material zinc can be produced by pyrometallurgical or hydrometallurgical method. Pyrometallurgical methods are used in other parts of the world but have gradually lost the importance, considering the mix world-wide in the pattern of the production processes producing zinc, the energy needed in the smelting step is 21.09 GJ/t assuming that 80 % is done by hydrometallurgical and 20 % by pyrometallurgical route. Norgate et al. (2007) report that zinc production from sulphide ore is done through electrolytic process with a energy requirement of 48 GJ/t of primary energy in overall process. Considering an average efficiency of 50 % due to the utilization of both thermoelectric and hydroelectric generation the energy requirement is 96 GJ/t. The imperial smelting process has an energy consumption of 72 GJ/t. Table 2.14 summarize the energy consumption in mining and refining of zinc, according to the aforementioned process used to obtain it.

Table 2.14: Energy consumption in the zinc production. Values expressed in GJ/ton of Zn.

	E_{mining}	E_{refining}	E_{total}
Boustead & Hancock (1979)			69.8
Chapman & Roberts (1983)	11.7	63.3	75
Yoshiki & Toguri (1993)	4.464	63.21	67.85
Ayres et al. (2002)	7.6	50	57.6
Classen et al. (2007)	0.62	21.09	21.71
IPPC (2009*a*)		14.76	

2.3 Summary

This chapter attempts to provide a basic understanding of the technology and energy usage of the mining industry. A description of main uses, physical, chemical and geological characteristics, producing countries and metallurgical production processes of several metals which will be used in the following chapters of this thesis, have been carried out. For each metal, a summary table of the energy consumptions during the mining and refining steps was presented. It is important to highlight that there is a wide range of energy values for each commodity as shown in each of the energy tables presented in this chapter due to different factors such as ore grade and technological constraints. Furthermore, it is difficult to know the energy requirements reported for those metals obtained as by-products. Due to the fact that there is very little data available on the mining industry for energy use by specific mining process utilized to produce by-products. Accordingly, Table 2.15 presents a summary of the energy requirements for each of the described metals as well as for the metals presented in Appendix A.

In the next chapter, the energy consumption of the mining industry (gold) is analyzed through the learning curve theory in order to know the influence that factors such as ore grade and technological improvements have in mining.

Table 2.15: Energy requirements for the production of mineral commodities. [GJ/t]

Metal	Mining and Beneficiation	Smelting and Refining
Aluminium (Gibbsite)	10.5	23.9
Antimony (Stibnite)	1.4	12.0
Arsenic (Arsenopyrite)	9.0	19.0
Beryllium (Beryl)	7.2	450.0
Bismuth (Bismuthinite)	3.6	52.8
Cadmium (Greenockite)	263.9	278.5
Chromium (Chromite)	0.1	36.3
Cobalt (Linnaeite)	9.2	129.0
Copper (Chalcopyrite)	28.8	21.4
Fluorite	1.5	-
Gold	107751.8	-
Iron ore (Hematite)	0.7	13.4
Lead (Galena)	0.9	3.3
Lithium (Spodumene)	12.5	420.0
Manganese (Pyrolusite)	0.2	57.4
Mercury (Cinnabar)	157.0	252.0
Molybdenum (Molybdenite)	136.0	12.0
Nickel sulph. (Pentlandite)	15.5	100.0
Nickel later. (Garnierite)	1.7	412.0
Potassium (Sylvite)	3.1	N.A.
REE (Bastnaesite)	10.2	374.0
Silicon (Quartz)	0.7	76.0
Silver (Argentite)	1281.4	284.8
Sodium (Halite)	3.3	39.6
Tantalum (Tantalite)	3082.8	8.1
Tin (Cassiterite)	15.2	11.4
Ti-Ilmenite	7.2	128.1
Ti-Rutile	13.8	243.8
Uranium (Uraninite)	188.8	N.A.
Vanadium	136.0	381.0
Wolfram (Scheelite)	213.0	381.0
Zinc (Sphalerite)	1.5	40.4
Zirconium (Zircon)	738.5	633.0

Chapter 3

Technical development in the mining industry

In the previous chapter, it was seen that factors such as ore grade and technological constraints play an important role when energy requirements in mining and metallurgical industry are evaluated. This chapter analyzes these variables through the learning curves theory, in order to know if energy required to mining ores decreases as technologies improve, if the amount of improvement decreases as time goes on and if technology improvements have more or less influence than ore grade declining in energy consumption. Furthermore, learning curves can be used as a tool to estimate future energy reductions in the mining industry.

3.1 Introduction

As described in chapter 1, the mining industry is experiencing groundbreaking changes such as commodity price fluctuating, rising energy demand, water and cyanide consumption, increasing costs, declining ore grades, green-house gas emissions, increasing waste volumes and the challenge to achieve sustainable industry. Thence, sustainability[1] practices have become important for most major mining companies in order to reach a balance between socio-political, economic and environmental issues.

In order to overcome the sustainability challenges in the mining industry, it is important to increase efficiency on resource extraction. One of the most powerful forces influencing the economic importance of natural resources in the future is technological change. Through technological innovations, it is possible to increase material efficiency in manufacturing processes and seek new substitute raw materials. Technology has always played an important role to transform mineral resources into mineral wealth and useful end-products. Nevertheless, technology breakthroughs of mineral extraction had been relatively slow until the Industrial Revolution when it showed a growth demand in commodities like coal, iron or copper. This fact lead to ever greater technological advances that even now are still used such as flotation, the blast furnace, railways, geophysics, drilling, trucks and transport, etc., allowing the mining of lower ore-grade mines.

[1] For Placer Dome Inc. which is one of the world's largest gold producers "sustainability means the exploration, design, construction, operation and closure of mines in a manner that respects and responds to the social, environmental and economic needs of present generations and anticipates those of future generations in the communities and countries where it works" Milton (1998).

According to the ad-hoc Working Group (2010), the technological progress in exploring, mining and processing mineral raw materials has actually been the key driver that has allowed supply to keep up with demand in the past. Sohn (2006) states that over the last 25 years, powerful advances in exploration techniques in the mining sector, such as remote sensing imagery, have located new and major deposits. Breakthroughs in mining machinery, the extensive use of computers, more effective chemicals and reagents, and better use of explosives in the mines, are some of the examples that allows for cost reductions and energy efficiency. Therefore, more efficient processing methods can have a great impact on future availability of mineral resources.

That said, there is a debate about the availability of commodities in the future, because there are two counteracting trends. First, general trends suggest a long-term decline in ore grade, which rises energy consumption per ton of metal extracted, and second technological transitions, which may hamper this trend. Jolliet et al. (2003) argue that if the quality of a mined abiotic resource is reduced over time, the effort to extract the remaining resource will increase.

Technological learning has been widely used and it has acquired support in many applications as the energy analysis proposed in this thesis. The aim of this chapter is to become acquainted if technological breakthroughs that have occurred can preclude the rising energy demand for the gold mining industry as a case study. As experience is acquired, material and energy efficiency increase and technical changes can be expressed through the so called learning curves. In this chapter these opposite issues are analyzed through the survey of data sets of 17 major gold producing countries, with the aim to establish relationships among resource extraction and energy use; therefore it allows being aware if actual mining processes are leading the gold mining sector towards sustainability. Nevertheless, technical efficiency cannot improve indefinitely and it can never overcome thermodynamic bounds.

3.2 Ore grade evolution

In the mining industry, energy consumption trend is strongly influenced by the decline in ore grades. Declining ore grades are indicative of a shift from "easier and cheaper" to more "complex and expensive" processing, which implies declining in productivity and the consequential rise in the energy intensity of mineral processing. Giurco et al. (2010) state that almost all minerals are being produced today at greater rates than at any time in history.

Historical data compiled by different authors such as Mudd (2007*a*,*b*,*c*, 2010), Page & Creasey (1975), Skinner (1986), Norgate & Jahanshahi (2010, 2011) reveal that ore grades have declined dramatically throughout the last century. The best mines with the highest grades have been already extracted and today mining companies need to go further and deeper to find profitable ores. Consequently, much more energy is required per ton of mineral extracted, as depicted in Fig. 3.1. But not only that, the use of water, chemicals and waste-rock produced is also increasing strongly, leading to serious environmental problems. Hence, production and cost trends show an increment as explained promptly.

That said, although there is evidence supporting the long-term decline in gold ore grades, there also exists the possibility that technological learning will overwhelm this fact. Hence, in the next sections the relationship between two issues: the decline in ore grades and the rising in energy consumption per ton of metal extracted, is analyzed.

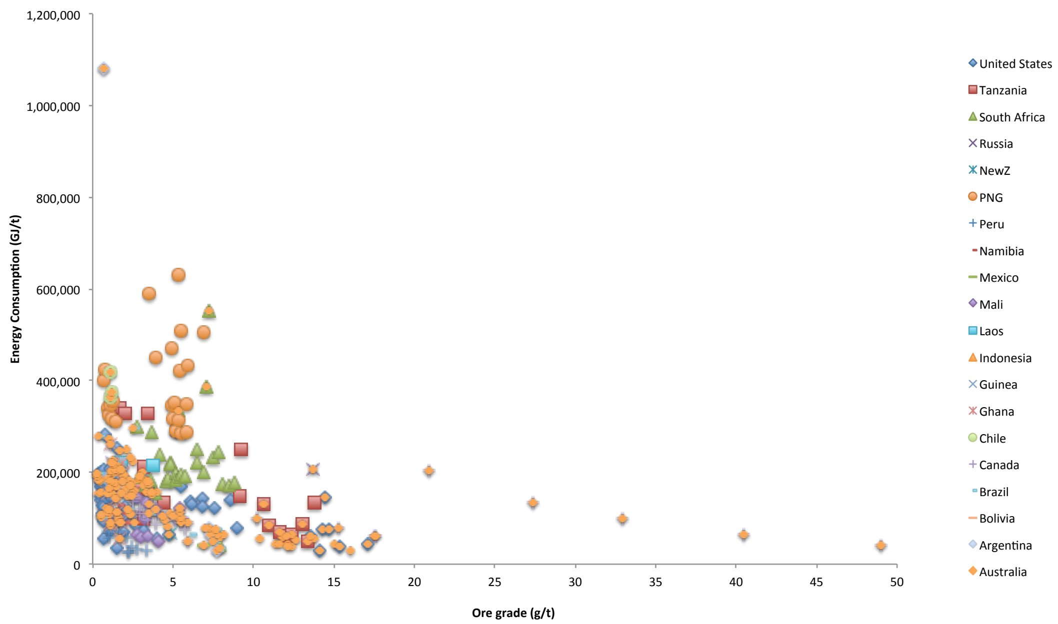


Figure 3.1: Energy consumption as a function of ore grade in global gold mining. Data from Mudd (2007*b*).

3.3 Evolution in technology in the minerals industry

Natural resources are the main inputs into mining production. The problem is their non-renewable character. As mineral and energy deposits are depleted, the quality and accessibility of remaining reserves usually decline, requiring more complex extraction techniques as well as greater costs. Hence, the importance of a deeper understanding of the role of technology in the mining industry.

Technology has always been, and remains, a key issue of the mining industry and its ability to transform mineral resources into mineral wealth and useful end-products. According to Giurco et al. (2010), improved technological performance has allowed the industry to:

- improve exploration capabilities
- decrease costs and increase efficiency when processing complex ores
- restrict the cost associated with environmental regulations
- reduce cost of labour by increasing mechanisation
- diminish input cost due to energy or chemicals
- recover resources from wastes

The development and widespread use of new technologies has made possible the growing in mineral supply to meet increasing demand. The latter is the main reasoning against mineral depletion. Nonetheless, this historical situation may change due to declining in ore grades.

The role of technology in mineral exploration, mining, processing, manufacturing and recycling has been critical in the minerals industry. A major breakthrough in mineral exploration was the emergence of geophysics, besides drilling, remote sensing, bio-prospecting, complex geological modelling tools, field analysis instruments, and so on. The main techniques of mining remain the same, however increasing mechanisation in underground mining allows to reach greater depths. In open cut mining, increasing truck sizes, safer and cheaper explosives and cheap diesel fuel, are the factors that have made possible the long-term growth. Whilst, flotation, gravity and dense media separation, carbon-in-pulp and heap leaching solvent extraction electrowinning (SX-EW), are the technologies developed to reduce energy intensity and improve metals recovery during minerals processing. Technology in manufacturing plays an important role because it allows to reduce the metal used in products as well as to design products in such way that recycling at their end of life be more easy.

Technical change is a gradual process that entails technical knowledge and investment, but also an increase in material and energy efficiency. Ruth (1993) claims that both material and energy efficiency increase independently and changes can be led to the learning by doing concept. In accordance to Söderholm & Sundqvist (2007), technical change is introduced by implementing technology learning rates, which specify the quantitative relationship between the cumulative experiences of the technology and cost reductions.

3.4 The learning curve theory applied to the mining industry

Learning curves come out as an empirical method to assess the effect of learning on technical change. Learning curves are used to analyze a well known observed fact. Because of the experience, humans become increasingly efficient. As experience is acquired, cost decline, efficiency and quality upgrade and waste is reduced.

There is a widespread use of learning curves because of their usefulness to quantify the impact of increased experience and learning of a given technology, allowing to obtain a representation of technical change with a variety of different indicators of technological performance.

A good number of studies based on the learning curves theory have been carried out. For instance, Söderholm & Sundqvist (2007) used learning curves for assessing the economic outlook of renewable energy technologies to link future cost developments to current investment in new technology. Other studies about the impact of quality on learning that suggest that learning is the link between quality improvement and productivity increase have been accomplished by various authors like Li & Rajagopalan (1997) and Jaber & Guiffrida (2008).

The rate of improvement is not subjective, it is a function of the process itself. Limitations to improve the process often requires a capital investment and remove the limitations inherent in the process. Learning curves describe long-term improvement through the knowledge of

- How fast can you improve to a energy saving of x?
- What are the limitations to improve the process?
- Are forceful goal achievable?

Yelle (1979) states that the simplest and most frequently representation of learning curve in energy technology studies is the Wright's log-linear model:

$$Y_x = Y_0 x^b \tag{3.1}$$

where Y_x represents the energy required to produce the x^th unit, Y_0 is the theoretical energy of the first production unit, x is the sequential number of the unit for which the energy is to be computed and b is a constant reflecting the rate energy decrease from year to year (learning index) and is calculated as:

$$b = \frac{lnS}{ln2} \tag{3.2}$$

where S is the energy slope expressed as a decimal value (learning rate), while (1-S) is defined as the progress ratio which express the fraction to which energy requirements are reduced with cumulated production.

However, Ruth (1995*b*) asserts that there is a limit on the energy use to ore production that cannot be exceed with increasing experience and in this case it is the minimum theoretical energy required to concentrate a substance from an ideal mixture of components. This limit can be calculated through the concentration exergy presented in Chapter 4 and expressed in Eq. 4.28. Accordingly, considering the energy limiting value, the learning curve can be expressed as Eq. 3.3 which integrates thermodynamic concepts to the learning curve analysis.

$$Y - b_c = Y_0 x^b \tag{3.3}$$

In the mining industry, the technology learning rates state the correspondence between the cumulative experience of the technology and the energy requirement reductions. These reductions are the result of learning by doing. For instance, performance improves as new technologies and mining methods are implemented. Accordingly, learning curves will be used to empirically quantify the impact of accomplishing new mining practices on the energy consumptions of ore mining.

Kahouli-Brahmi (2008) has performed an enhancement for the simplest learning curve by applying a factor related with research and development. These extended formulation is known as the two factor learning curve (TFLC) expressed as follows:

$$Y(x, KS) = Y_0 x^b * KS^c \tag{3.4}$$

where KS is the knowledge stock and c is the elasticity of learning by researching.

According to Weiss et al. (2010), both types of learning curves are the most commonly used to assess technology learning rates in the energy sector. However, Jamasb & Kohler (2007) declare that a multiple-factor learning curves that account for other independent variables besides cumulative production represent an approach to get a better understand of technological learning by enhancing the knowledge base.

Learning rates depend on the data points that are chosen. Previous surveys, as the one performed by Kahouli-Brahmi (2008) reveals significant variability in estimated rates between different energy technologies, which ranges from 1% to 41.5%. On the other hand, the study developed by McDonald & Schrattenholzer (2001) show that the average value of learning rates for energy technologies is 16-17% and learning rates for manufacturing is 19-20%. Negative learning rates can be interpreted as a consequence of experience depreciation, if no important external factors (such as declining ore grades in mining technologies) are influencing the production process.

The estimating of learning curves using econometric techniques has some highlights. For instance, the need to survey the effect of detach single observations especially outliers that may effect the learning rate estimate or the impact of using different variable definitions. Another issue is related with the way in which technology learning is operationalized in order to know if the indicator of learning by doing selected is assuredly capturing the impact of learning by doing activities or if it is following a general trend of technical progress. Also is important to investigate differences in learning rates across different technologies. Söderholm & Sundqvist (2007) assert that a further point is the assumption in the model when the independent variable is defined as well as the influence of other variables on this.

The use of learning curves implies that a technology had been already invented and implemented. Ruth (1993) argues that as more awareness is obtained in using materials and energy to produce outputs with a determined technology, changes in its performance occur slowly. This can suggest that a high level of expertise in ore mining with a specific technology will result in a discontinuity in learning. Further interruptions or discontinuities in the learning curve occur when intermittent production is presented, e.g. mine rehabilitation. Afterwards, learning curves may start again with a new technological breakthrough, a radical innovation or a paradigm change, according to Wellmer & Becker-Platen (2002). Also, Schoots et al. (2008) aver that breakthroughs may influence the progress ratio.

Wellmer & Becker-Platen (2002) avow that learning curves for mining sector are driven by financial rewards, directly (i.e. by the discovery of a very economic deposit or a price increase of a commodity) or indirectly (by a penalty).

3.5 Learning Curves applied to Global Gold Mining

In this section, the analysis of data set on historic gold mining in the main gold producing countries was carried out by means of linking resource extraction with energy use through the learning curves approach. Learning curves were originally developed to evaluate the effect of learning by doing in manufacturing. However, there are new applications such as analysis innovation and technical change in energy technology.

This section looks over energy data on gold mining for Australia, North America, Africa and the Asia-Pacific compiled by Mudd (2007*b*,*c*), who pointed out the critical aspects of mineral resource sustainability such as resource intensity linked to technology.

Learning rates and progress ratios were calculated for each mine using Eq. 3.2 and Eq. 3.3. The information was grouped according to the different mining technologies used, because learning by doing will differ between mines, countries and technologies.

Progress ratios are different for each country and even for each mine although they use the same recovery process technology. This is due to inherent factors to each mine such as project age, depth, ore types, etc. Results of the analysis performed for different mining operations and recovery processes are shown in Table 3.1. The assorted configurations of gold mines like open pit (OP), underground (UG) or mixed (MIX), as well as the energy source (diesel, coal, hydro, gas or any mix among them) are factors that influenced the progress ratio.

Recovery process technologies show average progress ratios around ±25% as shown in Fig. 3.2. Open pit operations with heap leach technology (HL) as recovery process as well as underground operations using carbon in pulp (CIP)[2] technology are the mining options with the greatest progress ratios.

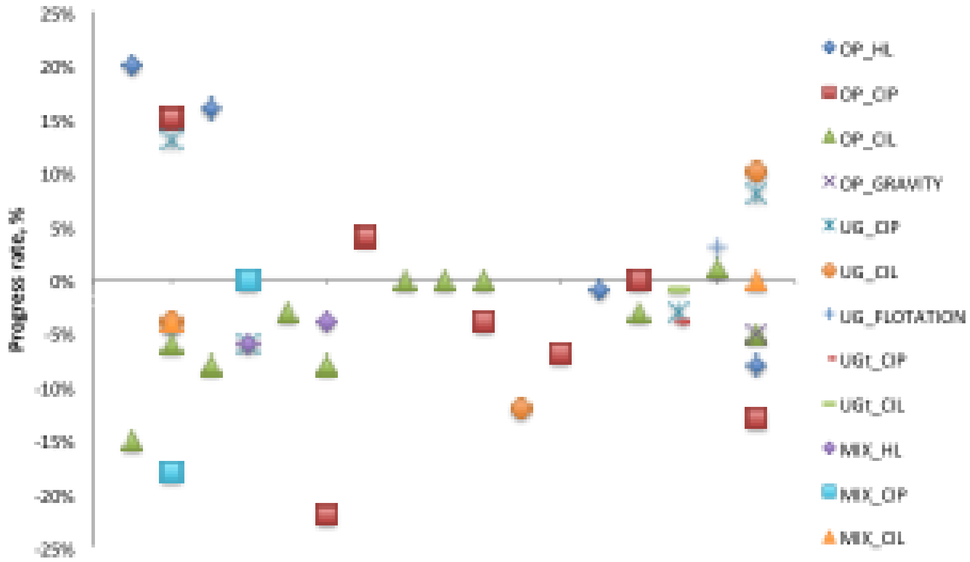


Figure 3.2: Distribution of average progress ratios for gold mining industry.

Negative progress ratios convey that technological learning has been unable to overcome the increase in energy consumption during mining operations due to the declining in ore grade. On the other side, positive progress ratios imply that mining recovery processes have achieved to maintain or decrease the energy consumption during mining operations throughout time. Accordingly, the progress ratio becomes an indicator to identify those mines where mining practices are successful when saving energy.

Table 3.1: Progress ratio for global gold mining.

Country	Mines	Operation	Recovery process	Energy consumption (GJ/t Au)	Average ore grade (g/t Au)	Progress ratio by mine (%)
Argentina	Veladero	OP	HL	476.295	1,2	20%
	Cerro Vanguardia	OP	CIL	57.568	7,4	-15%
Australia	Granny Smith	OP	CIP	48.010	12	-1%
	Kidston	OP	CIP	95.494	10,5	-7%
	Henty	UG	CIL	91.984	5,6	-31%
	Kalgoorlie West	MIX	CIL	88.191	39,3	-8%
	Agnew	MIX	CIP	171.934	21,6	-22%
	Hill 50	MIX	CIL	76.790	12,2	-6%

[2]The difference between carbon-in-pulp and carbon-in-leach processes is that for the first one the adsorption occurs after the leaching cascade section of the plant, whilst for the second one leaching and adsorption occur simultaneously De Andrade (2007).

Country	Mines	Operation	Recovery process	Energy consumption (GJ/t Au)	Average ore grade (g/t Au)	Progress ratio by mine (%)
	St Ives	MIX	CIP, HL	47.554	12,9	4%
	Central Norseman	MIX	CIL	148.309	8,4	1%
	Plutonic	UG	CIP, HL	155.778	3,5	2%
	Darlot	UG	CIL	181.927	1,5	14%
	Lawlers	UG	CIL	168.441	2	4%
	SuperPit	OP	CIL	141.350	2,1	-4%
	Mt Leyshon	OP	CIP	117.687	2,9	5%
	Tanami-Granites	MIX	CIP/CIL	174.270	1,6	-30%
	Boddington	OP	CIL	498.021	1,1	-14%
	Pajingo	UG	CIP	112.653	4,3	24%
	Bronzewing	MIX	CIL	63.504	7,5	4%
	Jundee	MIX	CIL	144.078	3,9	-19%
	Sunrise Dam	OP	CIL	180.196	0,4	1%
	Challenger	MIX	CIP	210.419	0,5	-26%
	Ravenswood	OP	CIP	236.498	1,5	18%
	Stawell	UG	CIL	87.669	1,1	-4%
	Fosterville	OP	BIOX, CIL	167.234	1,2	-5%
	Peak (NSW)	MIX	CIL	162.455	3,3	6%
Brazil	Mineracao	OP	HL	73.567	6,9	-4%
	Serra Grande	OP	CIL	64.707	6,3	-23%
	Amapari	OP	HL	208.293	2,4	29%
	Morro do Ouro	OP	CIL	176.444	0,5	1%
	Paracatu	OP	CIL	191.369	0,3	-2%
	Maricunga	OP	HL	163.089	0,4	24%
Canada	Dome-Porcupine	MIX	CIP	113.562	2,9	0%
	Hemlo	MIX	HL	102.457	4,6	-6%
	Musselwhite	UG	CIP	91.984	5,6	-16%
	Campbell	UG	CIL/CIP	67.688	16,8	-2%
	Eskay Creek	UG		88.191	39,3	-16%
	Red Lake	UG	CIP	22.401	79,7	0%
Chile	La Coipa	OP	CIL	385.254	1,1	-3%
Ghana	Tarkwa	OP	CIL	110.248	1	-4%
	Damang	OP	CIL	166.186	1,4	-11%
	Iduapriem	OP	CIP	130.283	1,8	-22%
	Obuasi	MIX	HL	192.560	2,1	-4%
Guinea	Siguiri	OP	CIP	189.244	1,1	4%
Indonesia	Kelian	OP	CIL	190.161	2,4	0%

Country	Mines	Operation	Recovery process	Energy consumption (GJ/t Au)	Average ore grade (g/t Au)	Progress ratio by mine (%)
Laos	Sepon Au	OP	CIL	217.951	2,4	0%
Mali	Sadiola	OP	CIP	102.837	2,9	-9%
	Yatela	OP	CIP	56.497	3,5	1%
	Morila	OP	CIL	125.031	4,2	0%
Mexico	San Dimas	UG	CIL/CIP	59.814	7,3	-12%
Namibia	Navachab	OP	CIP	110.056	1,8	-7%
Peru	Pierina	OP	HL	64.597	1,9	-9%
	Lagunas Norte	OP	HL, CIP/CIL	37.261	2,2	7%
PNG	Misima	OP	CIP	352.899	1,1	-2%
	Porgera	OP	CIP	431.600	5,2	2%
	Lihir	OP	CIL	374.258	5,4	-3%
South Africa	Harmony Group	UG-tails	CIP/CIL	205.291	5	-4%
	Beatrix	UG-tails	CIL	195.083	4,5	-1%
	Driefontein	UG-tails	CIP	204.009	5,1	-1%
	Kloof	UG-tails	CIP	229.860	7	-12%
	West Wits Field	UG-tails	CIP	175.272	8,5	0%
	South Deep	UG	CIP	424.041	6,5	-3%
	Vaal River	UG-tails	CIP, CIL	170.913	3,4	-2%
Tanzania	Geita	OP	CIL	257.028	2,3	-18%
	North Mara	OP	CIL	201.729	3,5	12%
	Tulawaka	OP	CIL	178.024	10,7	11%
	Bulyanhulu	UG	FLOTATION	78.621	12	3%
United States	Round Mountain	OP	GRAVITY	151.530	0,6	-5%
	Marigold	OP	HL	157.725	0,7	-5%
	Bald Mountain	OP	HL	129.211	1,1	-33%
	Cripple Creek-Victor JV	OP	HL	148.190	0,6	-3%
	Golden Sunlight	OP	CIP	131.676	2,6	-13%
	Cortez	OP	CIL	124.621	2,5	-5%
	Fort Knox	OP	HL	187.460	0,8	1%
	Wharf	OP	HL	146.938	1	-1%
	Goldstrike	MIX	CIL	138.706	6,8	0%
	Turquoise Ridge	UG	CIL	49.936	14,9	10%
	Pogo	UG	CIP	111.056	14,6	8%

3.5.1 Australia

Global demand for Australian minerals and metals continues to rise. However, energy inputs to mining are rising, direct employment from mining is relatively low and productivity is declining. Giurco et al. (2010) avow that being Australia very dependent on mining exports, strategies to assure long-term national benefits from minerals including social, economic and environmental issues should be developed.

Australian data was compiled by Mudd (2007*b*) who asserts that industry will be challenged by declining ore grades and the increase of environmental and social costs or resource intensity. Other authors such as Prior et al. (2012) reveal that mineral production in Australia is currently unsustainable, not because of resources being finite, but because of the impacts associated with its processing and use. Notwithstanding it, commodities mining in Australia has been and continues to be a very important issue of Australian industry, representing approximately 7.7% of Australia's GDP in 2008-2009, as stated by Giurco et al. (2010).

Gold is produced in almost 30 mines, including open pit, underground and mixed. In this chapter an analysis of the influence of technical development and declining ore grades on the availability of Australian gold resources was accomplished. Obtained results suggests that although progress in technology has been made, in most cases energy requirements are increasing, because the main variable is the ore grade. Progress ratios represent the amount of improvement in mining technologies for several mines in Australia, such as Kidston, Henty, Kalgoorlie, Agnew, St Ives, Plutonic, Darlot, Lawers, Superpit, Mt. Leyshon, Tanami, Boddington, Pajingo, Sunrise Dam, Challenger, Ravenswood and Peak. Available data from 1990 through 2008, is shown in Fig. 3.3.

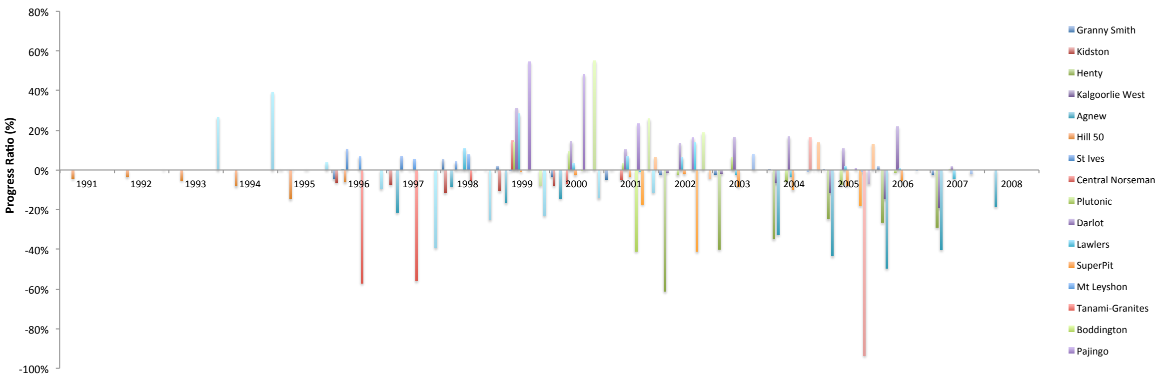


Figure 3.3: Progress ratios for gold mines in Australia.

Australia has a rising trend in energy consumption as well as in learning rates from 1857 to 2009, as shown in Figure 3.4. During this period its cumulative production was 11,565 t of gold. The general trend is a rising energy requirement throughout time, but there are some mines such as Agnew, Challenger, Plutonic, Super Pit, Fosterville, Tanami-Granites and Jundee, which show a reduction in its energy consumptions through the time. Another important issue when analyzing the energy consumption is the ore grade. As the concentration of the ore in a deposit tends to zero, the energy required to separate the substance from the mine tends to infinity. This is a consequence of the Second Law of Thermodynamics and is an empirical fact.

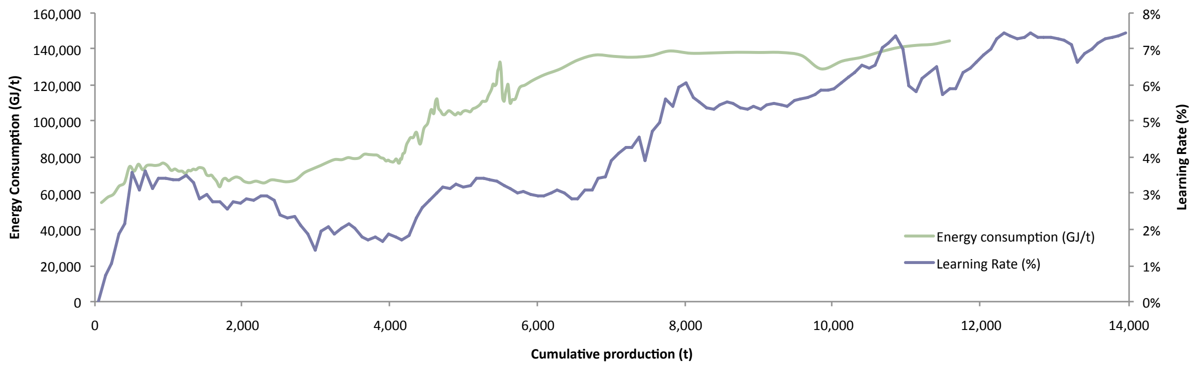


Figure 3.4: Learning curve for gold mining.

The scatter in gold data is due to factors such as the assorted configuration of gold mines (open pit, underground or mixed), the different kind of process used in the processing (heap leach versus CIP), the energy source (diesel, coal, hydro, gas or any mix between them) as well as inherent factors to each mine (project age, depth, ore types, etc.).

Hence, to analyze the real behavior of these data some differentiations between the type of mine and ore grades was carried out, in order to compare similar data, as shown in Fig. 3.5 which depicts the progress ratios classified according to ore grades and mining types.

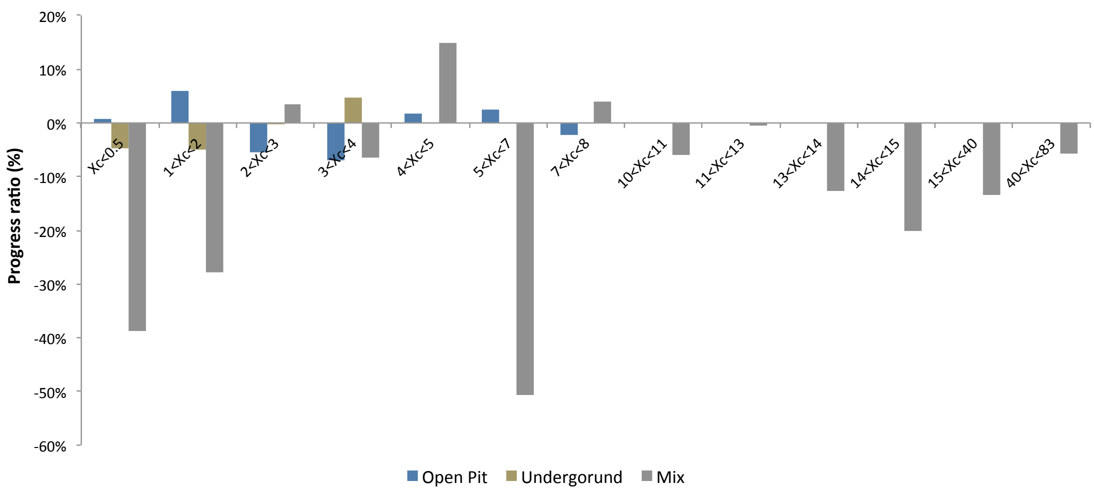


Figure 3.5: Progress ratios classified by ore grade for gold mining industry in Australia.

Furthermore, analysis taking into account variables such as: ore grade, years, mining type, primary fuel, energy consumption and cumulative production were performed. Figure 3.6 displays the aforementioned variables for an open pit mine in Australia. It can be observed that energy consumption decrease as cumulative production increase. Then, positive progress ratios were obtained from 1996 to 2007. A negative progress ratio or a reduction in progress ratios from one year to another is due to declines in ore grades.

The incoming general guidelines were obtained for the case of Australian gold mining:

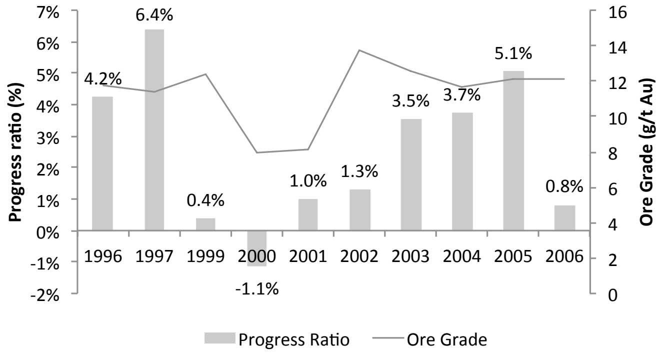


Figure 3.6: Progress ratios of an open pit mine in Australia.

1. Energy required to mining the ores is strongly related to ore grades variation and, to a lesser extent, to technological improvement.

2. The amount of improvement in mining technologies, represented in this work by the progress ratios calculated for each scope of ore grade, is not related to time, owing to the ore grade influence in progress ratios evolution. That is to say, if there are positive progress ratios over time these not necessarily increase as time goes on, because the key variable is the ore grade change.

3. Ore grades fluctuate across mines and mineral deposit regions. However average ore grades are declining, meaning that gold mining industry must shift from "simple and cheaper" to more "complex and expensive" mining methods.

3.5.2 Argentina

Gold is produced in two open pit mines; Veladero and Cerro Vanguardia. There is another important mine in Argentina named Bajo la Alumbrera in which gold and copper are produced. The Veladero mine belonging to *Barrick Company* (2013*a*) with typical ore grades under 2.5 g/t Au started its production on 2005 so it is a new mine that has been increasing its production with lower energy requirements. Hence positive learning rates are obtained when applying the learning curve approach. Otherwise, Cerro Vanguardia mine with ore grades between 7 and 8 g/t Au has been displaying a decline in its ore grade. Although cumulative production has grown, the energy per unit of gold produced has also increased and thereby negative progress ratios are presented. Available data from 2005 through 2007, is shown in Fig. 3.7.

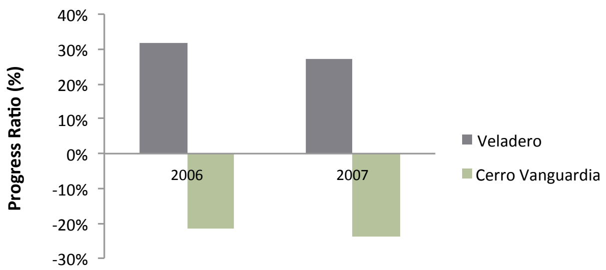


Figure 3.7: Progress ratios for gold mines in Argentina.

3.5.3 Brazil

There are two mines in which gold is extracted with an ore grade range less than 0.35 g/t Au, Maricunga and Paracatu owned by *Kinross* (2013). Maricunga mills only 35% of the total ore milled in Paracatu. In that case, the energy consumption in mining is related with quantity (cumulative production) and quality (ore grade) resulting a positive PR of 24% for Maricunga but not for Paracatu, which has a negative PR. Amapari mine owned by *Newgold* (2013) shows an improvement from 2005 to 2006 when it reduces its energy requirement almost 60% even though ore grade decreases. Hence, it presents the highest progress ratio of all mines analyzed. Available data from 2001 through 2007, is shown in Fig. 3.8.

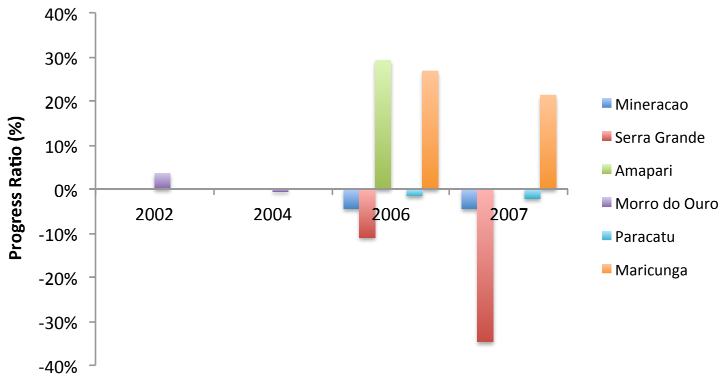


Figure 3.8: Progress ratios for gold mines in Brazil.

3.5.4 Canada

Dome-Porcupine mine belongs to *Goldcorp* (2013), these mine does not show variation in progress ratios although three situations were identified: 1) with the same ore grade in 1997 and 2005, an increment in energy consumption was presented, this can imply that there was no improvement in the process and that this increase can be caused by the deterioration in the mining equipment, 2) energy consumption can diminish although ore grade declines; for instance from 1997 to 1998, where energy reduction was influenced by the increase in the tons of ore milled, leading to a positive learning rate, and 3) the expected behavior of when ore grades decrease energy consumption increase and vice verse. Hemlo owned by *Barrick Company* (2013*a*), Musselwhite and Campbell mines belonging to *Goldcorp* (2013), show negative progress ratios as a result of ore grade declining, as well as the increment in energy consumption although ore grade remains constant.

Eskay Creek Mine belongs to Barrick's Company. This mine is a clear example of ore grade declining trend insomuch as ore grade in 2001 was 53.14 g/t Au and then in 2007 it was of 20.91 g/t Au. This situation have an effect on the energy consumption because in 2001 the energy required was 35.09 MJ/kg Au while in 2007 it reached 203.378 MJ/kg Au. Accordingly, negative progress ratios are presented. For values of ore grade between 40 and 90 g/t Au, besides Eskay Creek, there is another mine Red Lake from *Goldcorp* (2013). Available data from 1997 through 2007, is shown in Fig. 3.9.

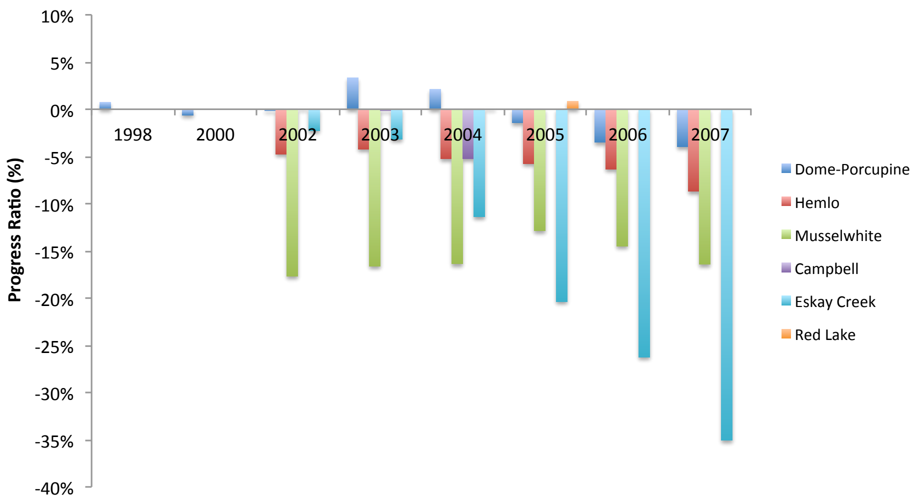


Figure 3.9: Progress ratios for gold mines in Canada.

3.5.5 Chile

Coipa mine uses conventional open pit mining methods and crushing, grinding and leaching operations to process gold (*Global Infomine* 2013). Energy consumption has been increasing over time, leading to negative progress ratios. Available data from 2003 through 2004.

3.5.6 Ghana

The main gold producing country in West Africa is Ghana. For ore grades below 1.5 g/t Au, there are two mines from Gold Fields Co.: Tarkwa Gold Mine and Damang Gold Mine owned by *Gold Fields* (2013). The first one consists of six open pits, two heap leach facilities, and a CIL plant. The operation is currently mining multiple-reef horizons from open pits and there is potential for underground mining in the future. Tarkwa has mineral resources equal to 433.75 gold tons and a mineral reserve of 280.6 tons. The second one is composed of multiple open pits, surface stockpile sources and a CIL plant, with a mineral resource of 133.2 gold tons and a mineral reserve of 59.5 tons. In accordance with the above information, it is reasonable that Damang mine has energy consumptions greater than Tarkwa mine for the same ore grade, leading to lower PR values. Furthermore, both mines show an increasing energy consumption trend under two conditions, when ore grades decrease and when cumulative production increase. Consequently, both mines have negative progress ratios, because under any circumstances there is an increase in energy consumption.

AngloGold Ashanti (2013) has two mines in Ghana: Iduapriem and Obuasi. The decrease in ore grade together with the rising energy consumption, result in negative progress ratios for both. Available data from 2004 through 2008, is shown in Fig. 3.10.

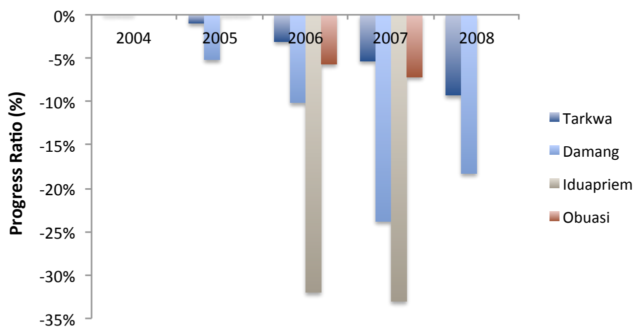


Figure 3.10: Progress ratios for gold mines in Ghana.

3.5.7 Guinea

Siguiri gold mine belongs to *AngloGold Ashanti* (2013). The annual production is 7.9 gold tons. It has a mineral resource of 138.9 gold tons and a mineral reserve of 73.7 tons. This mine fulfills the learning curve theory, since energy consumption decreases as cumulative production increases despite the ore grade is declining. Then, positive progress ratios are presented. Available data from 2005 through 2007.

3.5.8 Indonesia

Kelian Equatorial Mining is 90% owned by Rio Tinto (McGuire 2003). This open pit mine started its production in 1992 and finished it in 2004. The gold recovery process uses SAG and Ball Mills followed by gravity separation and carbon in leach (CIL) cyanidation. This mine shows a neutral PR. Available data from 2002 through 2004.

3.5.9 Laos

MMG Limited owns Seapon mine which has gold and copper operations. According to *Minmetals Resources Limited* (2013)Gold has been produced since 2002. In early 2005, an expansion of the original gold processing facility was completed doubling the capacity of the gold processing plant to 2.5 Mt/year, with a new crusher and mill allowing more flexibility and efficiency in the treatment of Seapon ore. The mine has a mineral resource of 93.5 gold tons and a mineral reserve of 5.1 tons. The Seapon gold mine is expected to be operational until 2012. There is not enough data to establish a trend in its energy consumption, then its PR is zero. Available data 2003 and 2005.

3.5.10 Mali

Sadiola Gold Mine owned by *IamGold Corporation* (2013) is operated by AngloGold Ashanti. Yatela Gold Mine performs the elution and smelting processes at the nearby Sadiola Gold mine. Morila Gold Mine is a joint venture company between Randgold (40%), AngloGold Ashanti Ltd (40%) and the State of Mali (20%) (*RandGold Resources* 2013) . During the first quarter of 2009, a successful transition was made from open pit mining to stockpile treatment. The operation is expected to come to an end in 2013 although the mine is currently investigating the opportunity to retreat the Tailings Storage Facility (TSF) material, which would extend the mine life by approximately five years. For ore grades under 3 g/t Au, energy consumption increases as cumulative production rises, leading to negative progress ratios. The positive progress ratio is due to the increment in ore grade. For the ore grades ranging between 3 and 6 g/t Au energy consumptions vary for each mine, but the general trend is a decreasing in energy consumption when cumulative production grows. Consequently, a null progress ratio is presented. Available data from 2005 through 2007, is shown in Fig. 3.11.

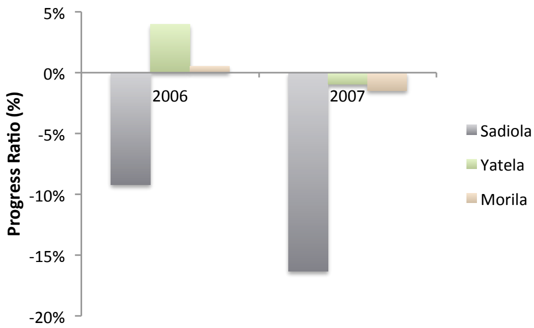


Figure 3.11: Progress ratios for gold mines in Mali.

3.5.11 Mexico

San Dimas Mine belonging to *Primero Mining* (2013) consists of five ore zones or blocks where underground gold and silver mining operations are carried out using mechanized cut-and-fill mining methods, with LHD equipment feed-ing either truck or rail haul to the mills. After milling, cyanidation, zinc precipitation and smelting, doré bars are poured and then transported to refineries in the United States. Over the last ten years investments have been made to significantly upgraded tailings management, increasing production and achieving a lower cost structure in the future. Besides, in 2005, crushing capacity was increased, as well as improvements to the chemical treatment and leaching area. Energy consumption increases although cumulative production grows and ore grade increases, but there is a change in 2005 where a reduction in energy requirements is presented despite the fact that ore grade decreases due to the improvement in the processes indicated above. Nevertheless, a negative progress ratio is presented. Available data from 2004 through 2006.

3.5.12 Namibia

Navachab gold mine recovers 85% of gold, according to *AditNow* (2013). After CIP extraction, elution and smelting, the unrefined bullion is sent to Switzerland, where it is refined. Energy consumption increase through the time due to the decline in ore grades, leading to a negative progress ratio. Available data from 2005 through 2007.

3.5.13 Peru

Pierina belonging to *Barrick Company* (2013*a*), is an open-pit mine, with truck and loader operations. Ore is crushed and transported through an overland conveyor to the leach pad area. Run-of-mine ore is trucked directly to a classic valley-fill type of leach pad. Pierina is currently engaged in energy efficiency optimization efforts which lead to decreasing energy consumptions or increasing energy efficiencies as well as reducing greenhouse gas emissions (*Barrick Company* 2013*b*). Over the last decade, improvements in the leach pad system as well as in the surface water management system have been made, as reported by *Ausenco* (2013). Despite the improvements made in the mine, energy consumptions continue growing due to the ore grade declining, leading to negative progress ratios. This can imply that technological efforts adopted by the mine are not enough to bring down the energy increasing trend. Yanacocha Gold Mine is the largest and most profitable gold mine in Latin America. It operates a complex of six open pit gold mines, five leach pads and two processing facilities. Gold is extracted from ore through a cyanide heap leach process, then the solution is treated by the Merrill Crowe process. After recovery, the contained metal is smelted and casted as bars containing 75% gold and 20% silver, according to *Mining Technology* (2013). Everything about Yanacocha facilities are enormous as well as its wealth, then this mine has the largest gold production with very low energy consumption.

Lagunas Norte mine is owned by *Barrick Company* (2013*a*). In 2006 began the development of a high grade area with a longer hauling cycle. Gold and silver are recovered in a conventional clarification and zinc precipitation circuit, using the Merrill-Crowe process. For this reason, a decrement in energy consumption from 2006 is observed, leading to a positive progress ratio, regardless the ore grade declining. Available data from 2001 through 2007, is shown in Fig. 3.12.

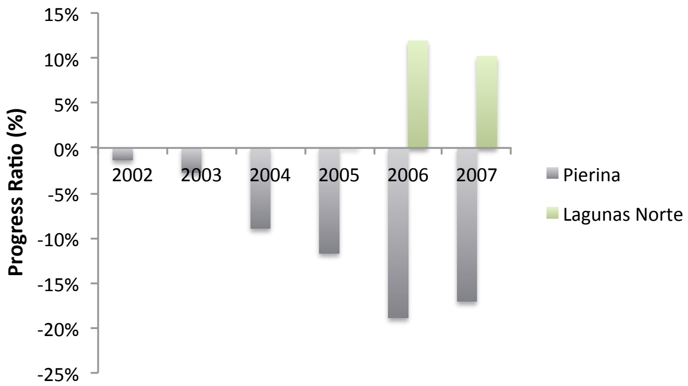


Figure 3.12: Progress ratios for gold mines in Peru.

3.5.14 Papua New Guinea

Misima gold/silver mine ends its operation in 2001 with stockpile milling anticipated to continue into 2004, as informed by *Mining Technology* (2013). Gold recovery uses a standard crushing, grinding and carbon-in-pulp (CIP) flowsheet. All data analyzed for this mine indicates that both cumulative production and energy consumption increase. Besides, ore grades are declining, resulting in negative progress ratios.

For ore grades varying between 3 and 5 g/t Au, there are two mines that are mined: Porgera and Lihir mines. Almost all data for this range is from Porgera mine, the energy consumption grows as cumulative production does, whilst progress ratios vary according to the ore grade changes. For the interval within 5 and 6 g/t Au of ore grade, Porgera mine reveals a slightly trend of ore grade decrease, whilst cumulative production increase. The result is a decreasing tendency of energy consumption prompting a positive progress ratio.

The Porgera gold mine is operated by a Barrick subsidiary. According to *Mining Technology* (2013), both open-pit and underground mining methods are employed because it was initially an underground operation until 1997, but was resumed in 2002. Additionally an open-pit mining became increasingly important from 1993. A lot of changes have been made into the mining processes. For instance, the open pit has been mined in five stages, with final-stage overburden removal taking place during 2001. The open-pit truck and shovel fleet was expanded in 1995 and 1997. Besides, in 1999 a flotation expansion was installed as well as and additional oxygen capacity to increase autoclave throughput. Run-of-mine ore is crushed and ground, then gold is recovered in a gravity circuit and flotation is used to recover a sulphide concentrate before the applying of CIP cyanide leaching process. The final step is the electrowinning process that produces bars of 88% gold average.

The Lihir gold mine is an open-pit mine consisting of two adjacent overlapping pits. Its operations include; crusher, SAG and ball mill circuit, flotation circuit, pressure oxidation and CIL processing facilities, and electrowinning and smelting facilities to produce gold dorè (*Global Infomine* 2013). Available data from 1997 through 2007, is shown in Fig. 3.13.

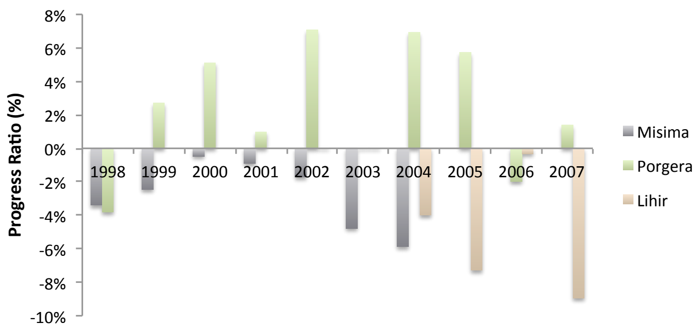


Figure 3.13: Progress ratios for gold mines in Papua New Guinea.

3.5.15 South Africa

In South Africa the data are from the following mines: Harmony Group, Vaal River, Beatrix, Driefontein, South Deep, Kloof and West Field. Gold Fields company owns Beatrix, Driefontein, South Deep and Kloof.

Beatrix Gold Mine owned by *Gold Fields* (2013) consists of four surface operating shafts that mine various gold bearing reefs from open ground and pillars. Ore is processed at two metallurgical plants, where milling, CIL process, elution and gravity circuits, electrowinning and smelting operations are carried out.

Driefontein Gold Mine owned by *Gold Fields* (2013) includes eight shaft systems that mine various gold bearing reefs from open ground and pillars. Ore extracted from the bearing reefs is processed at three metallurgical plants. It has a centralized elution and carbon treatment facility since 2001. The mineral processing technology was based on SAG milling circuit following by a cyanide leaching until the year 2003, when the-se processes were replaced by the CIP plant.

Kloof Gold Mine owned by *Gold Fields* (2013) is composed of five shaft systems and two gold plants, the gold is produced from a combination of underground mining and processing of surface waste rock dump material. For the mineral processing, two operational metallurgical facilities are used, including a central elution and smelting facility. In 2001 and ACC Pump Cell CIP circuit was installed to replace the less efficient drum filtration and zinc precipitation. Also, the upgrade included the installation of continuous electrowinning sludge reactors.

South Deep Gold Mine owned by *Gold Fields* (2013) incorporates two shaft systems that mine various auriferous conglomerates from open ground and pillars. The ore is processed at a central metallurgical plant. The mineral processing includes a milling circuit SAG, a CIP circuit, an elution system to finally recover gold by electrowinning and smelting processes.

Great Noligwa underground gold mine is situated close to the Vaal River, it comprises four gold plants, one uranium plant and a sulphuric acid plant. Great Noligwa has its own milling and treatment plant which applies conventional crushing, screening, grinding and CIL processes to threat the ore and extract the gold, as informed by *Mining Technology* (2013).

Harmony (2013) Group in South Africa include the next mines: Bambanani, Doornkop, Kusasalethu, Evander, Joel, Kalgold, Masimong, Phakisa, Phoenix, Target, Tshepong and Virginia . Sometimes the value of ore milled is too large compared with the values of other mines in the same ore grade scope. Therefore, it is probably that these data are referred to several mines. West Wits Operations include Driefontein, Kloof and South Deep.

Harmony Group reports the highest energy consumption value, leading to a negative progress ratio. For ore grades from 6 to 7 g/t Au, the only existing mine is Kloof, which shows an increase in the energy consumption for the same ore grade value from 2004 to 2008, therefore a negative progress ratio is shown. Data in the span between 8 and 9 g/t Au is from West Wits Field, even though ore grade decrease, energy consumption decrease too, leading to a null positive progress ratio. Available data from 2003 through 2008, is shown in Fig. 3.14.

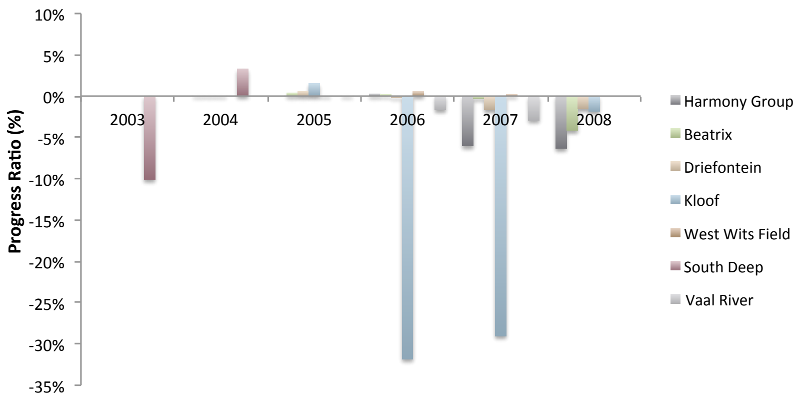


Figure 3.14: Progress ratios for gold mines in SA.

3.5.16 Tanzania

North Mara gold mine consists of three open pit deposits and belongs to Placer Dome Company. *AngloGold Ashanti* (2013) owns Geita gold mine, which began production in 2000. Geita is a multiple open-pit operation with underground potential. For ore grades between 3 and 5 g/t Au, most of the data is from North Mara, during 2003 and 2004 the ore grade is the same but the energy consumption differ greatly, almost by a 50%, the same situation is repeated for years 2005 and 2007, despite of the-se observations, there is a declining trend in energy consumption, resulting in a positive progress ratio of 12%.

Tulawaka Gold mine consists of a completed open pit mine with an underground access ramp, an ore stockpile area and crushing plant, a processing plant. The ore processing method includes SAG, gravity recovery and CIL (*Global Infomine* 2013). It is the only mine which report data in the span of 9 and 14 g/t Au, within this large ore grades the energy consumption falls as cumulative production increase, hence a positive progress ratio of 11% is shown.

Bulyanhulu Mine is owned by Barrick Gold Corp. Bulyanhulu is an underground trackless operation using long hole and drift and fill as its principal toping methods (*Gold mining in Tanzania* 2013). It shows a clear downtrend in ore grade that results in an energy consumption increase as cumulative production rises. However, due to the fact that ore grade vary from one year to another without a clear trend of increase or de-crease and this variation is not significant, the progress ratio is positive. Available data from 2001 through 2007, is shown in Fig. 3.15.

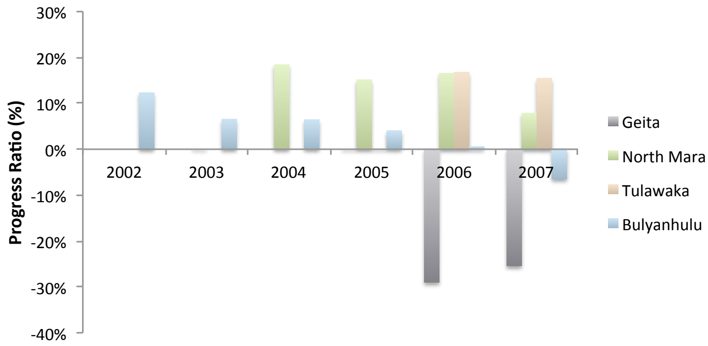


Figure 3.15: Progress ratios for gold mines in Tanzania.

3.5.17 United States

Barrick Company (2013*a*) in USA owns several mines. Bald Mountain mine is an open pit, run-of mine with conventional heap leaching technology and carbon absorption for ore treatment. Cortez mine is mined by conventional open-pit methods. It employs three different metallurgical processes to recover gold. Lower-grade oxide ore is heap leached, while higher grade ore is treated in a conventional mill using cyanidation and a CIL process. Heap leached ore is hauled directly to leach pads for gold recovery.

Golden Sunlight mine is mined by conventional open-pit methods. The ore treatment plant uses conventional CIP technology as well as San Tailing Retreatment (SRT). Goldstrike complex includes an open pit mine and two underground mines. The open pit is a truck and shovel operation using large electric shovels. While one of the underground mines is a high grade ore body which is mined by transverse longhole stoping, underhand drift and fill mining methods, while the other is a trackless operation, using two different underground mining methods: longhole open stoping and drift and fill. Also, it consists of two processing facilities that are used for both the surface and underground operations: (1) an autoclave circuit and (2) the roaster.

Marigold mine is an open-pit operation that uses heap-leaching to process its ore. Round Mountain mine is a conventional open-pit operation that uses multiple processing methods including crushed ore leaching, run of mine ore leaching, milling of higher grade ore and the gravity concentration circuit.

Turquoise Ridge mine uses underhand cut and fill mining methods. Ore is transported to an external mill for processing. The refractory gold ore is treated by pressure oxidation technology and gold is recovered using conventional CIL technology.

Cripple Creek Victor JV gold mine is a low-grade, open pit operation. The ore is treated using a valley-type, heap leach process with activated carbon used to recover the gold. The resulting doré buttons are shipped to a refinery for final processing, according to *Mining Technology* (2013).

Fort Knox mine belonging to *Kinross* (2013) is an open pit mine, that uses as processing methods CIP mill, heap leach and gravity. According to *Mining Technology* (2013), production from heap leach began in late 2009. Ridgeway underground mine produces gold and copper. It is in the process of transitioning from the sub-level cave to a block cave beneath the existing mine. Crushed ore from the underground is delivered by conveyor to a surface stockpile; then, gold and copper are recovered in a conventional floatation circuit to produce a copper concentrate containing elevated gold levels. The next step is to pump to the filtration plant where it is dewatered prior to being transported to export to smelters throughout East Asia.

Wharf owned by *Goldcorp* (2013) is an open pit and heap leach mine that has been in operation since 1983. *Global Infomine* (2013) state that Barneys Canyon gold mine is an open pit mine that started production in 1989. Mining and milling ended in 2001. Gold production from stockpiles continued until 2005. The Kettle River-Buckhorn gold mine belonging to *Kinross* (2013), was originally conceived as an open pit mine, but then it was redesigned and developed as an underground mine. The primary mining method employed is cut and fill. Its ore is processed through milling, flotation and CIP processes. Pogo gold mine is an underground mine that utilizes a cut and fill drift method. The milling operation includes grinding, sulfide flotation, paste thickening, leach/CIP, cyanide detoxification, tailings filtration and gravity recovery (*Global Infomine* 2013).

Open pit mining in USA is characterized by negative progress ratios, but underground mining using CIL and CIP shows positive progress ratios. Available data from 2002 through 2007, is shown in Fig. 3.16.

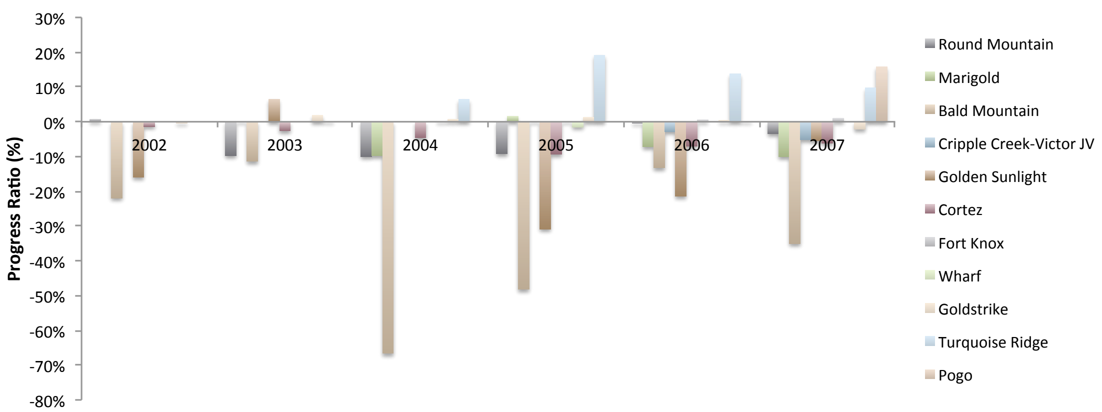


Figure 3.16: Progress ratios for gold mines in United States of America.

3.6 Progress ratios in the gold mining industry

Assuming that all mines of the same kind of operation as well as recovery process for a specific country are comparable, progress ratios can be presented as Fig. 3.17 displays. Average progress ratios obtained between different operation and recovery processes ranged from + 20% to – 22%.

Australia has an excellent progress ratio when CIP technology is used either in open pit or underground mines. This can imply that gold mining industry in Australia has overcome the declining in ore grades through technological learning. A compilation of the best practices and all mining process in general would be very useful for mines using the same recovery process around the world. The sharing of operational and technical experiences, with countries such as Papua New Guinea would be an excellent way to improve the efficiency in the gold mining sector.

For the United States, positive progress ratios can be observed when underground mining is performed (either when CIP or CIL process are applied). Hence, the relevant fact here is the kind of mining operation used: underground. Performance benchmarking of gold mines in Canada can be a worthwhile action to improve practices in the gold mining industry.

In South America, countries like Argentina and Brazil show great positive progress ratio when operations in open pit mines with heap in leach technology as recovery process is employed. Again, it would be very useful an extended compilation of their best practices in order to share this information with countries that have mines with the same geological and technological characteristics, such as mines in Peru.

3.7 Summary

In this chapter the influence of technical development and declining ore grades on the availability of world gold resources has been studied, applying the learning curves approach and estimating progress ratios for each country. The latter allowed to identify mines in which mining operations have proved to be successful when the goal is to save energy. Therefore these estimates can be used to point out best mining practices and serve as a reference for other mines with similar conditions. Results for Australia gold mining industry were published in Valero, Valero & Domínguez (2011), afterwards results for global gold mining were published in Domínguez & Valero (2013).

It should be pointed out, that the improvement in mining technologies, represented in this survey by the progress ratios calculated for different countries, mines operations and recovery processes are not related to time or cumulative production as it happens to conventional applications (such as manufacturing) when the theory of learning curves is applied. In the mining sector, an additional factor needs to be taken into account, and that is the key variable ore grade change. The learning effect is measured in terms of reduction in the energy requirements of mining operations. This way, an improvement in the energy efficiency of the processes does not necessarily imply an overall energy reduction, since the decrease in the ore grade may dominate.

General results suggest that although progress in technology has been made, in most cases energy requirements are increasing, because the main variable is the ore grade. Therefore, it can be asserted that technology cannot in general avert the rising energy demand for gold mining

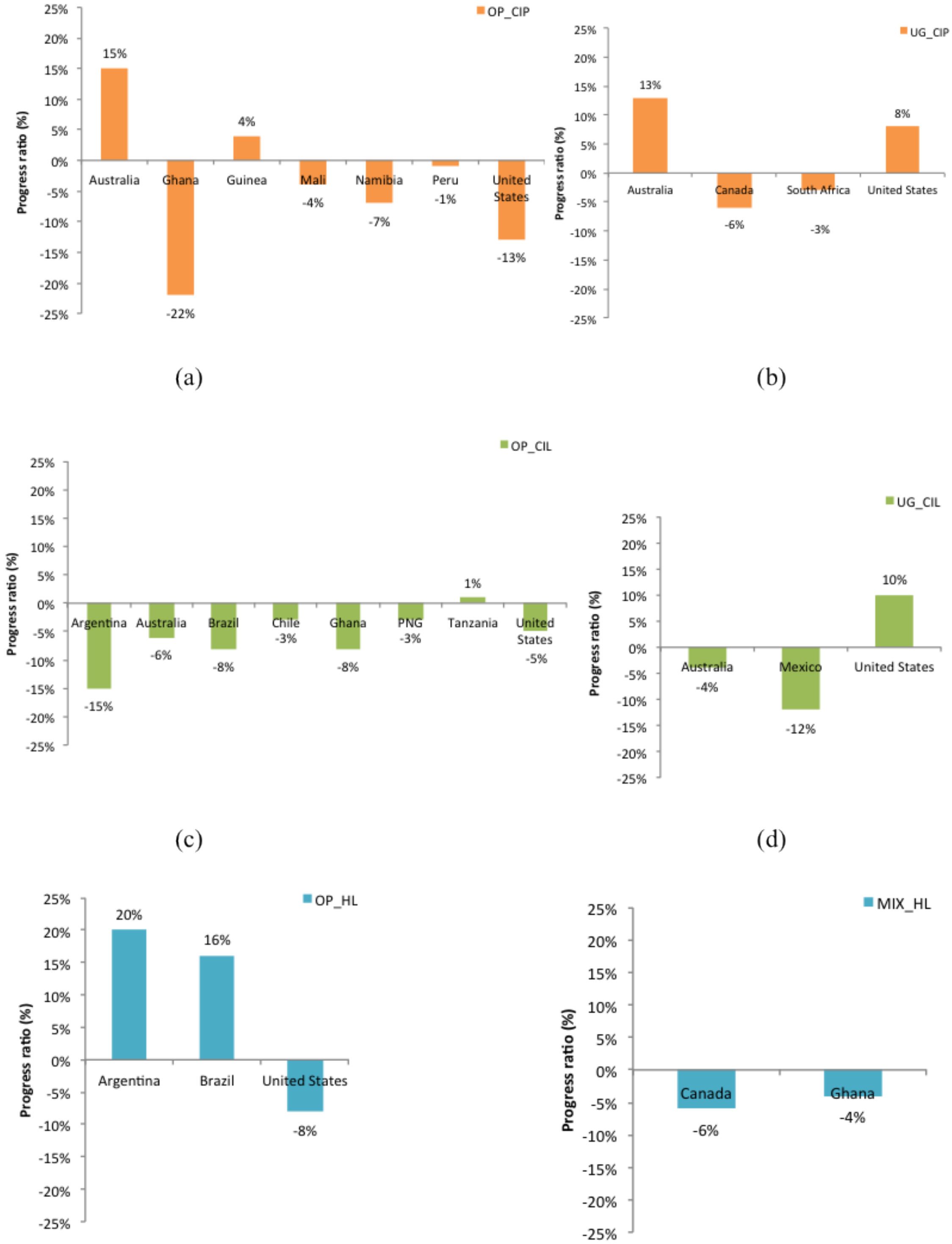


Figure 3.17: Progress ratio for different recovery process and countries in gold mining industry.

in the future if no major changes are performed in gold mines around the world. Hence, energy consumptions will continue to increase threatening the capability to fulfill the prospective demand.

It is crucial to analyze carefully those countries that are and will be the major gold producers such as Australia, South Africa, Russia, Chile, United States and Indonesia. The data analyzed reveals that South Africa and Australia show the greatest energy consumptions and hence should increase their efforts in improving their mining practices. Additionally, due to the strategic position of China in the gold mining industry, analyzing its data sets in energy consumptions and ore grades would be also very interesting and profitable.

This analysis allow us to have a more suitable understanding of the mining sector and the outcomes of technology evolution together with ore grade declining. Furthermore, this analysis lets us understand the general trends in resource consumption in the mining industry by means of identifying best mining practices around the world. Learning models can be used to survey the effect of policies and research and development resources applied in the mining sector in order to accelerate technical progress. Nevertheless, the accuracy of the estimated learning rates and progress ratios remains a major issue.

This chapter closes the analysis of energy consumption in the mining industry performed in this thesis. Hence, the next chapter presents an overview of thermodynamics and the methodologies that can be used to analyze mining industry from a thermodynamic point of view.

Chapter 4

Thermoeconomic Analysis

The aim of this chapter is to provide the thermodynamic background to assess mineral resources and their corresponding mining and metallurgical processes. Particularly, it introduces Thermoeconomics, the Thermoecological cost and the Exergoecological approach, which will be later combined so as to adequately cover the requirements of the mining industry.

4.1 Thermodynamics and the evaluation of natural resources

The use of thermodynamics to evaluate natural resources began with Georgescu-Roegen (1971) who draw on the idea of entropic degradation as a fundamental restriction for economic activity. He pointed out that the increasing rates of extraction of natural resources, leads to the entropic degradation of the earth. Afterwards, authors such as Naredo (1987) and Cleveland & Ruth (1997) studied the implications for material and energy use in economic development and the ecological systems, taking into account thermodynamic constraints. Within this research line, in Naredo & Valero (1998), Valero proposed a new approach to calculate the exergy replacement cost of natural resources. This method based on exergy has led several research works which in turn have given birth to two new disciplines: Physical Hydronomics and Physical Geonomics.

The former is concerned with water analyzes. The first study on this topic was performed by Zaleta et al. (1998), who applied the methodology to the water of a river. Martinez (2009) refined the methodology for undertaking exergy cost assessments of water bodies. Physical Geonomics meanwhile, is concerned with mineral analysis. In this respect, an exergy cost analysis of the Earth's mineral wealth was firstly accomplished by Ranz (1999). Later on, Botero (2000) carried out an exergy assessment of natural resources (including minerals, water and fossil fuels) and Valero Delgado (2008) performed a research work focused on the exergy evolution of the mineral capital on Earth which has led to many publications in this field (see section 4.6). This thesis continues with this research line with the aim of addressing unresolved issues that remained open in Valero Delgado (2008) such as the assessment of the exergy cost and ore grade in global mining.

A brief review of thermoeconomic concepts taken from Valero & Lozano (1994) are presented in the next section, so as to give an overview of the different tools used in this thesis.

4.2 Fundamentals of Exergy Analysis and Thermoeconomics

The exergy analysis is based on both the first and second laws of thermodynamics. Its aim is to calculate the useful energy associated with a thermodynamic system or with each flow stream in a given process, thereby identifying and evaluating the inefficiencies of the system. Exergy analysis provides two important messages: one is that it allows quantifying and locating thermodynamic losses. The second is, it allows to concentrate on the relevant part of the energy, namely "useful" energy. These analyzes can solve problems related to complex energy systems that could not be solved by using conventional energy analyzes.

Nevertheless, exergy analysis (Thermodynamics) is necessary but not sufficient to determine the origin of losses and the potential for energy saving as will be see in the next sections. Accordingly, it is necessary to include the concept of purpose (Economics) by means of the definition of efficiency. Exergy efficiency compares the performance of a real process to an ideal one of the same type. The conceptual link between these two disciplines is Thermoeconomics, which is a general theory for energy saving, that integrates thermodynamics (exergy analysis) and economics (exergy cost) by means of the Second Law, for the analysis, optimization and diagnosis of complex energy systems Lozano & Valero (1993). In this kind of systems, energy flows are easily converted into exergy ones and their value is an indication of quality. Among other applications, thermoeconomics is used for:

- Rational prices assessment of plant products based on physical criteria.
- Optimization of specific process unit variables to minimize the final product cost, i.e. global and local optimisation.
- Detection of inefficiencies and calculation of their economic effects in operating plants, i.e. plant operation thermoeconomic diagnosis.
- Evaluation of various design alternatives or operation decisions and profitability maximization.
- Energy audits.

4.2.1 Exergy

As already explained, exergy is an adequate thermodynamic property to account for energy quality. The exergy of a thermodynamic flow is the minimum amount of technical work needed for its production, from a given reference environment. Exergy provides a thermodynamic value of any energy stream with respect to reference conditions, and can be rigorously obtained from the laws of thermodynamics, which allows precise measurements. Valero & Torres (2004) argue that exergy may be regarded as a measure of the capacity of a given form of energy to produce work and is reasonable to assess the price of energy products on the basis of its exergy content.

Exergy is also a worthwhile concept in Economics. Exergy puts forward an approach to assess resource depletion and environmental destruction. Szargut (1993) pointed out that "the concept of exergy is crucial not only to efficiency studies but also to cost accounting and economic analysis". Hence, exergy is a pragmatic tool for evaluating: fuels and resources, process, devices and system efficiencies and their costs, as well as the value and cost of systems outputs.

In the absence of nuclear, magnetic, electrical, and surface tension effects, the exergy B can be divided into four components: physical exergy B^{PH}, kinetic exergy B_K, potential exergy B_P and chemical exergy B_{CH}, that is:

$$B = B^{PH} + B^K + B^P + B^{CH} \tag{4.1}$$

The sum of the kinetic, potential, and physical exergies is also referred to as thermo-mechanical exergy.

4.2.2 Exergy balance

Conventional thermodynamics states that the exergy balance accounts for the degradation of the exergy. The incoming exergy will be always greater than the outgoing one:

Exergy Input - Exergy Output = Irreversibilities > 0

As stated in Valero, Uson, Torres & Valero (2010), this expression only points out the existence of irreversibilities within the process. However, Thermoeconomics includes in the equation the concept of purpose by means of an efficiency definition. There is an implicit classification of the flows crossing the boundary of the system: the production objective, P, the resources required to carry out the production, F, and those that are residuals or wastes, R. Nonetheless, resources cannot just be associated with input flows, nor the products with output flows. It is necessary to have a clear idea of what is to be produced before the definition of the efficiency. This way, the exergy balance now becomes:

Ex. Resources(F) - Ex. Products(P) = Ex. Wastes(R) + Irreversibilities(I) > 0

$$F - P - R = I > 0 \tag{4.2}$$

And the process efficiency is defined as:

Efficiency = Ex. Product / Ex. Resources

$$\varepsilon = \mathrm{P/F} \tag{4.3}$$

Efficiency measures the quality of a process. This is to say, there is an implicit classification of the flows crossing the boundary of the system, the flows that are the production objective, and those that are the resources required to carry out the production. Since the exergy of resources is greater than that of the products, this efficiency is always positive and less than one.

4.2.3 Exergy Cost

The *exergy cost* concept proposed by Valero et al. (1986) can be defined as the sum of all resources required to build a product from its component parts, expressed in exergy units. The exergy cost of a mass or energy stream is the amount of exergy required to produce it. Almost simultaneously Szargut & Morris (1987) proposed the *cumulative exergy consumption* theory (see Section 4.4). Both concepts represent embodied exergy. In fact, the exergy cost is isomorphous with the Input-Output analysis (see Appendix B).

The unit exergy cost of a mass or energy stream represents the amount of exergy required to obtain a unit of exergy of the product stream. If B_i represents the exergy of the *i-th* product stream and B_i^* its exergy cost, the unit average exergy cost is written as:

$$k_i^* = \frac{B_i^*}{B_i} \tag{4.4}$$

The physical cost measured in exergy units of all manufactured products as well as the exergy needed for their use, maintenance, repair and disposal is named Exergy Life Cycle Assessment and provides average exergy costs because it is focused in obtaining round numbers which could be used as ecological indexes of sustainability.

4.3 Thermoeconomic Input-Output Analysis

Thermoeconomic Input-Output Analysis is a methodology for the analysis of the productive structure, and the natural resources consumption process in energy systems. According to Torres (1991) it appears as a technique, based on the Exergy Cost Theory, to obtain general equations, which relate the overall efficiency of an energy system and other thermoeconomic variables as fuel, product, exergy cost, with the efficiency of each component which forms it. By means of the equations obtained, it is possible to analyze the influence of the individual consumption of each component on the total amount of external resources required to obtain a product.

This approach is based on the Input-Output analysis explained in Appendix B. In thermoeconomics, the input-output table is transformed into a Fuel-Product model, in which the Second Law of Thermodynamics is used in the analysis of the processes. The Fuel-Product table (see Table 4.1) represents the productive structure which shows the resources distribution throughout the plant. The rows represent the destination of the production of each component: as fuel of other components, as disposable waste, or as a primary product of the system. The first row represents the external resources entering the system. Meanwhile, the columns represent the source of the fuel of each component: either coming from the production of other components or as resources coming from outside the boundaries of the system.

Table 4.1: Fuel-Product Table

			Process Resources					
		Final Product	1	$\cdots$	j	$\cdots$	n	Total
External Resources			B_{01}	$\cdots$	B_{0j}	$\cdots$	B_{0n}	P_0
	1	B_{10}	B_{11}	$\cdots$	B_{1j}	$\cdots$	B_{1n}	P_1
	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
Process Products	i	B_{i0}	B_{i1}	$\cdots$	B_{ij}	$\cdots$	B_{in}	P_i
	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
	n	B_{n0}	B_{n1}	$\cdots$	B_{nj}	$\cdots$	B_{nn}	P_n
Total		F_0	F_1	$\cdots$	F_j	$\cdots$	F_n	

According to this representation, the production of a productive component is used as fuel of other components or as a primary product of the system. Mathematically, this could be expressed as the sum of the element of each fuel-product table row:

$$P_i = B_{i0} + \sum_{j=1}^{n} B_{ij}, \qquad i = 1, \cdots, n \tag{4.5}$$

where P_i is the exergy of the process i production, which is used in part to meet the intermediate requirement as input resources of other process and in part to meet the final demand of the system, B_{ij} is the exergy of process i uses as a resource for process j, E_{0i} is the exergy of process i uses as a resource for the final product coming from the exergy of environment 0. Otherwise, the resources entering each component, could be expressed as:

$$F_i = B_{0i} + \sum_{j=1}^{n} B_{ji}, \qquad i = 0, 1, \cdots, n \tag{4.6}$$

where F_i is in part coming from external resources, say B_{0i}, entering to the system, which go into the i^{th} component. Therefore, the total product and fuel of the system could be expressed as:

$$P_T \equiv F_0 = \sum_{j=1}^{n} B_{j0} \tag{4.7}$$

$$F_T \equiv P_0 = \sum_{j=1}^{n} B_{0j} \tag{4.8}$$

The fuel and product Eqs. (4.5 - 4.6) could be rewritten in terms of exergy cost as:

$$P_i^* = B_{i0}^* + \sum_{j=1}^{n} B_{ij}^*, \qquad i = 1, \cdots, n \tag{4.9}$$

$$F_i^* = B_{0i}^* + \sum_{j=1}^{n} E_{ji}^*, \qquad i = 0, 1, \cdots, n \tag{4.10}$$

where B_{ij}^* denotes de exergy costs of the flow B_{ij}, and P_i^* and F_i^* are the cost of product and fuel of process i, respectively.

The Fuel-Product model provides two possible representations, the Demand driven model, from product to fuel (PF) and the Supply driven model, from fuel to product (FP), introduced in next sections.

4.3.1 The Demand Driven Model

The analysis of any system requires studying the behavior of the productive structure as a function of the total production or demand objectives. The demand driven model relates the thermoeconomic variables of the system with the total plant product, the efficiency of its components, and a new type of parameter called junction ratio.

The junction coefficients r_{ij}, are the portion of the resources of the j^{th} component coming from the i^{th} product, expressed as:

$$r_{ij} = \frac{B_{ij}}{F_j} \tag{4.11}$$

that verifies the sum of all junction ratios of a component is equal to one:

$$\sum_{i=0}^{n} r_{ji} = 1 \tag{4.12}$$

Applying Eq. 4.11 to Eq. 4.5 could be written as:

$$P_i = B_{i0} + \sum_{j=1}^{n} r_{ij} P_j \qquad i = 1, \cdots, n \tag{4.13}$$

As stated by Valero, Uson, Torres & Valero (2010), the exergy balance expressed by Eq. 4.2, is the point in understanding the difference between the Input-Output quantity model and the Thermoeconomic approach. The only numeraire (kg, m^3, kJ, ...) defining F, P and R that satisfies the Second Law Analysis is exergy. Since all elements in the fuel-product table are measured in the same quantity exergy, it is possible to add not only the rows (products) but also columns (fuels) for each component and compare them.

In matrix notation, Eq. 4.13 may be compacted and expressed as:

$$P = P_s + \langle KP \rangle P \tag{4.14}$$

The vector P_s $(nx1)$ contains the exergy values of the final product obtained in each component, and $\langle KP \rangle$ is a (nxn) matrix which elements are the junction coefficients r_{ij}. The matrix $\langle KP \rangle$ is, in the input-output methodology, the matrix of direct requirement (**A**) because it shows the quantity of product i required directly in the production of one unit of process j, and the technical coefficients could also be considered as unit exergy consumptions.

Therefore, the production of each process could be expressed as:

$$P = |P\rangle P_s \qquad where \qquad |P\rangle = (U_D - \langle KP \rangle) \tag{4.15}$$

The matrix $|P\rangle$ is called, in the input-output methodology, the *Leontief inverse matrix* (**L**), and its elements, say p_{ij} represents the total production requirement of process i in the production of a unit of process j, both direct and indirect.

The cost of the resources used in each component is given by:

$$\mathbf{k}_P^* = \langle KP \rangle \mathbf{k}_P^* + \kappa_e \tag{4.16}$$

where κ_e is a $(nx1)$ vector that represents the known cost of the external resources entering the components. Likewise, the unit exergy cost of each process as a function of the local unit exergy consumptions of all the processes of the system is:

$$\mathbf{k}_P^* = {}^t|KP\rangle \kappa_e \tag{4.17}$$

In the input-output methodology presented in Appendix B, κ_e corresponds to b, whilst $\mathbf{k}_P^*$ is the unit cost c.

4.3.2 The Supply Driven Model

The supply driven model allows to obtain all flows of the productive structure of the system starting from the external resources, those consumed by the system from the environment.

It is based on the distribution coefficients y_{ij}, which are the portion of the production of the j^{th} used as resources in the i^{th} component, expressed as:

$$y_{ij} = \frac{B_{ji}}{P_j} \tag{4.18}$$

and verifies that the sum of all distribution ratios of a component is equal to one:

$$\sum_{i=0}^{n} y_{ji} = 1 \tag{4.19}$$

Applying Eq. 4.18 to Eq. 4.6 could be written as:

$$F_i = B_{0i} + \sum_{j=1}^{n} y_{ij} P_j \qquad i = 1, \cdots, n \tag{4.20}$$

The previous Eq. 4.20 could be written in matrix notation as:

$$F = F_e + \langle FP \rangle P \tag{4.21}$$

The vector F_e $(nx1)$ contains the exergy values of the external resources for each component, and $\langle FP \rangle$ is a (nxn) matrix which elements are the distribution coefficients y_{ij}.

Therefore, the production exergy cost of all the process of the system, as a function of the external resources and the distribution ratios, could be expressed as:

$$P^* =^t \langle P^* | F_e \qquad where \qquad \langle P^* | = (U_D - \langle FP \rangle)^{-1} \tag{4.22}$$

4.4 Thermoecological Cost (TEC)

In this section the Thermo-ecological cost method is introduced, which will be used in Chapter 6 to analyze the mineral processing of several metals. The Thermo-ecological cost derives from Szargut et al. (1988*a*) where the *cumulative exergy consumption* concept is defined as the cumulative consumption of non-renewable exergy connected with the fabrication of a particular product with additional inclusion of the consumption resulting from the necessity of compensation of environmental losses caused by rejection of harmful substances to the environment. The thermo-ecological cost is in essence the same concept of the exergy cost proposed by Valero et al. (1986) which can be defined as the sum of all resources required to build a product from its component parts, expressed in exergy units.

The TEC index is calculated by solving a system of linear input-output equations (Eq.4.23), in order to determine the exergy cost for the j^{th} process within the bounds defined by the process under study as Fig. 4.1 depicts. It should be noted that in the case of TEC the boundary reaches up to natural resources deposits.

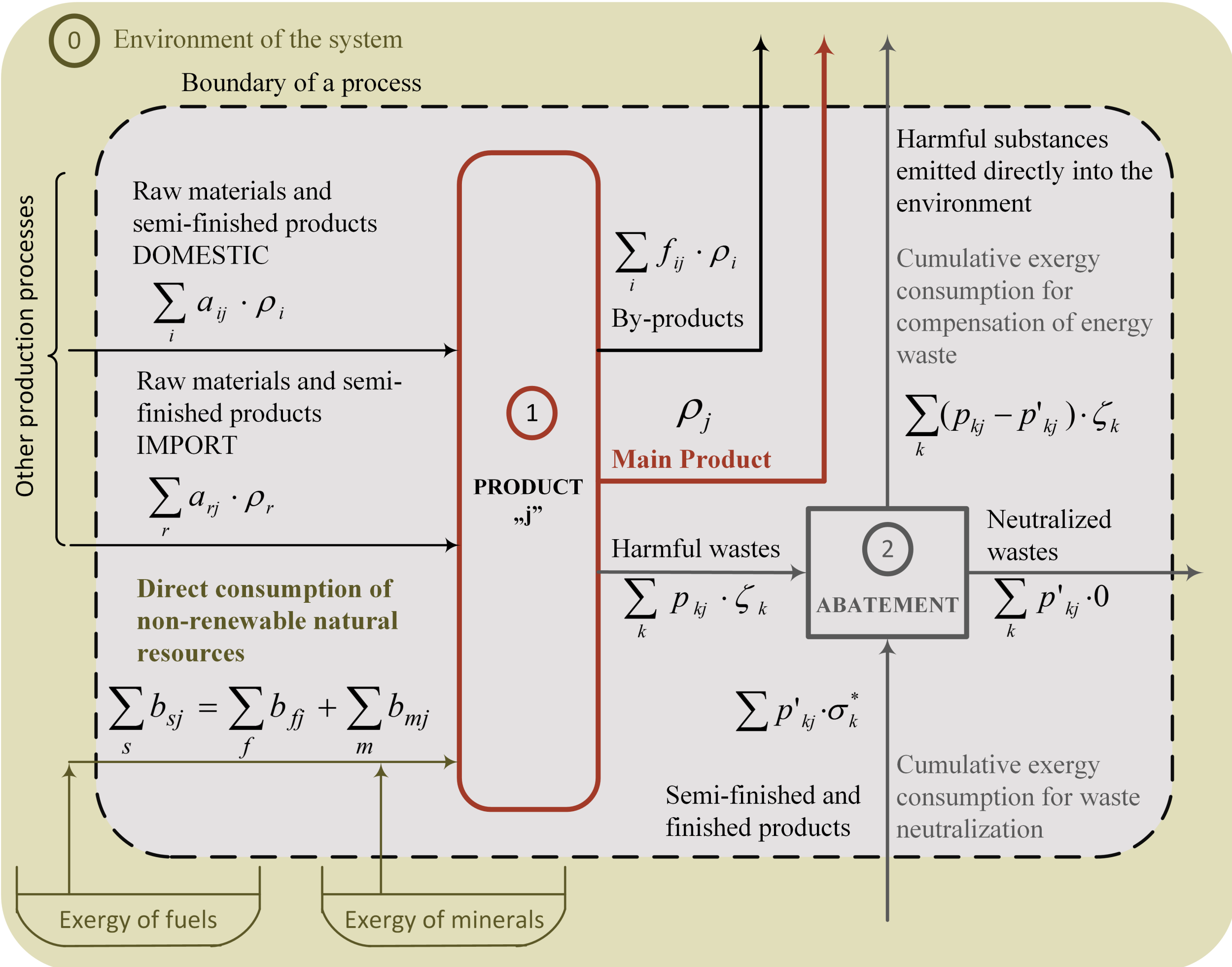


Figure 4.1: TEC balance equation. Piekarczyk et al. (2012).

Recently, the TEC methodology has been further developed in Szargut et al. (2002). This new approach states that differentiation between the TEC resulting from fuel or non-fuel mineral resources is worthy. This is because fuel resources could be substituted by renewable natural resources, yet non-fuel minerals cannot be easily replaced by any other resource. Moreover, it is important to keep in mind that current technology allows only for partial substitutions of fuel and material resources, whilst recycling processes allows to recover only some of the mineral resources at their end of life.

The first set of equations used to perform the balance of Thermo-Ecological Cost for a system, like the one presented in Fig. 4.1, is expressed as:

$$\rho_j + \sum_i (f_{ij} - a_{ij})\rho_i = \sum_f b_{fj} + \sum_m b_{mj} + \sum_k p_{kj}\zeta_k \tag{4.23}$$

where ρ_j is the specific TEC of a main product j^{th} of the considered process, ρ_i is the specific TEC of a raw material or semi-finished product i^{th} of the considered process, f_{ij} is the coefficient of production of the i^{th} by-product per unit of the j^{th} main product, a_{ij} is the coefficient of consumption of the i^{th} raw material and semi-finished product per unit of the j^{th} main product, b_{fj} is the exergy of the fuel ($_f$) and b_{mj} is the exergy of the mineral ($_m$) immediately extracted from nature per unit of the j^{th} main product, p_{kj} is coefficient of the production of the k^{th} rejected harmful waste product per unit of the j^{th} main product, and ζ_k is the TEC of compensation of the deleterious impact of the k^{th} rejected waste product.

Distinctness of the TEC into a fuel part TEC_f and mineral part TEC_m allows to identify the kind and amount of exergy consumed in the course of the production process. Accordingly, it is necessary to include a second set of equations used to determine the fuel part of TEC through the expression:

$$z_j \rho_j + \sum_i (f_{ij} - a_{ij}) z_i \rho_i = \sum_f b_{fj} + \sum_k p_{kj} z_k \zeta_k \tag{4.24}$$

where z_j is the fraction of TEC of a main product j^{th} due to fuel consumption and z_i is the fraction of TEC of a raw material or semi-finished product i^{th} due to fuel consumption. The fraction of TEC of a raw material or semi-finished product i^{th} due to mineral consumption does not appear in Eq. 4.24 because this equation is evaluating only the fuel part. Hence, the fraction of TEC of a main product j^{th} due to mineral consumption will be the difference (1-z_j), whilst (1-z_i) will be the fraction of TEC of a raw material or semi-finished product i^{th} due to mineral consumption.

Szargut (1986) proposed that the TEC part due to rejections of harmful substances to the natural environmental can be assessed by means of:

$$\zeta_k = \frac{B w_k}{GDP + \sum_k P_k w_k} \tag{4.25}$$

where ζ_k is the Thermo-Ecological Cost due to the emission of a unit of the k^{th} waste product, B is the exergy extracted per year from the domestic non-renewable natural resources, w_k is a monetary index of harmfulness of k^{th} substances, GDP is the Gross Domestic Product and P_k is the nominal flow rate of the k^{th} deleterious waste product rejected to the environment.

Finally, the TEC can be the basis for determining the index of sustainability which expresses the ratio between Thermo-Ecological Cost of the useful i^{th} product and its specific chemical exergy:

$$r_i = \frac{\rho_i}{b_i} \tag{4.26}$$

A lower index of sustainability means fewer cumulative exergy consumption of natural resources per unit of exergy of a given useful product. Accordingly, the lower the index of sustainability, the better the product from an ecological point of view.

4.5 Similarities and differences between Thermoecological Cost and Thermoeconmic Input-Output Analysis

As aforementioned, the *exergy cost* proposed by Valero et al. (1986) in their "General Theory of Exergy Saving" can be defined as the amount of exergy required to produce a mass or energy stream. Whilst, the *thermoecological cost* proposed by Szargut & Morris (1987) almost simultaneously in their "Cumulative Exergy Consumption Theory" can be defined as the cumulative consumption of non-renewable exergy connected with the fabrication of a particular product. Basically, both concepts represent embodied exergy.

The *Thermoeconomic Input-Output Analysis* is in essence the same concept of the *Thermoecological Cost*, which can be defined as the sum of all resources required to build a product from its component parts, expressed in exergy units. In fact both are isomorphous with the Input-Output analysis (see Appendix B) as described in section 4.3.

The Eq. 4.13 from thermoeconomic input-output analysis, expresses the same that Eq. 4.23 from the thermoecological cost. Here, the exergy of the process P_i is equivalent to the specific thermoecological cost ρ_j. Whilst the specific TEC of a raw material or semi-finished product i^{th} of the considered process ρ_i is analogous to P_j. The exergy of the fuel b_{fj} and the exergy of the mineral b_{mj} in the TEC methodology correspond to the exergy of process i coming from the exergy of environment E_{0i}. Finally, the junction coefficients r_{ij}, are the coefficient of consumption a_{ij} of TEC.

Both, the exergy of the process P_i calculated through the Thermoeconomic Input-Output analysis and the Thermoecological cost ρ_j, account for the by-products or wastes obtained in a system. The Thermoecological cost perform this analysis through the coefficients of production of the i^{th} by-product per unit of the j^{th} main product, f_{ij}. The Thermoeconomic Input-Output analysis meanwhile has been applied to develop a method for the allocation of the cost of wastes, presented in Agudelo, Valero & Torres (2011). Besides, both methodologies analyze the emissions related to the use of fossil fuels. The Thermoecological cost has an additional inclusion of the consumption resulting from the necessity of compensation of environmental losses caused by rejection of harmful substances to the environment. The Thermoeconomic Input-Output analyze carbon emissions through the abatement costs (Agudelo, Valero & Uson 2011). The latter methodology allows to perform an exergy decompostion in order to know the contributions of every external resource to each stream of a system, revealing how energy resources are used along productive processes. In the same way, the Thermoecological cost method performs a differentiation between the TEC resulting from fuel or non-fuel mineral resources. However, the TEC can be applied on a regional scale, involving the thermo-ecological cost associated with the imported raw materials and semi-finished products.

When the analysis of any system is performed, the matrix system obtained from the Thermoeconomic Input-Output Analysis can be solved using an Excel spreadsheet. Whilst, the system of linear input-output equations derived from Thermoecological Cost Analysis requires a software package used for solution of systems of equations, like EES (Engineering Equation Solver), Matlab, etcetera.

4.6 The exergoecology approach and the degraded Earth Thanatia

The methodologies presented in the previous sections allow to analyze the path "cradle to grave" in a LCA of mining industry, because processes such as raw material extraction, refining, product manufacturing, recycling and disposal can be evaluated. Nevertheless, the "grave to cradle" path still needs to be assessed for an absolute LCA (see Fig. 4.2).

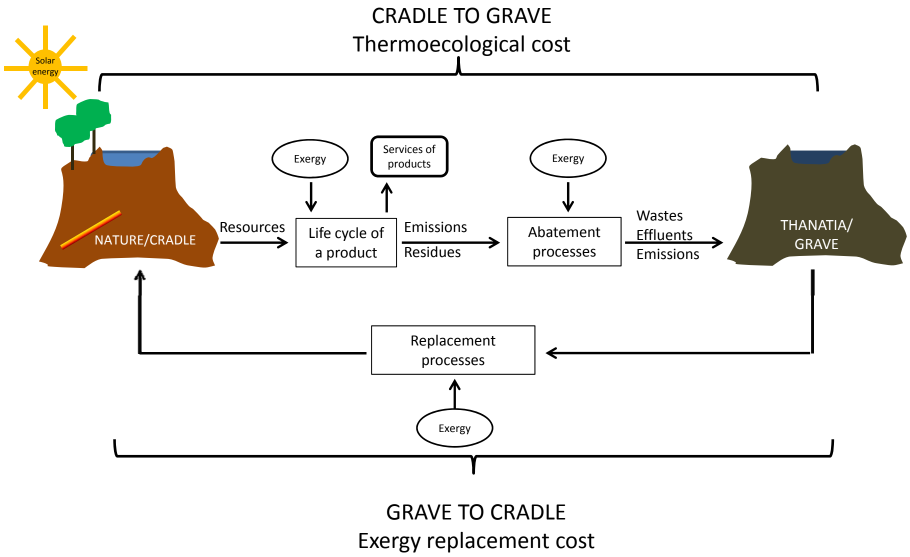


Figure 4.2: Conceptual diagram of cradle-to-grave and grave-to-cradle methodologies. Valero & Valero D. (2014).

The exergoecological approach proposed by Valero (1998), Valero et al. (2003) is used for assessing the exergy of any natural resource from a defined dispersed state of the Earth. Conceptually, the Exergoecological method allows an evaluation of mineral resources through the Exergy Replacement Cost, which is the exergy required to return to the initial state of concentration and composition found in mines, the minerals that have been totally dispersed throughout the crust once their useful lives have come to an end. That is to say, the Exergy Replacement Cost quantifies the amount of exergy that man saves when resources are extracted from a mine, instead of from a pool of materials contained in a hypothetical Earth that has reached the maximum level of deterioration.

The dispersed state is assimilated to an Earth where all fossil fuels have been burnt and all mines have been commercially exhausted and dispersed. The model for this "commercial end" of the planet developed by Valero Delgado (2008), is the Crepuscular Earth model of the theoretical Earth state *Thanatia*. It represents a degraded planet with an exhausted atmosphere, hydrosphere and continental crust. Nevertheless, as opposed to that of the current Earth, the crepuscular crust contains no mineral deposits with all non-fuel minerals having been extracted and dispersed and all fossil fuels having been burnt. Valero, Agudelo & Valero (2010) assert that as a consequence, the CO_2 concentration of the crepuscular atmosphere is much higher than it is at present. Similarly, all water available in the hydrosphere, except for a tiny 2.5% due to the hydrological cycle as it is now, is saline due to all freshwater and saltwater having mixed. The crust model proposed by Valero, Valero & Gomez (2011) is a first approximation of the average mineralogical composition of the upper crust and provides the composition and concentration of the most common 294 minerals currently found on Earth. These concentrations represent the lower limit of ore grades, and once it is achieved, the natural exergy of a mine becomes zero (Fig. 4.3). Although closely related the concept of Thanatia should not be mixed up with that of the well known Reference Environment (R.E.) commonly used for the calculation of chemical exergies. For the calculation of ERC, the concentration of all minerals in a dispersed crust are required, something which is missing in conventional R.E. That said, the Reference Environment is still required for the assessment of the chemical exergy of minerals and in fact Thanatia has chemical exergy with respect to the R.E. (see Fig. 4.3).

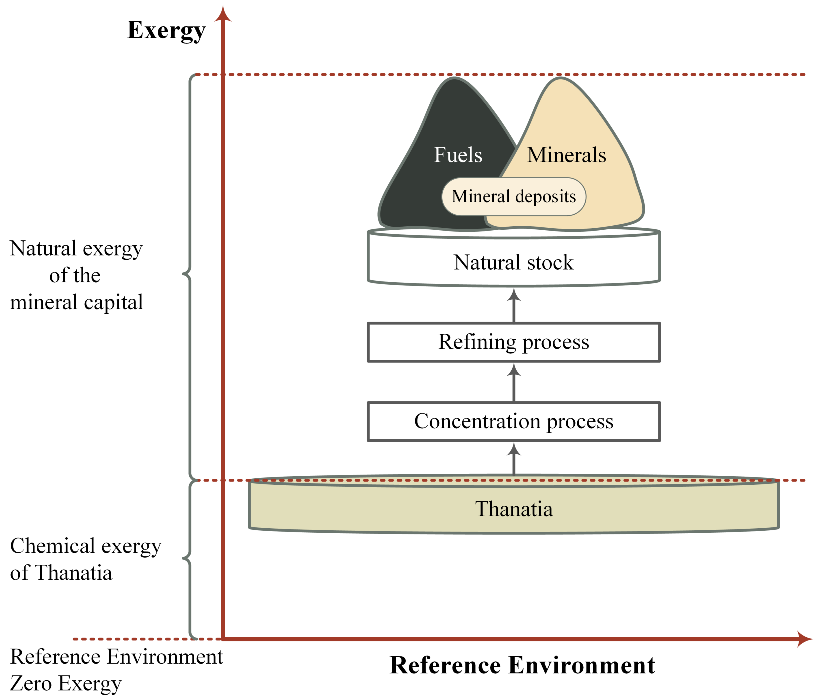


Figure 4.3: Conceptual diagram of RE and Crepuscular Earth for the evaluation of mineral capital. Valero, Valero & Gomez (2011).

In the exergoecology approach, a resource is not only valued according to its mass or chemical composition. Mineral resources are assessed according to its differentiation with the environment. The greater the ore grade of the mineral with respect to the dispersed state, the greater its thermodynamic value. This is because the value of a mineral is related with the amount of exergy needed to return it from the depleted state of Thanatia to the conditions of the mine where it was originally found. Valero & Valero D. (2014) assert that the exergy difference between Thanatia and the mine increases with the mine's quality (e.g. with its ore grade) and decrease when the mineral deposits become exhausted. At the threshold when all natural resources have been extracted and dispersed, the planet has lost all its natural bonus. Valero, Valero & Gomez (2011) claim that the mining of highly concentrated mines is "penalised" since they have greater associated exergy replacement costs. For instance, mines with high-grade ores do not need so much energy during the mining and concentration processes, however if ores of high exergy content are being depleted, inexorably its exergy replacement costs will be high. On the contrary, mines with low-grade ores require high amounts of energy during the mining and beneficiation processes, but their exergy replacement costs will remain low. And each time a mine is exploited, that exergy bonus gets lost and is therefore unavailable for future generations.

According to Valero & Valero (2010*a*), the exergoecology approach is based on two concepts: exergy and exergy cost. The first is defined as the minimum energy required to produce a natural resource with a specific structure and concentration from common materials in the reference environment, and the second accounts for the actual exergy required for accomplishing the same process with available technology, as shown in Fig. 4.3.

By means of these two concepts, the Exergy Replacement Costs (ERC) were preliminary calculated in Valero, Valero & Martínez (2010). The objective of the ERC is thus to determine the exergy bonus that Nature provides by having minerals concentrated in mines instead of having them dispersed throughout the Earth's crust. It can also be used alongside extraction data, to assess how Nature's stock is being degraded and dispersed by mankind and at which rate.

4.6.1 Reference Environment

As mentioned above, to calculate the chemical exergy of a mineral resource, it is necessary to define a reference environment (RE). Authors such as Ahrendts (1980), Kameyama et al. (1982), Szargut et al. (1988*a*) have proposed different references environments. The RE must be determined by the natural environment and is fixed by its chemical composition. The differences between standard chemical exergies of the elements obtained from different RE can be very significant. Each RE definition generate different exergies, therefore an appropriate RE is necessary.

There are criterion differences between the different RE proposals. For instance, the RE proposed by Ahrendts (1980) is based on the chemical equilibrium, however the natural environment is ar removed from such equilibrium. Kameyama et al. (1982) proposed a reference environment with the criterion of chemical stability, nonetheless the most stable compounds selected by this author are not the more common in the real environment. The RE proposed by Szargut et al. (1988*a*) is based on partial abundance, this author select the most stable substance among a group of reasonable abundant substances in order to satisfy the "earth similarity criterion". Further information of these RE and other partial RE has been carried out by Ranz (1999) and Valero Delgado (2008).

An appropriate RE to assess natural resources, has been proposed by Valero Delgado (2008). This reference environment is based on that developed by Szargut et al. (1988*a*) and is an updated of the RE proposed by Ranz (1999). The update takes into account new data of the standard chemical exergy of chemical compounds as well as the gaseous, solid and liquid reference substances.

4.6.2 Assessment of mineral resource depletion

Exergy of mineral resources

The exergy of a mineral resource has at least three components: one associated with its chemical composition (b_{ch}), one associated with its concentration (b_c) and one associated with comminution processes (b_{com}).

The chemical exergy[1] b_{ch} of the resource can be calculated by means of an exergy balance of the reversible formation reaction, as proposed by Szargut et al. (1988*a*).

$$b_{ch} = \sum_k \upsilon_k b^0_{ch,k} + \Delta G_{mineral} \tag{4.27}$$

Where $b^0_{ch,k}$ is the standard chemical exergy of the elements that compose the mineral, υ_k is the number of moles of element k in the mineral and $\Delta G_{mineral}$ is the standard normal free energy of formation of the mineral (Gibbs free energy). In a recent survey, Valero & Valero (2012) have obtained a database of enthalpy and Gibbs free energy of formation of minerals in order to calculate thermodynamic properties such as the chemical exergy of about 300 natural substances.

The concentration exergy (b_c), meanwhile, is the minimum amount of energy associated with the concentration of a substance from an ideal mixture of two components, was defined by Faber (1984) as:

$$b_{c\,i} = -\bar{R}T^0\left[lnx_i + \frac{(1-x_i)}{x_i}ln(1-x_i)\right] \tag{4.28}$$

where $\bar{R}$ is the universal gas constant (8.314 kJ/kmolK), T_0 is the temperature of the reference environment (298.15 K) and x_i is the concentration of the substance i. The exergy accounting of mineral resources implies to know the ore grade which is the average mineral concentration in a mine x_m as well as the average concentration in the Earth's crust (in Thanatia) x_c. The value of $x[g/g]$ in Eq. 4.28 is replaced by x_c or x_m to obtain their respective exergies, $b_c(x = x_c)$ and $b_c(x = x_m)$ whilst the difference between them $\Delta b_c(x_c \to x_m)$ represents the minimum energy (exergy) required to form the mineral from the concentration in the Earth's crust to the concentration in the mineral deposits as:

$$\Delta b_c(x_c \to x_m) = b_c(x = x_c) - b_c(x = x_m) \tag{4.29}$$

In the case of concentrating two solids, another term must be added: the variation in cohesion exergy between the final and the initial state. Minerals in the crust are commonly embedded in a sillicate matrix and its cohesion exergy is its comminution exergy (b_{com}), or minimum exergy needed to comminute the mineral between two given sizes Valero & Valero D. (2012). Considering that the size of the bare rock of the Crepuscular Earth model d_θ is so large compared to the geometrical mean size d_M of the natural fragments found in the mine, the comminution exergy cost (b^*_{com}) of a mineral in a mine of size d_M is defined as:

$$b^*_{com} = 10W_i(1/\sqrt{(d_M)} - 1/\sqrt{(d_\theta)}) \tag{4.30}$$

[1] Chemical exergy is *the work that can be obtained by a substance having the parameters T_0 and P_0 to a state of thermodynamic equilibrium with the datum level components of the environment* (Szargut et al. (1988*b*)).

Where W_i is the Bond work index [kWh/t][μm]$^{0.5}$. If the differences in size are not substantial and the mineral is present in the same sillicate matrix, this comminution exergy variation may be neglected in a first approach.

Exergy Replacement Cost

From the 2nd Law of Thermodynamics, Eq. 4.28 indicates that as the concentration of the substance tends to zero, the exergy required to separate it tends to infinity. So Thermodynamics provides the tendency of the behavior. The real energy required is several orders of magnitude greater than what the Thermodynamics of reversible processes dictates. In fact, mixing and separating are the most irreversible processes. When salt and sugar are mixed, the energy that is liberated in the mixture is almost imperceptible. If the process were reversible, the same amount of energy would be required to separate the mixture. But that is obviously not the case in the real world and when this happens in everyday life, it is easier to throw out the mixture than trying to separate it. Hence, it should be noted that if minerals are assessed solely in exergy terms, the results obtained would be very far removed from "socially accepted" values given to minerals. This is because exergy measures minimum thermodynamic values. Man's technology is however very far removed from reversibility conditions and this is why we need to resort to the exergy replacement costs, including the so called unit exergy costs (k). The latter factor is defined as the ratio between the exergy consumed in the real mining process ($E_{realprocess}$) used to obtain the mineral from the ore grade x_c to the commercial grade x_r and the minimum exergy ($\Delta b_{mineral}$) required to accomplish the same process, expressed as:

$$k_m = \frac{E_{realprocess}}{\Delta b_{mineral}} \tag{4.31}$$

Accordingly k is a measure of the irreversibility of man-made processes and amplify minimum exergies by a factor of ten to several thousand times, depending on the commodity analyzed. Consequently, the Exergy Replacement Cost of a mineral would require k times the minimum exergy, and can be calculated with the following expression:

$$b_t^* = k_{ch} \cdot b_{ch} + k_c \cdot b_c + b_{com}^* \tag{4.32}$$

The exergy replacement cost is defined as the total exergy required to concentrate the mineral resources from Thanatia, with the best available technologies. Therefore, these are not absolute and universal values, as opposed to property exergy. Domínguez & Valero (2013) argue that the exergy costs are a function of the extraction and separation technologies, which in turn vary with time, with the type of mineral analyzed, and with man's ability to extract it, i.e. with its learning curve. See Section 3.4.

For most case studies, the chemical component of Eq. 4.32 is zero because there is no need to chemically produce the mineral from Thanatia again, since the Crepuscular Earth model already contains the substance, but at a significant lower concentration. Whilst, the comminution exergy cost of a mineral can be neglected if the differences in size are not substantial, as considered in the analyzes carried out in this paper. Therefore, one only needs to account for the exergy required to concentrate the mineral from the dispersed conditions found in Thanatia, until the original concentration found in the mines.

As aforementioned, in Eq.4.33 the unit exergy cost k is the ratio between the real cumulative energy required to accomplish the real process to concentrate the mineral from the ore grade

x_m to the commercial grade x_r and the minimum thermodynamic exergy required to accomplish the same process as, it can be expressed also as:

$$k = \frac{E_{(x_m \to x_r)}}{\Delta b(x_m \to x_r)} \tag{4.33}$$

The general procedure to calculate the exergy replacement cost of mineral resources is presented in Fig. 4.4.

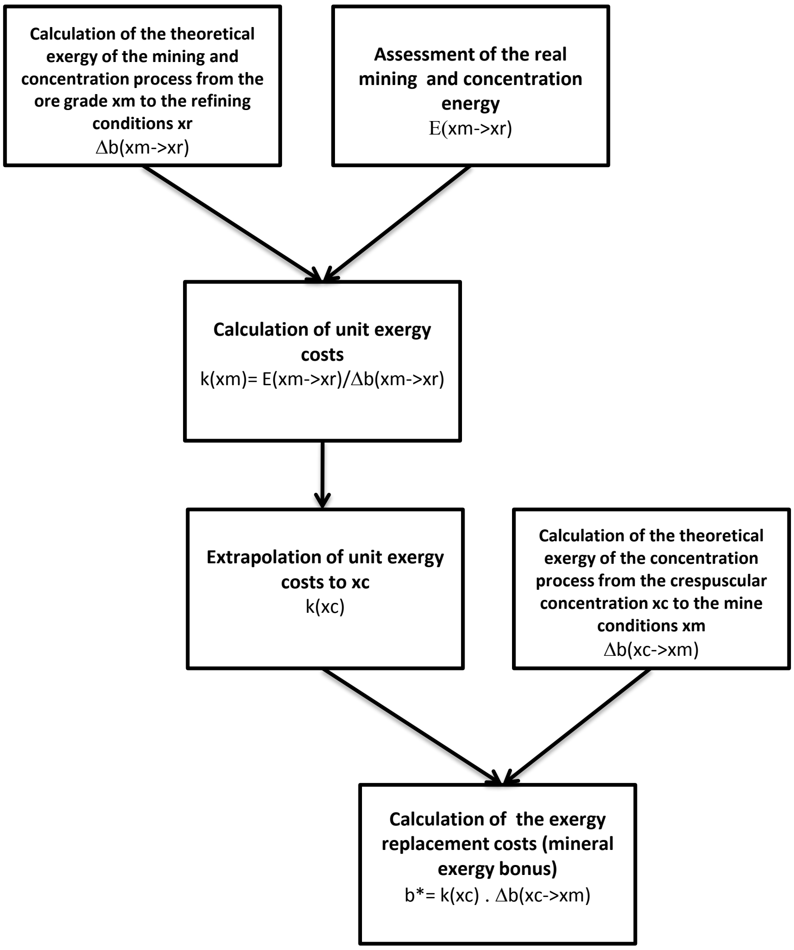


Figure 4.4: Calculation procedure for obtaining a mineral's exergy replacement costs. Valero & Valero D. (2014).

The energy required for mining is a function of the ore grade of the mine and of the technology used, thence it can be defined as the unit exergy cost. Moreover, both variables have an opposite effect on the energy used, as Ruth (1993, 1995*a*,*b*,*c*) states. The lower the ore grade, the more energy is required for mining. On the contrary, technological development usually improves the efficiency of mining processes and hence, decrease the energy consumption. In other words, the unit exergy cost depends on the ore grade (x_m) and the time (t) that is considered through the improvements in mining techniques, which in turn are reflected in the real energy consumptions.

$$k = k(x, t) \tag{4.34}$$

Hence, the temporal function k is only definable for the past and for each particular mineral. It is therefore difficult to extrapolate it towards the future for the practical impossibility to predict changes in the scientific and technological knowledge that will eventually appear.

The second problem with k is that it is not a continuous function. The technology applied can also vary with the concentration ranges of a particular deposit. And in turn, each mining technique (i.e. underground or open-pit mining), has a particular effect on the energy consumption due to different factors such as ore grade, grind size, nature, depth and processing route. These factors have been analyzed in Norgate & Haque (2010), Norgate & Jahanshahi (2010, 2011), for different commodities such as for copper, nickel aluminium and iron through the life cycle assessment methodology.

Bearing in mind these limitations and the kind of data available for mining (which is usually very scarce) in this survey it is assumed that the same technology is applied for the range of concentration between the ore grade x_m in the mine and the refining grade x_r, than between the dispersed state of the crepuscular crust x_c and x_m. This way, an analysis of the average energy vs. ore grade trends for different minerals is carried out, in order to calculate the corresponding unit exergy cost values and extrapolate them to ore grades equal to those of the dispersed conditions of Thanatia.

4.7 Summary

In this chapter a brief review of the main thermoeconomic concepts was presented, in order to introduce the concepts that allow to assess natural resources. In this regard, two methodologies: Thermoeconomic Input-Output and Thermoecological Cost were explained and compared. Both methods will be applied in several case studies of mining and metallurgical industry in Chapters 5 and 6 of this PhD. These methods are used to analyze the path "cradle to grave" in a LCA of mining industry, because processes such as raw material extraction, refining, product manufacturing, recycling and disposal can be evaluated.

Afterwards, the Exergoecology approach and the exergy replacement costs were presented as tools to evaluate the "grave to cradle" path. In this way, the cycle of natural resource assessment is closed and an absolute LCA "cradle-to-cradle" can be performed. The importance of the exergy replacement costs lies in their ability to establish a scarcity factor of mineral resources which should be accounted for, when assessing the sustainability of mining and metallurgical processes. Accordingly, in next chapter an exergy analysis of mineral resources and metallurgical systems will be carried out, and the exergy replacement cost of several metals will be calculated. Additionally, the problem of cost allocation when two or more commodities are produced in the same mining operation will be settled.

Chapter 5

Exergy analysis of mineral resources and mining by-products

This chapter is aimed at providing a thermodynamic outlook of mineral resources and the metallurgical processes required to produce them. Accordingly, the first objective of this chapter is to analyze the energy requirements as a function of the ore grade, in order to calculate the exergy replacement costs. However, in the mining industry, with each ore, two or more products, by-products and residues are produced simultaneously. Hence, the LCA is confronted with the difficult and often rather complicated problem of assigning costs to their by-products and joint products. In this regard, the second objective of this chapter is to develop a new cost allocation methodology based on the exergy replacement costs. The final aim is to estimate the exergy cost and eventually economic, technology and environmental bearings of each commodity produced.

5.1 Introduction to exergy analysis of mineral resources

Future availability of mineral resources is increasingly gaining importance in strategic plans of governments, as it is a high-priority issue for economic development. The availability is not related to the quantity of minerals included in the crust. The whole continental crust is composed of minerals that could be eventually extracted. Mineral availability is rather related to accessibility, which in turn is tightly connected with energy consumption. Mining, transport, crushing and grinding, smelting, refining, etc. are all processes that require significant amounts of energy. Notwithstanding, it is important to highlight that energy requirements become an important issue, because nowadays it comes mainly from non-renewable resources.

An assessment of the energy consumption required to produce commodities can provide an overview of the implications needed to achieve sustainability. Authors such as Chapman & Roberts (1983) pointed out that the energy required to produce a metal provided a useful guide to its resource implications. Otherwise, trough different works like those performed by Valero & Valero (2011), Valero et al. (2008), Valero, Valero & Martínez (2010) it has been demonstrated that exergy analysis is a useful tool to assess natural resources because it takes into account variables such as composition, concentration (ore grade), cohesion and the state of technology.

As stated in Chapter 4, section 4.6, the exergy of any natural resource is defined as the minimum energy required to produce it with a specific structure and concentration from common materials in the reference environment. The exergy of a system gives an idea of its differentiation with the environment. The case of a mineral deposit is clear; it has exergy because the minerals contained in it have a specific concentration and composition different from the common bedrock. Hence, the higher the grade of a mineral deposit, the more exergy it has. Hence, minerals can be considered as a carrier of exergy.

When the mineral is mined, the exergy content of the mineral is kept constant, and if it is enriched the exergy content increases. A meager deposit of mineral contains less exergy and will require a substantial input of external exergy to be utilized. Finally, when a concentrated mineral is dispersed, the exergy content decreases. A mine loses its natural exergy when the ore grade declines through extraction, and becomes zero when this ore grade equals to that of the surrounding environment.

But exergy only represents the thermodynamic minimum. And this minimum is very far removed from reality. If mineral resources had to be created and concentrated with current available technology from the bedrock (from Thanatia), much more energy would be required. Accordingly, the first objective of this chapter will be accomplished through the analysis of the energy requirements as a function of the ore grade in order to calculate the exergy replacement costs. This will allow to physically assess mineral resources and will give an idea of how far is the mining industry from sustainability.

5.2 Exergy Replacement Costs of minerals resources

This section appraises the energy requirements for mineral production through an exergy approach taking into account the long-term decline in ore grades. In this context, the exergy replacement costs are defined as the exergy required for restoring mineral resources from a complete dispersed state where no deposits exist into the same conditions in which they were delivered by the ecosystems with the available technology. The exergy replacement cost is the point of reference in order to evaluate in a single variable, characteristics such as composition, concentration (ore grade) and the state of technology of mineral resources. With empirical data of energy requirements in mining as a function of the ore grade, the exergy replacement costs of cobalt, copper, gold, nickel and uranium are obtained. Additionally, a general expression of mining energy vs. ore grade is derived for those mineral commodities where no empirical data is presented.

The first step in obtaining the unit exergy cost for the commodities analyzed is to obtain their real energy consumptions in the mining and concentrating processes (going from x_m to x_r) as a function of the ore grade (x_m). This information can be obtained from data published in the literature. In a parallel way, the theoretical exergy of the same process is calculated as the difference in concentration exergy (Eq. 4.28) when $x = x_m$ and $x = x_r$. A calculation of the refining grade x_r requires a careful analysis of the different processes involved in the concentrating steps. Finally, the unit exergy costs are calculated with Eq. 4.33 as a function of the ore grade. The latter can be extrapolated to obtain the unit costs at the crepuscular grade x_c, which will eventually serve for calculating the exergy replacement costs of the mineral wealth on Earth with Eq. 4.32. The values used for the crepuscular grade are those x_c published in Valero, Valero & Gomez (2011). Average values for x_m have been obtained from several studies such as Cox & Singer (1992), Kellogg (1977), Mudd (2007*c*, 2010), Norgate & Jahanshahi (2010).

5.2.1 Cobalt

Cobalt is mainly produced as a by-product and recovery of other abundant metals such as copper, platinum or nickel. In this survey it is considered that cobalt comes mainly from nickel sulphide ore. The energy consumption as function of the ore grade shown in Fig. 5.1 is obtained from the data set of Ni-Cu-Co provided by Mudd (2010). The allocation of the energy among different metals was carried out in Mudd's study according to their tonnage. Furthermore, it was assumed that 60% of the overall energy is consumed for mining and concentrating cobalt from sulphide ore, while 40% for refining[1]. In addition, it was assumed the same Exergy replacement cost for nickel sulphide ores and for cobalt, since the latter is "free" mineral obtained in nickel production. Accordingly, it is considered that the proportion of Co in Ni-sulphides is $0.07 g_{Co}/g_{Ni}$ from the Minara Murrin mine. Consequently the Exergy replacement costs for cobalt in GJ/ton$_{Co}$ are calculated as the exergy costs for nickel sulphides divided by 0.07.

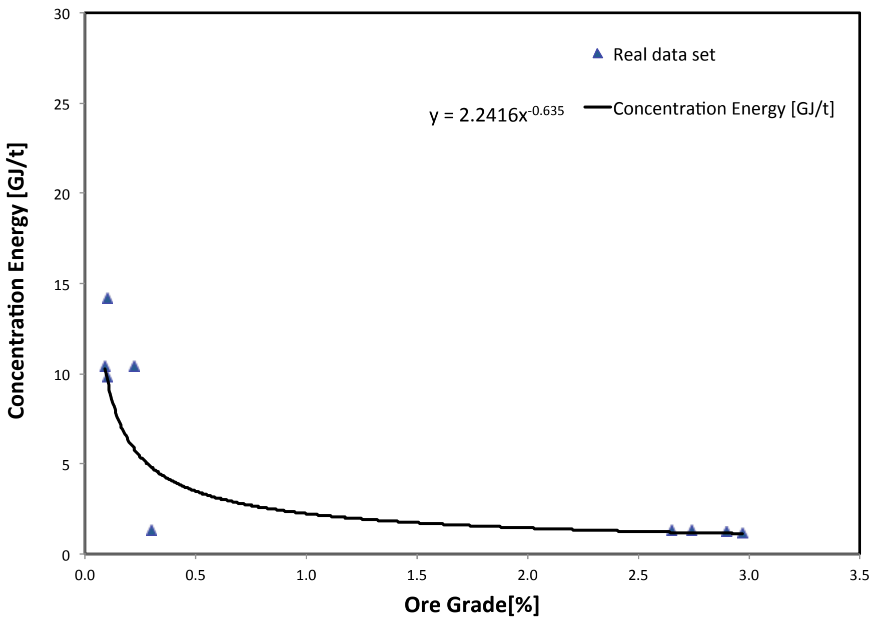


Figure 5.1: Energy requirements for cobalt production form sulphide ores as a function of the ore grade. Adapted from Mudd (2010).

5.2.2 Copper

Copper is always associated with other metals, commonly nickel, molybdenum and platinium group metals. Copper in mineral deposits is usually found in nature in association with sulphur, as chalcopyrite ($CuFeS_2$). This ore has a crustal concentration of $x_c = 6.64E^{-05}$g/g, as reported in Valero, Valero & Gomez (2011). According to Cox & Singer (1992), the average ore grade assumed is $x_m = 1.67E^{-02}$ g/g. Data sets for energy requirements as a function of the copper ore grade are obtained from the study of Mudd (2010) of sulphidic ores, which contain

[1]This assumption comes from an extrapolation of published data: according to Botero (2000), the energy requirement for mining and concentration is 193 GJ/t, while the energy consumption in the refining process to obtain pure cobalt is reported by Chapman & Roberts (1983) as 129 GJ/t.

also cobalt and nickel. Energy was allocated in such study among the minerals according to their tonnage. It was assumed that 60% of the whole energy recorded is used for the mining and concentration processes. Additionally, *Kennecott Utah Copper Corporation* (2004) reports an average grade for Cu after beneficiation of $x_r = 28.00E^{-02}$g/g. Fig. 5.2 shows the trends for an ore grade range including the average value reported by Cox & Singer (1992).

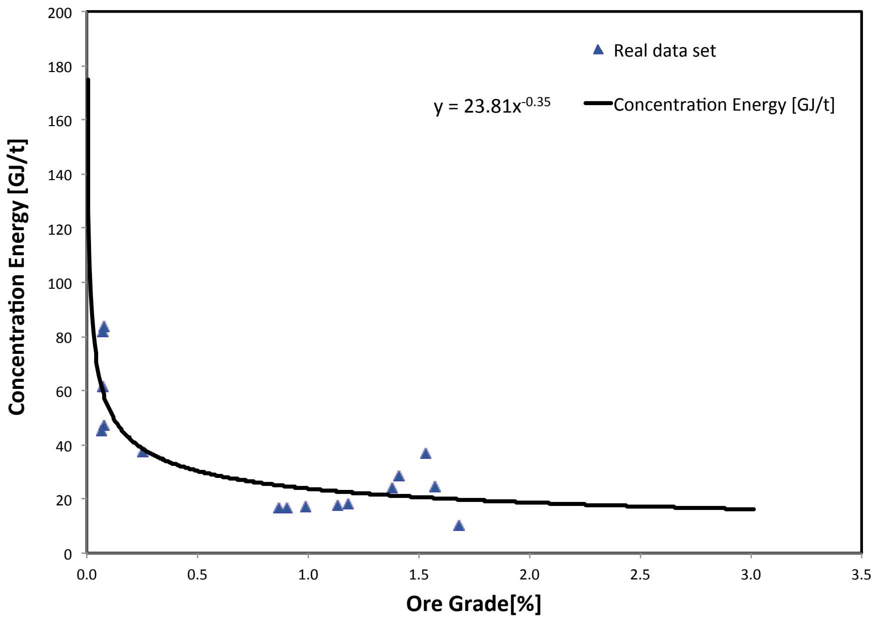


Figure 5.2: Energy requirements for copper production as a function of the ore grade. Adapted from Mudd (2010).

5.2.3 Gold

Mudd (2007*c*) studied in detail the global trend of gold extraction (see Fig. 5.3) finding a clear declining ore grade trend in the countries reviewed, namely Brazil, Australia, South Africa, Canada and the United States. In Australia for instance, ore grades have declined from 37 g/t in 1859, to the current 2 g/t. The average ore grade of the gold deposits studied by Mudd (2007*c*) is $x_m = 2.244$ g/ton.

The average energy consumption of mines worldwide meanwhile is reported at 143,000 GJ/ton. However, the latter value includes all the processes of gold production: mining, beneficiating, smelting, converting and refining. However, only the first two steps need to be taken into account for the calculation of ERC. *Kennecott Utah Copper Corporation* (2006) reports an energy share for gold production of 27% for mining, 54% for concentrating, 12% for smelting, 6% for refining and 1% for tailings. Hence, it is assumed that 81% of the energy consumption in gold production is used for the mining and concentrating steps. Furthermore, the same company reports that 1 kg of gold is obtained from 2,180 kg of blister copper, which in turn is produced from concentrated copper after the beneficiating process at around 30% Cu-purity. Hence, and in the absence of other sources of information, it is assumed that after beneficiation, gold has a concentration of $x_r = 1.38E^{-04}$g/g.

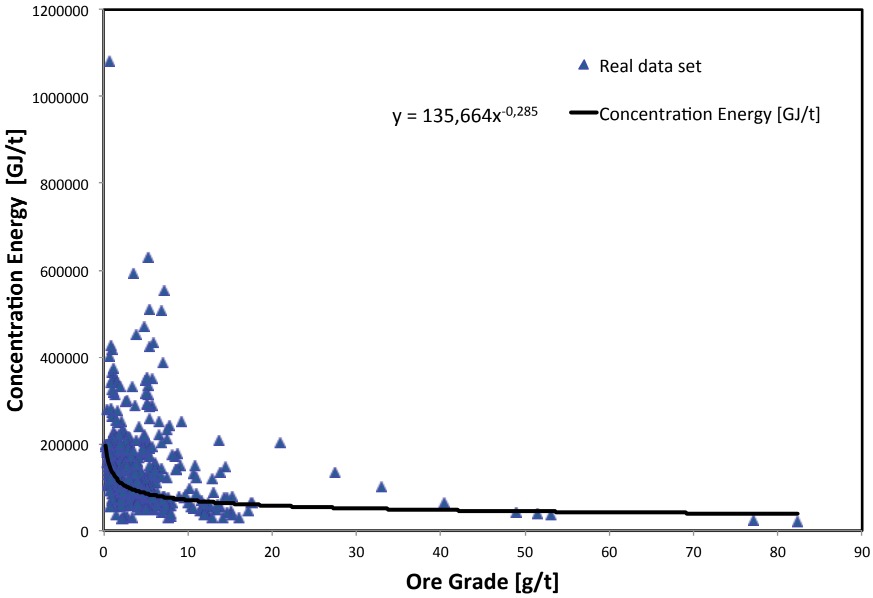


Figure 5.3: Energy requirements for gold production as a function of the ore grade. Adapted from Mudd (2007*c*).

5.2.4 Nickel

Nickel is always associated with other metals, predominantly copper, cobalt and platinum group metals. It is produced from oxidic (laterite and saprolite) or sulphidic ores. Although the majority of economic resources are contained in laterite ores (around 60% vs. 40% for sulphide ores), the bulk of historic Ni production has been derived from sulphide ores since laterites require more complex processing (60% of extraction from sulphide vs. 40% from laterite ores). Sulphide ores are predominantly produced by underground mining whilst lateritic ores are generally produced by open pit mining.

It is assumed that the lateritic ore from which nickel is produced is garnierite, which has crustal concentration of $x_c = 4.10E^{-06}$g/g, reported by Valero, Valero & Gomez (2011). It has an average ore grade of $x_m = 4.42E^{-02}$ g/g, according to Norgate & Jahanshahi (2010). In IPPC (2009*b*) the refining grade of laterite ores with a maximum nickel content of 3% is reported as $x_r = 8E^{-02}$ g/g. The energy consumption as a function of the ore grade is obtained from the study for sulphidic Cu-Ni-Co ores performed by Mudd (2010) where values from 252 to 572 GJ/ton of metal are reported in the re-fining process. A mean value of 412 GJ/ton of nickel is considered in this survey.

Otherwise, pentlandite is the sulphidic ore from which most nickel is produced, and has a crustal concentration of $x_c = 5.75E^{-05}$g/g, according to Valero, Valero & Gomez (2011). It has an average ore grade of $x_m = 3.36E^{-02}$ g/g, reported by Mudd (2010). IPPC (2009*b*) reports that nickel concentrates, generally contain 7 - 25% Ni. Assuming a mean value of 16 % results in the refining grade of $x_r = 4.68E^{-01}$ g/g. The energy requirements as a function of the ore grade are obtained from the study of Mudd (2010) for sulphidic Cu-Ni-Co ores.

Figure 5.4 shows the trends of energy consumption as a function of the ore grade for pentlandite. Undoubtedly, the processing of nickel from lateritic ores is more resource intensive than from sulphides, this is a spotlight issue because of the on going increase of nickel mining from laterites.

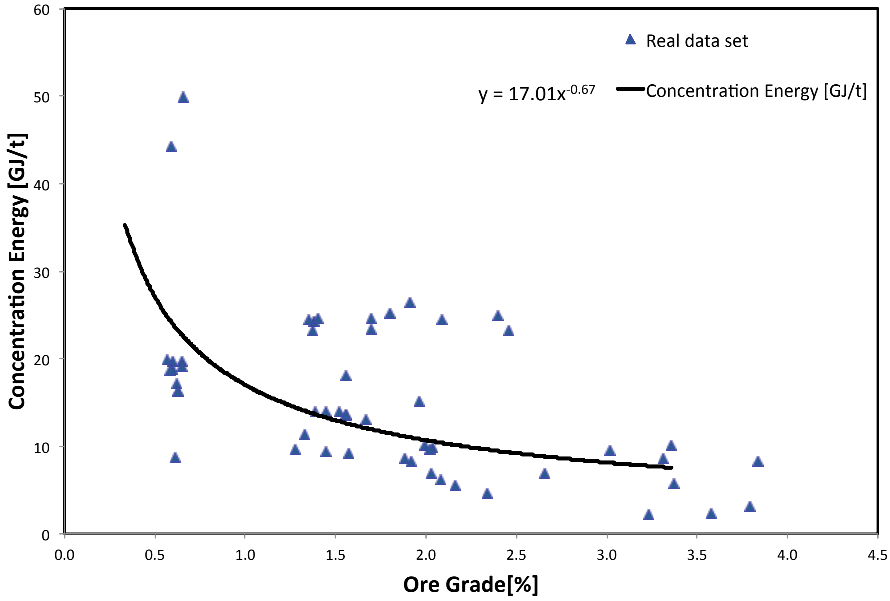


Figure 5.4: Energy requirements for nickel production as a function of the ore grade. Adapted from Mudd (2010).

5.2.5 Uranium

Uranium is widely distributed, with the most important ores uraninite UO_2 and carnotite. However, these are usually dispersed so that typical ores contain only about 0,1% of U content and many of the more readily exploited deposits are nearing exhaustion. It is assumed that uraninite is the only U-ore. Valero, Valero & Gomez (2011) calculates a crustal concentration of $x_c = 1.51E^{-06}$g/g, whilst the average ore grade is $x_m = 3.18E^{-03}$g/g, according to Cox & Singer (1992). The energy data used to obtain the exergy cost for this commodity was provided by Mudd & Diesendorf (2008) who did a detailed compilation and analysis of Australian uranium mining (as U_3O_8) (5.5). The refining grade is assumed at $x_r = 7.50E^{-01}$ g/g, in accordance with Gupta & Mukherjee (1990).

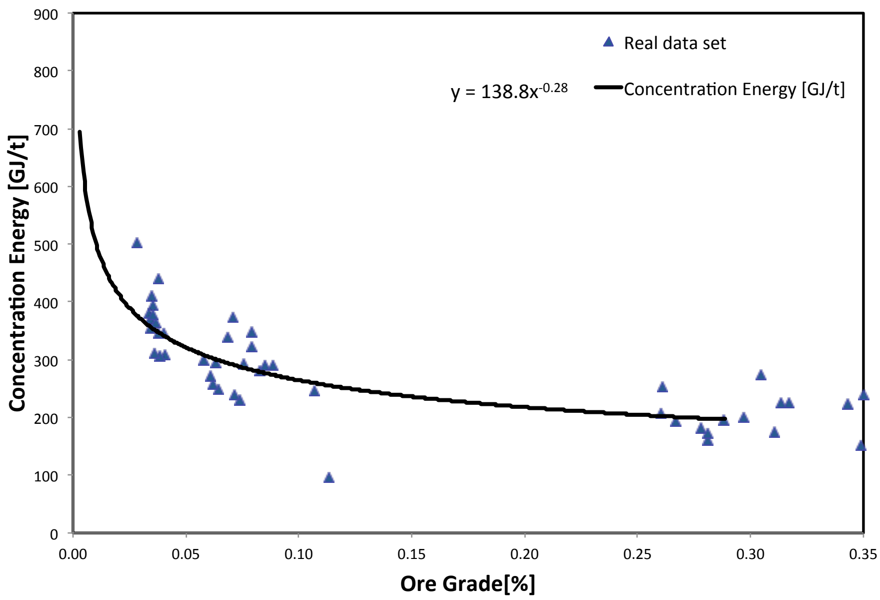


Figure 5.5: Trends of unit exergy costs and concentration energy in uranium mining (data referred to uranium oxide U_3O_8). Adapted from Mudd & Diesendorf (2008).

5.2.6 Summary of ERC obtained

A summary of all commodities analyzed previously is presented in Table 5.1. It contains the main values for each substance, such as x_c, x_m and x_r along with the equations to calculate the energy required to mining and concentrating a specific ore, the unit exergy cost and the exergy replacement cost.

Table 5.1: Exergy Replacement Costs. Values of x_c, x_m and x_r are referred to the assumed mineral that represents the ores from which the metal is extracted.

	$E(x)[GJ/t]$	$x_c[g/g]$	$x_m[g/g]$	$x_r[g/g]$	$k(x = x_c)$	$k(x = x_m)$	Exergy Replacement Cost
Cobalt (Linnaeite)	$E = 2.24x^{-0.64}$	$5.15E^{-09}$	$1.90E^{-03}$	$4.56E^{-02}$			10,872
Copper (Chalcopyrite)	$E = 23.81x^{-0.35}$	$6.64E^{-05}$	$1.67E^{-02}$	$8.09E^{-01}$	525	170	110
Gold	$E = 135,664x^{-0.285}$	$1.28E^{-09}$	$2.24E^{-06}$	$1.38E^{-04}$	6,380,357	2,135,879	583,668
Nickel (Sulphide - Pentlandite)	$E = 17.01x^{-0.67}$	$5.75E^{-05}$	$3.36E^{-02}$	$4.68E^{-01}$	13,039	585	761
Nickel (Laterite - Garnierite)	$E = 2.11x^{-0.5}$	$4.10E^{-06}$	$4.42E^{-02}$	$8.04E^{-02}$	876	136	167
Uranium (Uraninite)	$E = 138.8x^{-0.28}$	$1.51E^{-06}$	$3.18E^{-03}$	$7.50E^{-01}$	13,843	3,697	901

As stated before, the unit exergy cost is the ratio between the real energy required for mining and concentrating a substance and the minimum thermodynamic energy (exergy) required to achieve the same process. Hence, it provides a measure for the irreversibility (or technological ignorance) of the process. Generally, the energy value (nominator) increases more rapidly than the exergy one (denominator). An exception of this fact is found for elevated ore grades, where the opposite happens. Consequently, the lower the ore grade, the more energy is required for mining and concentrating the mineral and the more irreversible is the process.

For instance, gold has the highest unit exergy cost value associated to the deposits (when $x = x_m$) of the metals analyzed in this work, attributable to its low concentration in mines and the consequent amount of energy needed to concentrate it. Besides, the actual ore grade in mines is close to that in crepuscular Earth's crust. The opposite example is copper which has a lower k value ascribed to its actual high ore grade in mines.

But the state of technology plays also an important role. This fact is highlighted with nickel from sulphide ore. Even if its ore grade is similar to that of copper, the elevated value of k is an indicator of the significant irreversibility of the production process.

A particular case is that of nickel and its ores. Historically, the metal was likely obtained from sulphide ores due to the major energy requirement of laterites in the refining process. Nevertheless, more Ni resources are in the form of laterites than of sulphides. But focusing only in the concentration energy, sulphide ores have larger concentration requirements than lateritic ores, as revealed by the larger unit exergy costs. However, continuous sulphide ore grade decline, the increasing cost of underground mining coupled to the estimations that in the future nickel production will be obtained from lateritic ores in order to fulfil the nickel demand, augur an increase of the energy associated with nickel production.

Of special interest is the value of $k(x = x_c)$. This value multiplied by the minimum exergy required to concentrate the mineral from x_c to x_m represents the amount of energy required to mine and concentrate a substance from the bedrock (from Thanatia) to the current conditions in the mineral deposits and provides a measure of the exergy that Nature provides "for free" thanks of having minerals concentrated in mines instead of dispersed throughout the crust. The value of the crepuscular unit exergy cost of the different minerals is always greater than that of the current mineral deposits. The difference increases generally with the separation between the crepuscular grade and the average grade in the deposits. For instance, the crepuscular k-value of gold is in the same order of magnitude than the mine k-value, because the grade of gold is close to that found in Thanatia. The opposite happens with uranium, which has a small crepuscular grade compared to current average ore grades. Therefore its crepuscular k-value is considerably much larger compared to its unit exergy cost when the average ore grade in U-mines is taking into account.

Finally it is worth to note in Table 5.1 that the energy consumption as a function of the ore grade shows expression varying from $x^{-0.2}$ to $x^{-0.9}$. From this observation and recognising that empirical data for most of the minerals produced in the world is very limited, it is proposed the following general expression for the exponential curve applied to estimate the energy consumption as a function of the ore grade:

$$E(x_m) = A \cdot x_m^{-0.5} \qquad [x_m, \qquad \text{metal concentration } \%] \tag{5.1}$$

Coefficient A is determined for each mineral since generally, the average ore grade x_m and the energy required for concentrating and extracting the mineral at that grade $E(x_m)$ is known. It should be noted that x_m values are expressed in Eq. 5.1 as mass percentage of the element under consideration. This is a very rough approximation, but it is more in agreement with actual mining behaviour than the equation proposed by Chapman & Roberts (1983), where the energy is inversely proportional to the ore grade.

The same analysis was carried out for several commodities, which will be used in further chapters. Hence, Table 5.2 summarize the exergy replacement cost for different commodities. It can be observed that a mineral has a high exergy replacement cost when 1) the concentration of the mineral in the crepuscular crust (in Thanatia) is low and the difference between the ore grade of the current mines (x_m) is high and/or 2) when the energy required to extract the mineral and beneficiate it is significant. The exergy replacement cost is greater for critical elements (e.g. gold) than it is for those found in abundance (e.g. chromium).

Table 5.2: Exergy Replacement Costs for different commodities. Energy and exergy values are expressed in GJ/ton of mineral.

Mineral	$x_c\,[g/g]$	$x_m\,[g/g]$	$x_r\,[g/g]$	Concentration and beneficiation energy	Smelting and refining energy	Exergy replacement cost
Aluminium (Gibbsite)	$1.38E^{-03}$	$7.03E^{-01}$	$9.50E^{-01}$	10.55	23.87	627
Antimony (Stibnite)	$2.75E^{-07}$	$5.27E^{-02}$	$9.00E^{-01}$	1.4	12	474
Cadmium (Greenockite)	$1.16E^{-07}$	$1.28E^{-04}$	$3.86E^{-03}$	1.4	263.9	278.5
Chromium (Chromite)	$1.98E^{-04}$	$6.37E^{-01}$	$8.10E^{-01}$	0.01	36.3	5
Iron (Hematite)	$9.66E^{-04}$	$7.3E^{-01}$	$9.5E^{-01}$	0.7	13.4	18
Lead (Galena)	$6.67E^{-06}$	$2.37E^{-02}$	$6.35E^{-01}$	0.9	3.3	37
Manganese (Pyrolusite)	$4.90E^{-05}$	$5.00E^{-01}$	$6.71E^{-01}$	0.2	57.4	16
Molybdenum (Molybdenite)	$1.83E^{-06}$	$5.01E^{-04}$	$9.18E^{-01}$	136	12	908
Phosphate rock (Apatite)	$4.03E^{-04}$	$5.97E^{-03}$	$9.00E^{-01}$	0.3	4.6	0.4
Silver (Argentite)	$1.24E^{-08}$	$4.27E^{-06}$	$9.00E^{-01}$	1281.4	284.8	7371.4
Zinc (Sphalerite)	$9.96E^{-05}$	$6.05E^{-02}$	$7.90E^{-01}$	1.5	40.4	25
Rare Earth Metals						
Cerium (Monazite)	$1.03E^{-04}$	$3.00E^{-04}$	$8.0E^{-01}$	523.05	56.1	43.47
Gadolinium (Monazite)	$1.03E^{-04}$	$3.00E^{-04}$	$9.5E^{-01}$	3607.25	43.05	115.23
Lanthanum (Monazite)	$1.03E^{-04}$	$3.00E^{-04}$	$8.0E^{-01}$	296.75	53.45	16.77
Neodymium (Monazite)	$1.03E^{-04}$	$3.00E^{-04}$	$8.0E^{-01}$	591.7	53	31.88
Praseodymium (Monazite)	$7.10E^{-06}$	$3.00E^{-04}$	$8.0E^{-01}$	296.28	55	124.37
Yttrium (Monazite)	$1.03E^{-04}$	$3.00E^{-04}$	$9.5E^{-01}$	1198.25	47.6	32.01

5.3 Introduction to Exergy Cost Allocation of by-products in the mining industry

The long-term availability of mineral resources is a key factor to satisfy human activities, technology and economic activity, including those metals that do not generally are the primary production of mines, such as copper or nickel, but instead are mined as by-products during the mining of primary ores. In this regard, mining industry is confronted with the difficult and often rather complicated problem of assigning costs to their by-products and joint products, which have highly complex demand/supply and technology and investments requirements.

The availability of by-product metals depend on the availability of technology to recover those metals during or after the processing of host metal ores, as well as on the economic profit of by-product metal recovery. Mudd et al. (2013) proposed a set of parameters in order to evaluate by-product metal availability such as: (1) size and type of the by-product metal ore bodies; (2) the characteristics abundances of by-product metals in the host or hosts; (3) the typical recovery efficiencies for these by-product metals (mainly the different technologies used) and (4) models of the relative costs and benefits of by-product metal recovery.

However, in Mudd's proposed parameters there is a missing one related with energy consumption of by-product metals. In this respect, conventional LCA software usually performs allocations among products when one or more by-products come about in a mining or metallurgical process, based either on tonnage or on revenue (commercial prices). Both ways of allocating environmental costs entail many disadvantages, such as introducing subjectivity with price or underestimating burden for certain by-products when the tonnage is low. Specifically in the Ecoinvent database, the by-product allocation problem (the joint production of silver and lead, for instance) is undertaken by a subdivision of the sub-processes. The starting point for the estimation depends on the general profit expectations of the company, considering an arbitrary performance value of 10%. Hence, the allocation factors are based on revenue but these values are corrected by mass in order to keep up with the resource balance in the final commodity. Consequently, allocation methods are confronted with the difficult and often rather complicated problem of assigning costs to their by-products and joint products.

Furthermore, LCA uses computer software and database like Ecoinvent (Classen et al. 2007), which contains a very broad data on energy supply, resource extraction, raw material supply like chemicals, metals, explosives or water. However, most of such databases consider regional averages of environmental impacts associated with mineral processing, with arbitrary allocations among those operations using raw materials, hydro, gas, coal or nuclear generated electricity, or those occurring in different countries, or even any variations from process to process. In this way, authors like Yellishetty et al. (2009) have conducted a critical review of existing LCA methods in the minerals and metals sector in relation to allocation issues related to indicators of abiotic resource depletion, concluding that LCA issues of minerals and metals need to be investigated further to get more understanding, to facilitate the future use of LCA as a policy tool in the mining sector and increase objectivity with more scientific validity. There is clearly a need for better data related to mining industry such as, energy consumption, production efficiency at various levels of aggregation, waste disposal, fugitive emissions, among others. Authors such as Brown et al. (2012), McLellan et al. (2012) think that a global perspective on the current energy use and GHG emissions proceeding from minerals production is required. Espí (2009), Sagar & Frosch (1997) assert that this kind of information is crucial to perform analysis which allows a deeper understanding of mining sector. Since mineral extraction and processing constitutes the first stage of any given process, using conventional LCA software may lead to incorrect results. Aware of this problem, in this section, the second objective will be achieved through the development of a new cost allocation methodology based on the exergy replacement costs. The final aim is to estimate the energy consumption and eventually economic, technology and environmental bearings of each commodity produced. The novelty introduced with respect to what is already being done in conventional Thermoeconomic analysis is that when non-fuel minerals come into play, allocation is carried out through the exergy replacement costs instead of through chemical exergy, what was traditionally done in conventional thermoeconomic analyzes. In this way, the scarcity factor of minerals is taken into account.

In order to allocate costs among non-fuel minerals through the exergy replacement costs, 33 different mineral deposit models where 12 coupled products are obtained have been analyzed. Additionally, as study cases, exergy cost allocation was applied to nickel, copper, lead and REE production with its respective by-products.

The mineral deposits models used to develop the allocation methodology in this section, are taken from the comprehensive study of average ore grades accomplished by Cox & Singer (1992). In their study, a compendium of geologic models was presented, including 85 descriptive models identifying attributes of the deposit type and 60 grade-tonnage models giving estimated pre-mining tonnage's grades from over 3,900 well-characterized deposits all over the world. The average grade $\overline{x}_m$ of the different mineral deposits analyzed is calculated with Eq. 5.2, taking into account the tonnage (M) and ore grade (x_m) of each model and the number of deposits containing the mineral under consideration. Tables 5.3 through 5.9 are calculated with the mean average grade and tonnage of each deposit type.

$$\overline{x}_m = \frac{\int_0^M x_m dM}{\int_0^M dM} \tag{5.2}$$

Such models will serve to demonstrate why the allocation model presented in this thesis is more suitable than conventional approaches using tonnage or market prices.

5.4 Joint products and by-products in the mining industry

Products produced at the same time are classified as joint products or by-products; generally driven by the importance of the different products to the viability of the mine. The same metal may be treated differently based on differing grades and quantities of products. The decision as to whether these are joint products or one is only a by-product is important as it may affect the allocation costs.

Joint products are metals or minerals within an ore body which each have significant relative sales values. Hansen et al. (2009) state that they are produced simultaneously by the same process up to a "split-off" point and from a common raw material source. Joint products are related to each other such that one joint product cannot be produced without the other. Furthermore, an increase in the output of one increases the output of the others, although not necessarily in the same ratio. Up to the often called split-off point, it cannot be obtained more of one product without getting more of the other(s). The split-off point is the point at which the joint products become separate and identifiable.

By-products are metals or minerals within an ore body which have minor sales values when compared with the principal product or products. Is a secondary product recovered in the course of production or processing of a primary product. For instance, by-products resulting from scrap, trimmings, and so forth, of the main products. According to Mudd et al. (2013), these metals are known also as companion metals (e.g., cobalt, molybdenum, rhenium, selenium, germanium, gallium, tellurium and indium). Although these metals often have economic and technological importance, the economic driver for mining here is undoubtedly the major metal. Besides, there are some groups of metals such as PGMs or REE that may occur as "coupled elements" without a real carrier metal.

Otherwise, some metals generally produced as by-products may also be mined as target metals on their own if they occur in elevated concentrations (e.g. cobalt, bismuth, molybdenum, gold, silver, PGMs and tantalum) or if demand exceed the supply available from by-product and joint product output.

As previously explained, more than one metal is commonly produced by the same mining and refining processes. Metals such as lead and zinc are commonly found together; silver is often found with gold. These are only two examples of the many joint products that Nature provides. Figure 5.6 depicts that each carrier commodity metal is associated in Nature (geology) by a distinctive mix of valuable minor elements. The latter has led to metallurgical processing being sharpened to effectively recover most elements economically. This complex link of materials can be observed in the "Metal Wheel", in which each element has a unique position. Therefore, eliminating or disrupting the production of one element will have an effect over all other connected elements Verhoef et al. (2004).

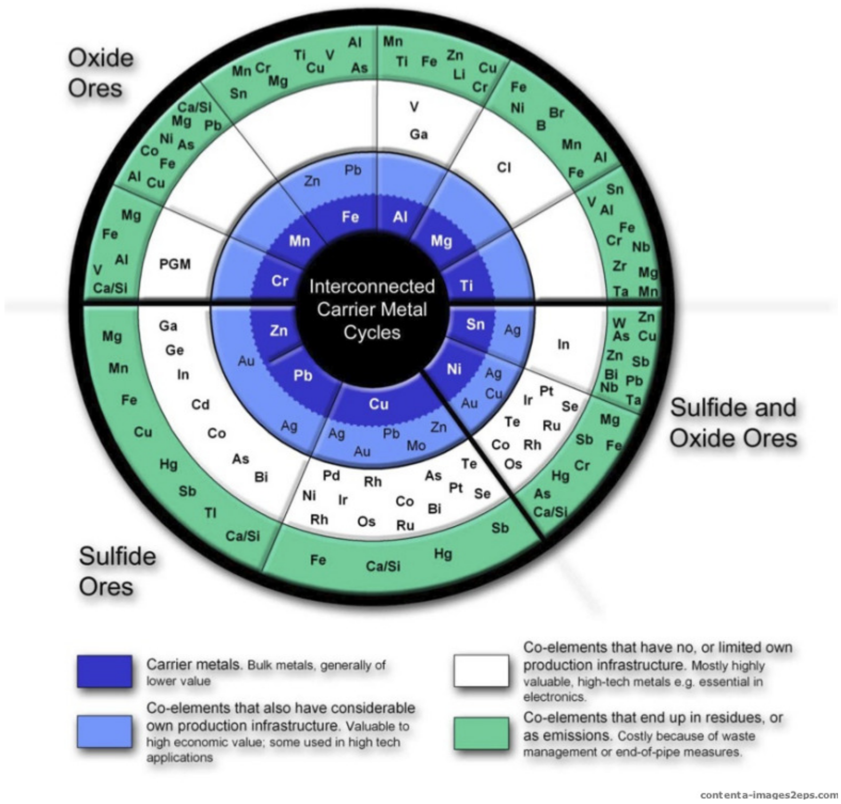


Figure 5.6: The metal wheel. Verhoef et al. (2004)

5.5 Approaches to allocating joint cost

As aforementioned, the Exergy Life Cycle Assessment provides average exergy costs of all manufactured products as well as the exergy needed for their use, maintenance, repair and disposal, it is focused in obtaining round numbers which could be used as ecological indexes of sustainability. However, the problem comes up when two or more products, by-products and residues are produced simultaneously. How to allocate costs? As stated by Valero & Lozano (1994), it is necessary to look inside the system in order to understand the process of cost formation, by identifying the internal relationships of all the structure components. Indeed, the main problem of allocating costs has been to find a function that adequately characterizes every one of the internal flows in a system and distributes cost proportionally. This function needs to be universal, sensitive and additive. That is, it needs to have an objective value for every possible material manifestations, it needs to be able to vary when these manifestations do so and each internal flow property needs to be represented additively. There is a wide international consensus that the best function, at least for energy systems, is exergy, which can contain in its own analytical structure the flow history.

Therefore three conditions are needed to allocate costs. First, the definition of the boundaries of the system. Second, a structure of the system in which all the components or processes are described in terms of black boxes interacting to each other through energy flows (or more generalized: energy, economic or information flows). Third, the definition of the purpose of production for each and every component.

The purposes of cost accounting could be stated in broad terms as: determination of the actual cost of products, settlement of a rational basis for pricing products and/or evaluation of their profitability as well as means for controlling costs.

Accordingly, cost allocation of mineral resources is not a simple task, due to the fact that an allocation method must allocates the cost on as reasonable basis as possible. As reported on PWC (2012), a systematic and rational basis of cost allocation should be applied when the conversion costs of a product are not separately identifiable.

Joint costs are the total of the raw material, labor, and overhead costs incurred up to the initial split-off point. Joint cost allocation is based on the proportional values of the products at the split-off point. Whilst, separable costs are those costs incurred after the split-off point; they can be easily traced to individual products.

For instance, if ore contains both iron and zinc, the direct material itself, is a joint product. Since neither zinc nor iron can be produced alone prior to the split-off point, the related processing costs of mining, crushing, and splitting the ore are also joint costs. The variety of products and the mutually beneficial costs, appear either because the material itself is a joint product or because processing results in the simultaneous output of more than one product.

By-products are not usually allocated any of the joint costs. Some mining entities assign to by-products only the costs of processing after the split-off point to by-products, because by-products are processed beyond the split-off point to bring them to a marketable form or to increase their value above their selling prince at the split-off point. Furthermore, the accounting treatment of by-products necessitates a reasonably complete knowledge of the technological factors underlying their manufacture, since the origins of by-products may differ.

As mentioned above, cost are either separable or not. Separable cost are easily traced to individual products and offer no particular problem. If not separable, they must be allocated to various products. All joint products benefit from the entire joint cost. The objective in joint cost allocation is to determine the most appropriate way to allocate a cost that is not really separable.

Although, there are variety methods for allocating costs to joint and by-products, they can be associated to two approaches, using market-based data or using physical measures. However, the physical measure of the individual products may have no relationship to their respective revenue-generating capacity. For example, in a gold mine that extracts ore containing gold, silver, and lead, the use of a common physical measure (tons) would result in almost all costs being allocated to lead, the product that weighs the most but has the lowest revenue-generating power. The physical method of cost allocation is inconsistent for this case, with the main reason that the mining company earns revenues from gold and silver, not lead. Thereby, Hansen et al. (2009) assert that there is no well-accepted theoretical way to determine which product incurs what part of the joint cost.

In this thesis, three different allocation methods are reviewed:

- Through *Tonnage*: For this allocation, the tonnage of each of the product and by-product is considered. External resources such as energy and raw materials are divided into the products according to its mass value.

- Through *Market Price*: The assignment based on price, considers the market price of each product obtained in the process.

- Through *Exergy Replacement Cost*: In this allotment, the exergy replacement cost of each element is taking into account. This allocation method introduces the depletion factor of mineral resources.

5.5.1 Tonnage Allocation of by-products

Under the physical units method, joint cost are distributed to products based on some physical measure of the joint products at the split-off point. However, cost allocation based on tonnage may be inappropriate if there is a significant difference between the relative sales values of the joint products, such as in a mine producing lead and silver. The costs allocated to the lower value product may exceed its net realisable value whilst the higher value product would result in "super" profits, as stated by Hansen et al. (2009).

Through tonnage allocation, the majority of environmental impacts would be ascribed to the most abundant product mined. The issue with this is, although based on physical phenomena, such a procedure does not reflect the physical value of minerals.

To exemplify, a tonnage allocation was done using the data of 33 mineral deposit models. Results presented in Tables 5.3 – 5.9, show that allocation based only on tonnage is not very suitable, due to the underestimating charges for certain by-products when the tonnage is low. For instance, Table 5.3 depicts the cost allocation for three mineral deposits developed by Cox & Singer (1992), where copper, gold and silver are found. It can be observed that cost allocation based on tonnage is not a reliable decision, because all cost would be attributed to copper, as in tonnage terms it is the most significant. Otherwise, the amount of silver and gold is very small, and consequently the cost associated with these metals would be almost neglected.

Table 5.3: Cost allocation of Cu-Au-Ag deposits as a function of tonnage, price and ERC.

Deposit	Porphyry Cu-Au				Cu skarn				Epith. quartz-alunite Au			
type	Ton.	Price		ERC	Ton.	Price		ERC	Ton.	Price		ERC
	[%]	[%]		[%]	[%]	[%]		[%]	[%]	[%]		[%]
		1980	2006			1980	2006			1980	2006	
Copper	99.96	56.6	81.3	70.3	99.86	43.3	73.3	46.1	98.9	3.1	9.5	5.3
Gold	0.01	38	17.4	28.2	0.01	40.3	21.7	50.0	0.3	90	86.7	92
Silver	0.03	5.4	1.4	1.5	0.13	16.3	5	3.9	0.7	6.9	3.8	2.7

5.5.2 Market Price Allocation of by-products

Metal price fluctuations depend on macroeconomic variables like industrial production, consumer prices, interest rates, stock prices and exchange rates, according to Labys et al. (1999). Kriechbaumer et al. (2014) assert that metal prices are the result of complex market and economic dynamics resulting in a great price fluctuation. Metal prices have been analyzed in several surveys by Brunetti & Gilbert (1995), Chen (2010), Dooley & Lenihan (2005), Figuerola & Gilbert (2001), McMillan & Speight (2001), Roberts (2009). Gleich et al. (2013) claim that in many cases commodity prices double or even triple within only few years. Humphreys (2013) argue that the price boom that started around 2004 has led to politicise metal supply.

However, authors like Gordon & Tilton (2008), assert that long-run trends in real prices of a mineral commodity provide a better indicator of trends in availability than physical measures indicating how much is left in the ground. This is because trends in real mineral-commodity prices can be upward or downward depending largely on whether new technology with the assistance of mineral substitution offsets the cost-increasing effects of depletion. Furthermore, Gordon & Tilton (2008) argue that if environmental impacts of mining industry are gradually included into cost structure of metal production (for instance, through carbon taxes) the price of metals will increase.

The most common allocation methods used to share out joint production costs to joint products at the split-off point, based on market data include: the sales value at split-off method, the net realizable value method, the constant gross-margin percentage method. These methods are preferred over the physical measures, because revenues are, in general, a better indicator of benefits received (PWC 2012). For instance, mining companies receive more benefits from 1 ton of gold than they do from 10 tons of copper. Besides, the physical measure of the individual products may have no relationship to their respective revenue-generating capacity. For example, in a gold mine that extracts ore containing gold, silver, and lead, the use of a common physical measure (tons) would result in almost all costs being allocated to lead, the product that weighs the most but has the lowest revenue-generating power. The physical method of cost allocation is inconsistent for this case, with the main reason that the mining company earns revenues from gold and silver, not lead.

In this section a market price allocation was done taking into account the unit value ($/ton) of the different commodities published in *U. S. Geological Survey* (USGS) from year 1900 to 2011. Chen (2010) asserts that metal prices rise to a peak in the 1980s, and in recent times, the price boom started around 2004, as stated by Humphreys (2013). Therefore, Tables 5.3 – 5.9 show the allocation factor for the year 1980 and 2006. Results depict great variations among years, commodities, by-products and models. The latter supports the idea that despite what price allocation supporters claim, market price is not a suitable indicator to assess mineral resources, because of the huge price volatility. Clearly therefore, resource consumption and greenhouse gas emissions need to be related to physical expenditures, not prices.

Table 5.4: Cost allocation of Cu-Au-Pb-Ag-Zn deposits as a function of tonnage, price and ERC.

Deposit	Zn-Pb skarn				Polymet. Replacement				Polymetallic vein			
type	Ton.	Price		ERC	Ton.	Price		ERC	Ton.	Price		ERC
	[%]	[%]		[%]	[%]	[%]		[%]	[%]	[%]		[%]
		1980	2006			1980	2006			1980	2006	
Copper	4.79	5.9	9.2	11.9	2.49	2.3	4.9	5.2	1.58	0.6	2.2	1.9
Gold	0.0005	5.1	2.5	6.2	0.001	6.2	4.3	4.0	0.001	1.7	2	3.3
Lead	33.54	17.3	15.9	27.7	54.82	20.9	26.6	37.7	74.58	12	25.6	30
Silver	0.12	43.7	12.4	19.8	0.21	56.4	22.1	29.0	0.72	82.3	54	58.4
Zinc	61.55	28	59.9	34.4	42.47	14.2	42.1	19.8	23.12	3.3	16.2	6.3

Deposit	Cyprus massive sulfide				Creede epith. vein				Comstock epith. vein			
type	Ton.	Price		ERC	Ton.	Price		ERC	Ton.	Price		ERC
	[%]	[%]		[%]	[%]	[%]		[%]	[%]	[%]		[%]
		1980	2006			1980	2006			1980	2006	
Copper	65.54	51.6	68.5	67.8	6.33	3.9	9.5	8.5	27.7	0.2	0.7	0.42
Gold	0.004	25.9	10.9	20.4	0.004	24.4	18.9	31.8	1	65.6	76.2	83.2
Lead	2.05	0.7	0.5	0.7	53.77	14.0	20	24	13.8	0.04	0.1	0.07
Silver	0.05	12.3	3.0	3.6	0.26	48.7	21.4	23.8	15.9	34	22.4	16.2
Zinc	32.36	9.4	17.1	7.5	39.64	9.1	30.1	12	41.5	0.1	0.6	0.14

Deposit	Kuroko mass. sulfide			
type	Ton.	Price		ERC
	[%]	[%]		[%]
		1980	2006	
Copper	26.13	30.3	38.9	45.9
Gold	0.002	16.6	6.8	15
Lead	15.55	7.6	5.7	9.1
Silver	0.06	20.6	4.8	7
Zinc	58.26	25	43.8	23

Table 5.4 shows the cost allocation for seven mineral deposits developed by Cox & Singer (1992), where copper, gold, lead, silver and zinc are found. In general, the high prices of gold and silver may drive the exploitation of the other commodities. However, it can be observed that cost allocation based on market price, not always attributes the cost to the most expensive commodity (e.g. gold). This is because the quantity of the produced metal is also considered.

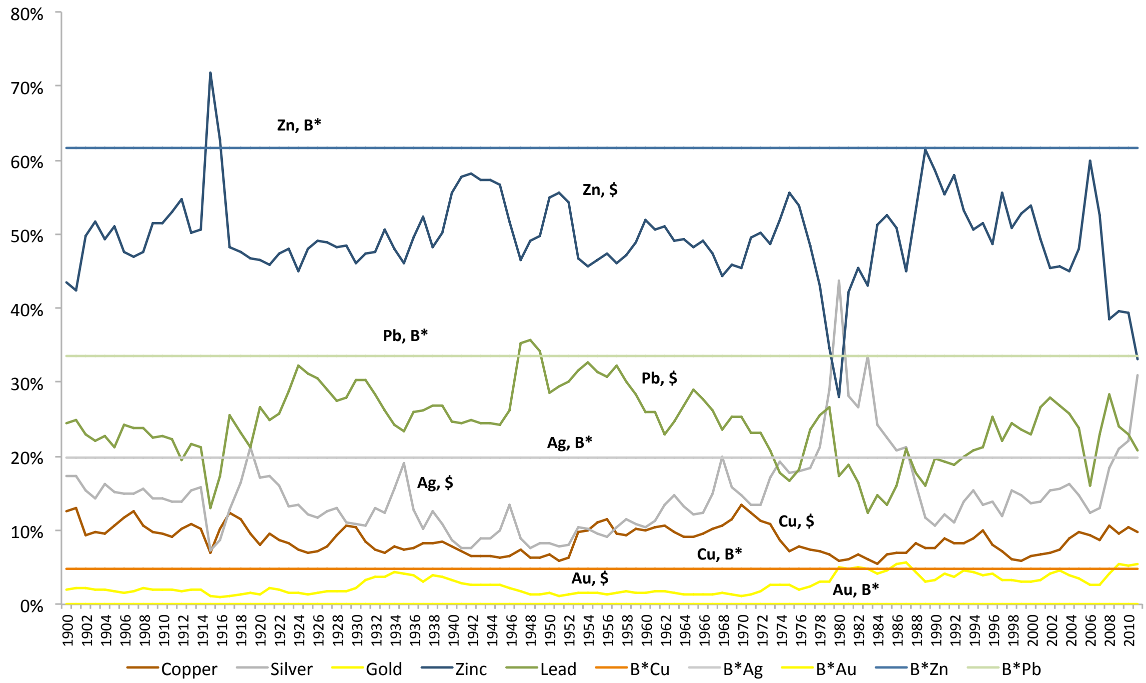


Figure 5.7: Cost allocation of Cu-Au-Pb-Ag-Zn deposits as a function of price and ERC.

The "Polymetallic vein" model of Table 5.4 shows a percentage allocation cost for silver of 82.3% in the year 1980 which decreases up to 54% in 2006. This is because of price volatility, depicted in Fig. 5.7. The problem with this allocation type is that burdens or energy consumption do not change at the same rate as price fluctuates (which in fact occurs frequently).

5.5.3 Exergy Cost Allocation of by-products

An alternative way to allocate costs as proposed in this thesis is through the Exergy Replacement Cost (ERC). ERC is greater for critical elements (e.g. gold, silver, cobalt) than it is for those found in abundance (e.g. limestone). A mineral has a high exergy replacement cost when 1) the concentration of the mineral in Thanatia is low and the difference between the ore grade of the current mines (x_m) is high and/or 2) when the energy required to extract the mineral and beneficiate it is significant. Consequently, when minerals are assessed through ERC, the exergy bonus that Nature provides by having minerals concentrated in mines instead of having them dispersed throughout the Earth's crust is taken into account.

Table 5.5: Cost allocation of Au – Ag deposits as a function of tonnage, price and ERC.

Deposit type	Placer Au-PGE Ton. [%]	Price [%] 1980	Price [%] 2006	ERC [%]	Carbonate-hosted Au-Ag Ton. [%]	Price [%] 1980	Price [%] 2006	ERC [%]	Low-sulfide Au-quartz veins Ton. [%]	Price [%] 1980	Price [%] 2006	ERC [%]
Gold	13	81.7	88.7	92.2	10.5	77.7	86	90.3	76.3	99	99.4	99.6
Silver	87	18.3	11.3	7.8	89.5	22.3	14	9.7	23.7	1	0.6	0.4

Deposit type	Homestake Au Ton. [%]	Price [%] 1980	Price [%] 2006	ERC [%]
Gold	85.1	99.4	99.7	99.8
Silver	14.9	0.6	0.3	0.2

Table 5.5 depicts the cost allocation for four mineral deposits developed by Cox & Singer (1992), where gold and silver are found. The fact that gold has a higher ERC than silver, lead to a great cost allocation for it, as Fig. 5.8 shows. The specific exergy replacement costs (GJ/t), shown in Table 5.5, need to be multiplied by the tonnage of the given commodity. The greater a commodity's replacement cost, the more energy (or environmental burden) is allocated to it and subsequently the strengths of price and tonnage as indicators are combined, with the highest importance placed on those minerals that are more"socially valued". It is thus a physical measure independent of monetary arbitrariness supported by the rigorous theory of Thermoeconomics.

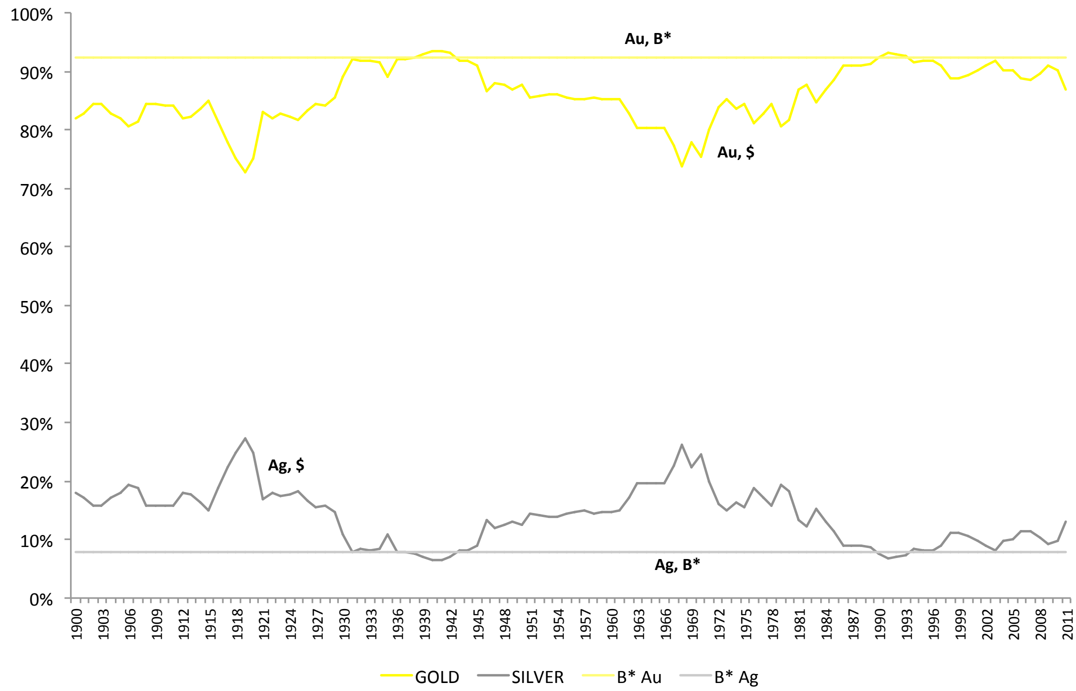


Figure 5.8: Cost allocation of Au-Ag deposits as a function of price and ERC.

5.6 Cost allocation of by-products applied to mineral deposits

Once the three allocation options have been explained, allocation among commodities are presented in Tables 5.3 – 5.9, which show how costs are allocated as a function of tonnage, price (for 1980 and 2006) and Exergy Replacement Cost of 33 mineral deposit models containing 12 commodities: phosphorous, manganese, iron, cobalt, nickel, copper, molybdenum, silver, gold, zinc, lead and antimony. Allocation was done from 1900 to 2011, however a summary of each deposit type is presented in the Tables 5.3 – 5.9 which are calculated with the mean average grade and tonnage of each deposit type.

Table 5.6: Cost allocation of Co-Au-Mo-Ag deposits as a function of tonnage, price and ERC.

Deposit type	Porphyry Cu				Porphyry Cu skarn-related				Porphyry Cu-Mo			
	Ton. [%]	Price [%]		ERC [%]	Ton. [%]	Price [%]		ER [%]	Ton. [%]	Price [%]		ERC [%]
		1980	2006			1980	2006			1980	2006	
Cobalt	98.2	68.5	81.7	42.6	97.9	61.3	78	41.7	95.4	64.5	71.6	70.2
Gold	0.002	13.5	5.1	50	0.003	18.2	7.4	50	0.0002	1.4	0.5	0.9
Molybdenum	1.8	11.8	11.9	6.5	2	11.6	12.5	7	4.5	28.5	26.8	27.5
Silver	0.03	6.2	1.3	0.9	0.05	8.9	2	1.4	0.03	5.6	1.1	1.4

According to the different allocation methods used, it can be observed that tonnage allocation is not a reliable indicator, as explained in section 5.5.3. For instance, in the case of copper and its more valuable by-products: gold and silver, if the tonnage indicator is selected, none of the burden is ascribed to gold or silver due to their much lower grade compared to copper. If exergy replacement cost is applied, the results are similar to those obtained via the price indicator. This supports the idea that the exergy replacement cost indicator is very close to the value society places on minerals. Nevertheless, contrarily to prices, exergy replacement cost does not fluctuate with external factors linked to market mechanisms but remains constant as can be seen in Figures 5.7 – 5.12. That said, exergy replacement costs are a function of the technology used and can be obtained from energy data published in different sources such as that provided by the Ecoinvent database. Hence, the values are as reliable as the sources used and are subject to improvements.

To have a general outlook of the cost allocation based on market price, Figures 5.7 - 5.12 show the historical trend of commodities prices from 1900 to 2011, for several mineral deposit models, where different commodities are obtained. From the figures, it can be clearly appreciated the great price fluctuation throughout time, being evident that the mining and metallurgical industry requires a more objective allocation method, like the one proposed in this thesis through the exergy replacement costs and represented in the figures by the straight line.

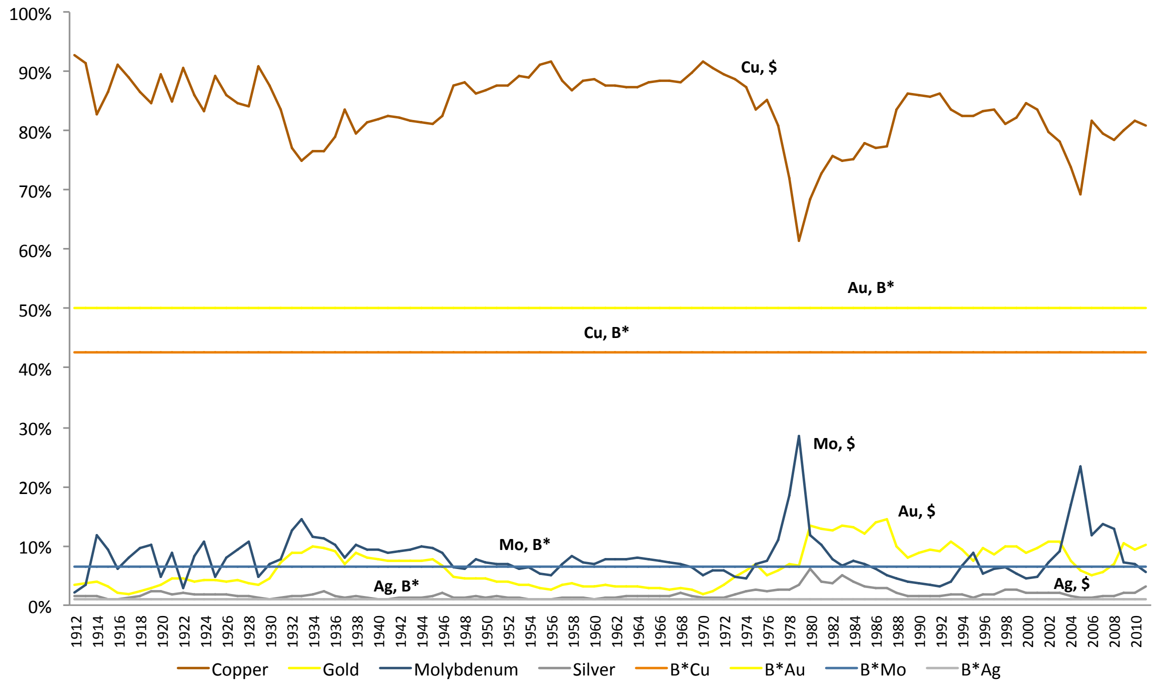


Figure 5.9: Cost allocation of Co-Au-Mo-Ag deposits as a function of price and ERC.

Table 5.7 shows two deposit models of copper and its by products: gold, silver and zinc. This table is important because it is based on real deposits founded in the Earth's crust and analyzed by Cox & Singer (1992). The allocation procedure through the three options explained previously were applied. It can be observed, that values of exergy allocation factor for copper and silver are very similar to those obtained in the case study presented in Table 5.10. For instance, the "Besshi massive sulfide" deposit show an exergy allocation factor of 80 % for copper and 2.2% for silver, whilst the case study show an exergy allocation factors of 89% and 2%, respectively.

Table 5.7: Cost allocation of Cu-Au-Ag-Zn deposits as a function of tonnage, price and ERC.

Deposit	Besshi massive sulfide				Sado epith. vein			
type	Ton. [%]	Price [%]		ERC [%]	Ton. [%]	Price [%]		ERC [%]
		1980	2006			1980	2006	
Copper	72.2	66.3	77.7	80.3	42.7	2.5	7.8	4.6
Gold	0.002	13.6	5.1	9.9	0.2	81.1	78.8	87.9
Silver	0.04	10.6	2.2	2.9	0.9	15.1	8.3	6.1
Zinc	27.71	9.4	15	6.9	56.2	1.2	5.2	1.4

Figure 5.10 shows the historical trend of commodity prices (market price allocation) from 1900 to 2011 for the "Besshi massive sulfide" deposit, where a great price fluctuation throughout time, can be noted. The exergy replacement costs (exergy allocation) is represented by the straight line.

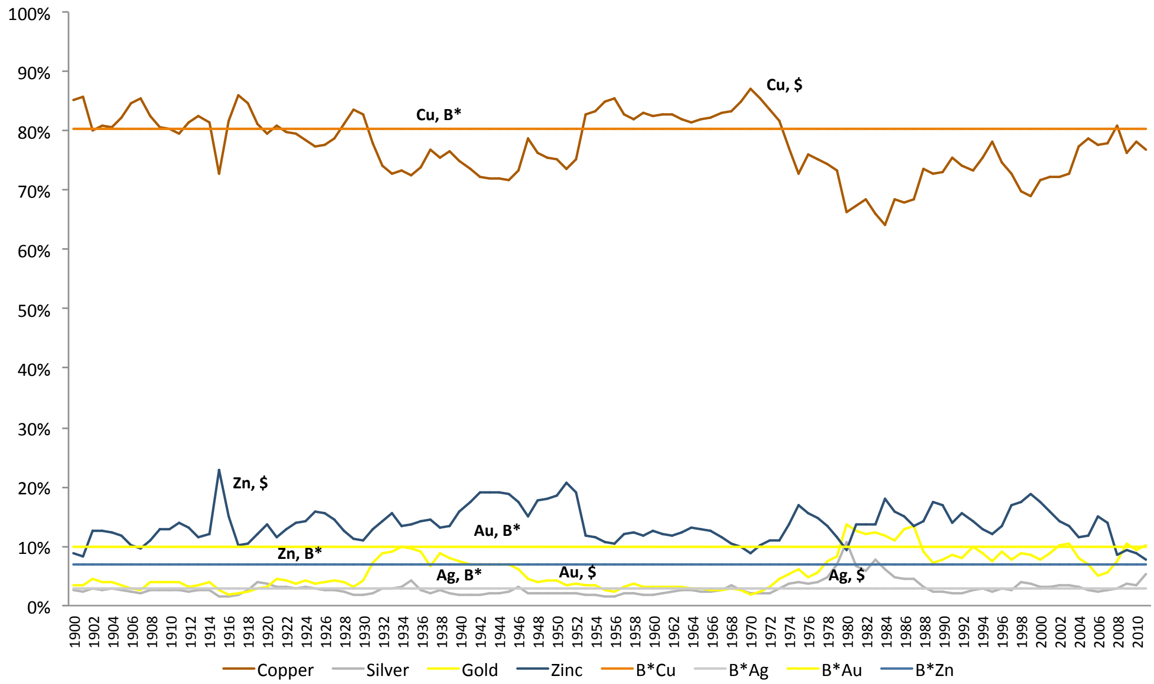


Figure 5.10: Cost allocation of Cu-Au-Ag-Zn deposits as a function of price and ERC.

Table 5.8 depicts three deposit models of cobalt and its by products: copper, gold and nickel. This deposit contains two of the commodities analyzed in this section, copper and cobalt. The allocation procedure through the three options explained previously were applied. It can be observed that values of exergy cost allocation for copper and cobalt are very different to those obtained in the case study presented in Table 5.10, due to the different tonnage. Hence, it is important to highlight that there is a general exergy allocation factor for each specific commodity, depending on the amount of mineral produced.

Table 5.8: Cost allocation of Co-Cu-Au-Ni deposits as a function of tonnage, price and ERC.

Deposit	Komatiite Ni-Cu				Dunitic Ni-Cu				Synorg.-synvolc. Ni-Cu			
type	Ton. [%]	Price [%]		ERC [%]	Ton. [%]	Price [%]		ERC [%]	Ton. [%]	Price [%]		ERC [%]
		1980	2006			1980	2006			1980	2006	
Cobalt	3.5	24	4.7	35.9	2.8	19.7	3.7	30.1	3.9	30	6.5	46
Copper	8.2	2.4	2.5	0.8	3.8	1.1	1.1	0.4	37.2	12.4	14.2	4.5
Gold	0.0002	0.6	0.2	0.1	0.0002	0.5	0.2	0.1	0.001	2.5	0.9	0.5
Nickel	88.3	73	92.7	63.2	93.4	78.6	95.1	69.4	58.9	55	78.4	49

Figure 5.11 shows the historical trend of the market price allocation from 1900 to 2011 for the "Komatite" deposit, as well as the exergy replacement costs allocation represented by the straight line (B*). It can be noted that price allocation could be above the exergy allocation (e.g. nickel) or below (e.g. cobalt).

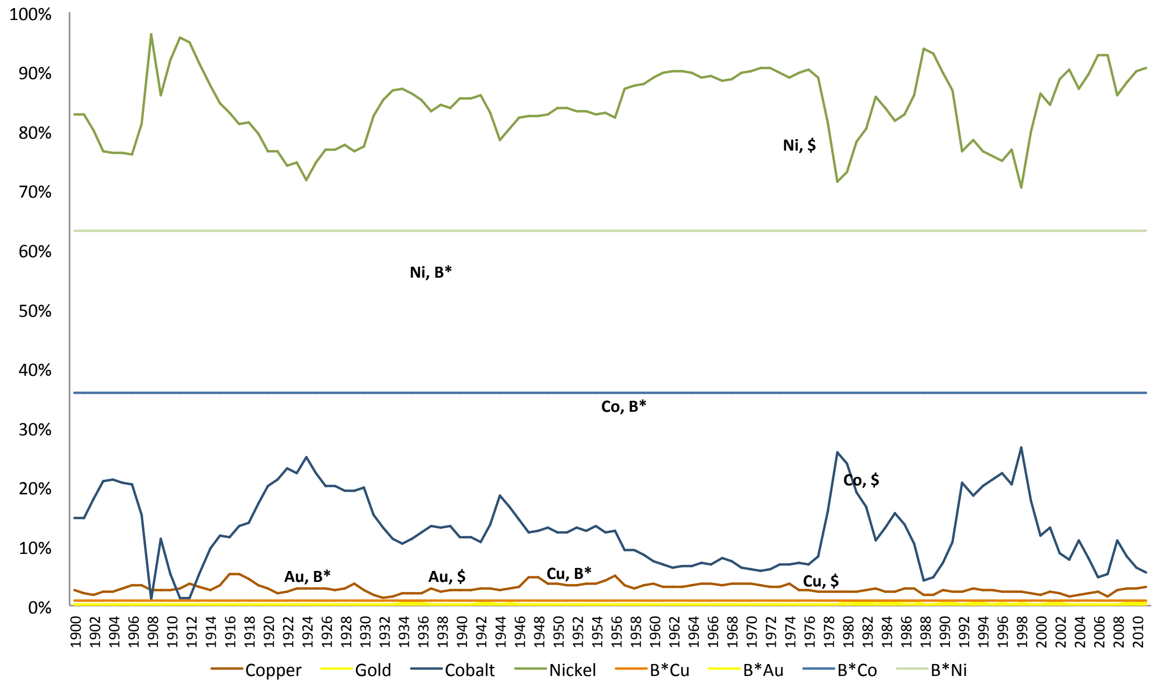


Figure 5.11: Cost allocation of Co-Cu-Au-Ni deposits as a function of price and ERC.

Table 5.9 depicts two deposit models of lead, silver and zinc. This deposit contains two of the commodities analyzed in this section, lead and silver.

Table 5.9: Cost allocation of Pb-Ag-Zn deposits as a function of tonnage, price and ERC.

Deposit	Sandstone-hosted Pb-Zn				Missouri / Appalach. Pb-Zn			
type	Ton. [%]	Price [%]		ERC [%]	Ton. [%]	Price [%]		ERC [%]
		1980	2006			1980	2006	
Lead	78.4	62.1	59.7	77.5	23.3	24	12.8	30.3
Silver	0.04	22.9	6.8	8.1	0.01	6.4	1.1	2.3
Zinc	21.5	15	33.5	14.4	76.7	69.6	86.2	67.4

Figure 5.12 shows the historical trend of the market price allocation from 1900 to 2011 for the "Sandstone" deposit, as well as the exergy replacement costs allocation represented by the straight line is close to the price allocation factor. This means that commodities have been valuated in a similar way in which it would be allocated taking into account the ERC.

Additional Tables and Figures of deposit models are presented in the Appendix C.

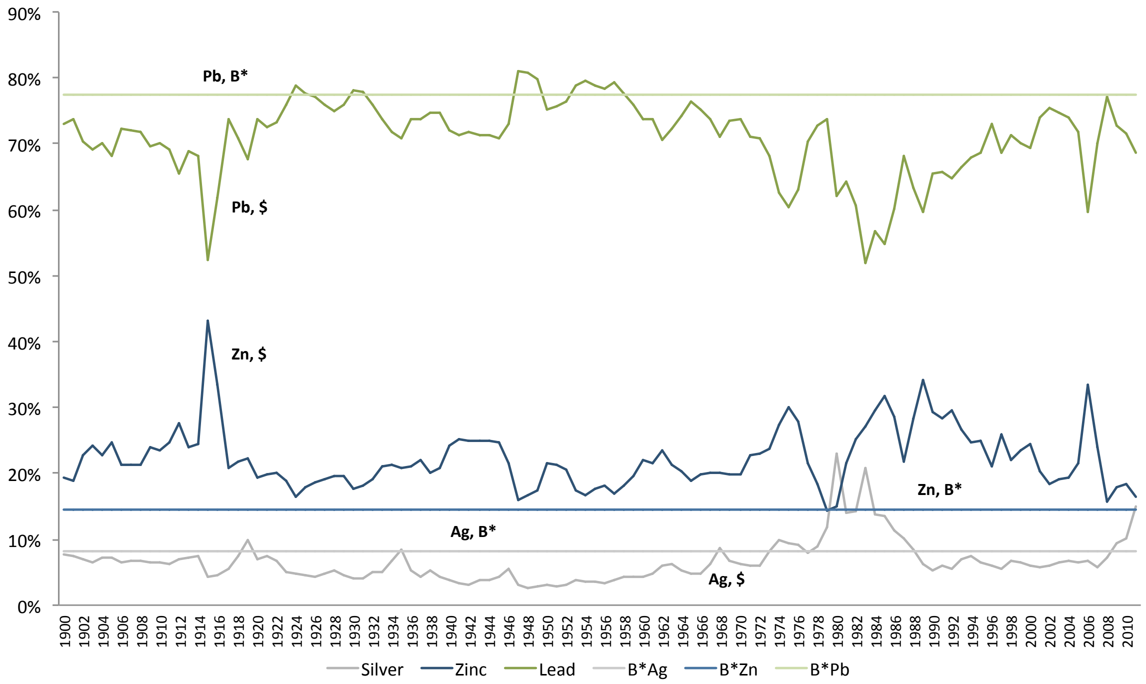


Figure 5.12: Cost allocation of Pb-Ag-Zn deposits as a function of price and ERC.

5.7 Exergy cost allocation applied to mining and metallurgical processes

Once the cost allocation has been done for specific deposits, the methodology can be applied to mining processes in order to allocate inputs of raw materials, utilities, emissions and so on. For this kind of allocation methods, it is necessary a detailed knowledge of the process involved in the commodities production. Data such as energy (fuel and electricity), ore and raw material mass, in each production stage is needed to perform the analysis.

In this section, the analysis of four case studies of mineral production is carried out. Due to lack of information about real processes, the case studies used in this section were proposed from information of different sections of Ecoinvent database (Classen et al. 2007) and do not represent a specific mining operation. A detailed analysis of a metallurgical process will be carried out in the following chapter. Hence, in this chapter only theoretical and simplified case studies are presented as a way to show how the allocation procedure works in the mining industry. The first case involves copper production and its by-products: molybdenum, silver and tellurium. The second case assesses nickel production and its by-products: copper and cobalt. The third case analyzes lead production and its by-products: zinc, silver and cadmium. The fourth case evaluates the rare earth elements: lanthanum, cerium, praseodymium, neodymium, gadolinium and yttrium.

5.7.1 Exergy Cost Allocation of Copper and its by-products

Copper is always associated with other metals, mainly nickel, molybdenum and platinum group metals. In this case, copper is extracted jointly with molybdenum, silver and tellurium. In order to assess the production process of copper, a Thermoeconomic Input-Output analysis (considering ERC as explained in Chapter 4) was performed.

Data of raw material and utilities (e.g. electricity, natural gas and fuel inputs) used during the production process were taken from Ecoinvent database Classen et al. (2007). According to the copper production process shown in Fig. 5.13, molybdenum is obtained right after the mining and beneficiation operations. Pretreatment, reduction and refining processes follow and by-products tellurium and silver are obtained from this second stage. Once the material flows have been identified, exergy cost allocation of inputs of electricity or natural gas among the products of the considered process is performed as depicted in Fig.5.14. In the same way, all inputs such as chemicals, raw materials and utilities are allocated.

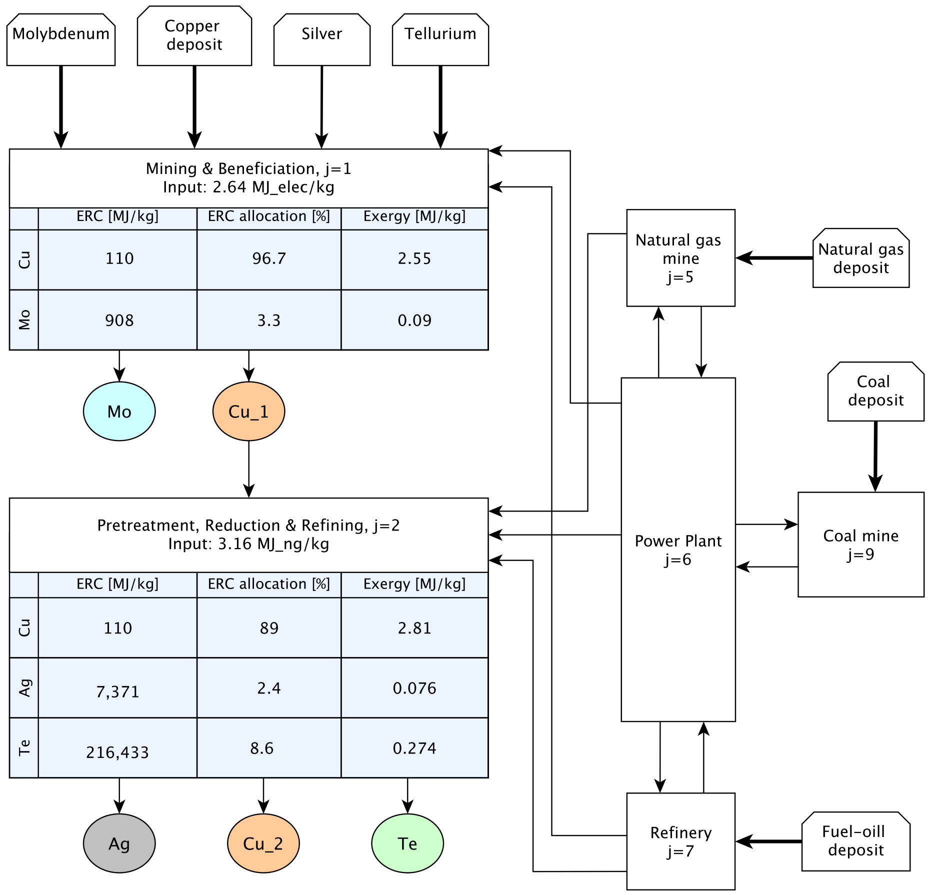


Figure 5.13: Exergy Cost allocation of Cu and its by-products Mo, Ag and Te.

Finally, a thermoeconomic analysis of the process allows to obtain the exergy cost of each of the commodities obtained, which in turn can be converted into monetary units considering the electricity price. Accordingly, one can compare the market price of the commodities with that considering the exergy costs required to produce them. Obviously market prices do not only take into account production costs, but also include other factors alien to the physical reality of commodities. In addition, prices do not take into account the fact that with extraction and the further dispersion of materials, the mineral heritage of the Earth is being destroyed and becoming thus unavailable for future generations.

Table 5.10 depicts the results obtained for the copper example. Amount of product obtained, unit price (market price of the commodity for the year 2011 according to *U. S. Geological Survey* (USGS)), exergy cost and their respective allocation factors (a.f.), as well as an additional allocation factor based on the chemical exergy, are shown.

Table 5.10: Allocation factors of copper and its by-products Mo, Ag and Te

Commodity	Output product [kg]	Exergy cost a.f. [%]	Exergy Cost [MJ/kg]	Unit price [$/kg]	Ton. a.f. [%]	Price a.f. [%]	b_{ch} a.f. [%]
Copper_1		97	44		99.6	98.5	99.7
Copper_2	1	89	186	9	99.956	94	99.99457
Molybdenum	0.00411	3	545	34	0.4	1.5	0.3
Tellurium	7.17E-06	8	73,324	349	0.040	5	0.00004
Silver	3.26E-04	2	6,419	1,130	0.005	1	0.00539

Figure 5.14 shows the commodity prices vs. the units of exergy required to produce 1 kilogram of metal. It can be seen that costs based on ERC show higher values respect the unit price value. Accordingly, a critical commodity such as tellurium, should have a higher unit price, in order to reflect properly its physical condition in Nature.

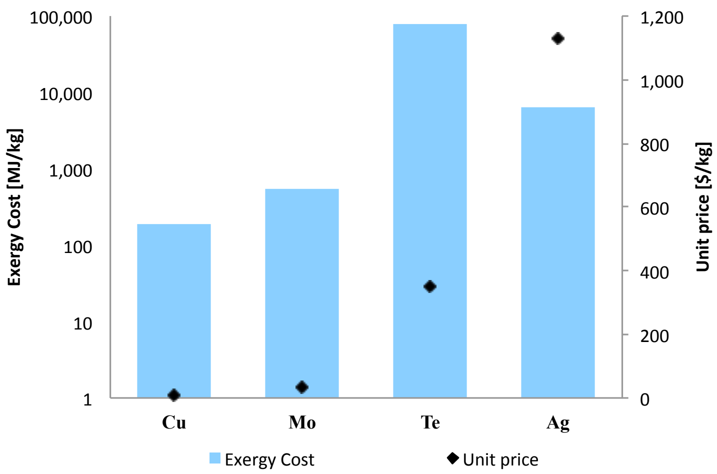


Figure 5.14: Cost allocation of Cu by-products, based on price and exergy.

5.7.2 Exergy Cost Allocation of Nickel and its by-products

Since nickel is always associated with other elements, its production generates other metals like copper and cobalt. A detailed study of the nickel production process is performed in Chapter 6. Thence, the exergy analysis required to obtain the exergy cost used in this section is taken from section 6.1.1. The production system for nickel production is shown in Fig. 5.15. The processing operations have been grouped into four general stages: 1) Mining and Beneficiation and 2) Drying, Roasting and Smelting, 3) Converting and 4)Electrolysis. Figure 5.15 depicts the input-output of utilities (e.g. electricity, natural gas, fuel oil and coal) and raw materials (e.g. ores from which nickel is produced).

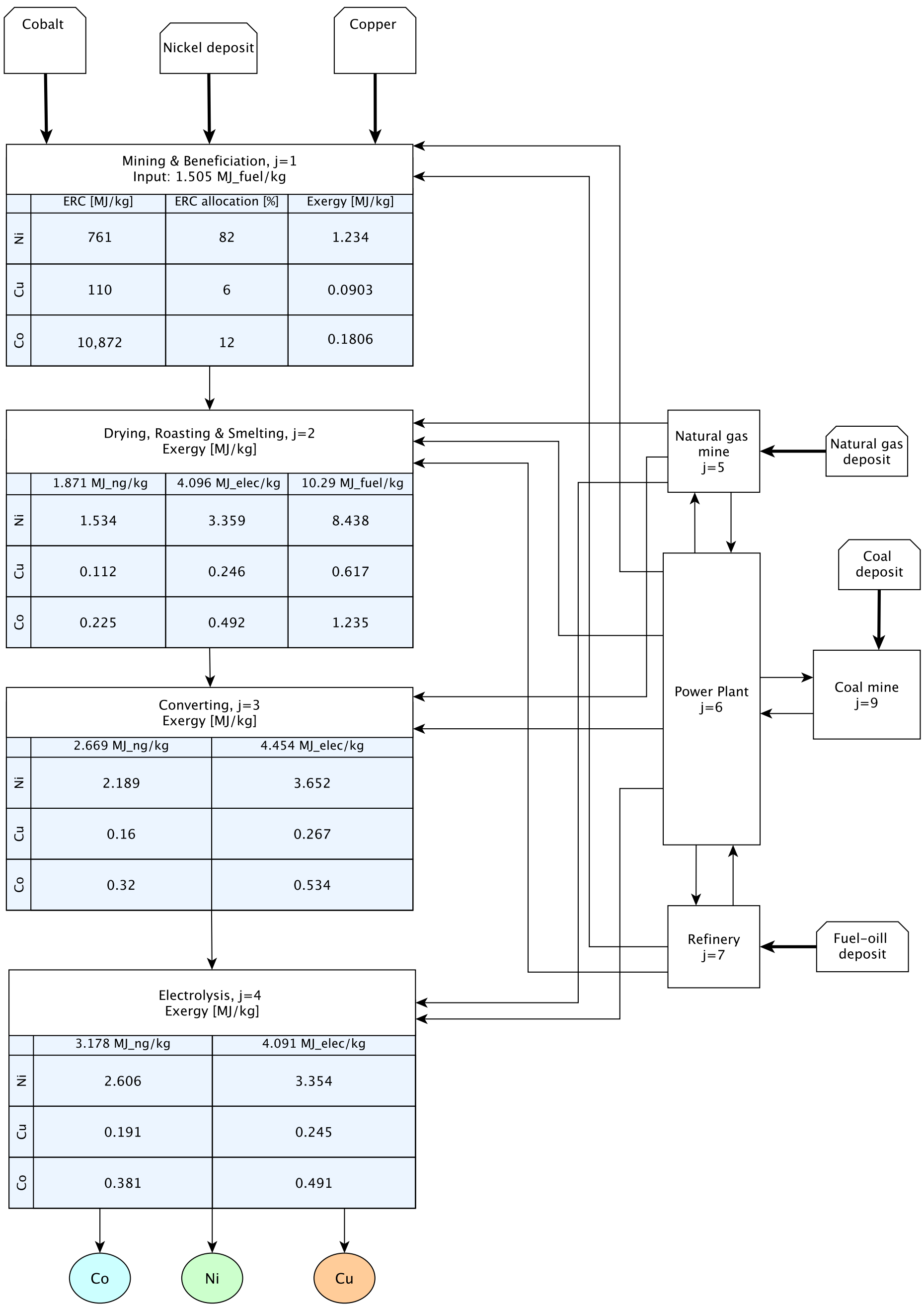


Figure 5.15: Exergy Cost allocation of Ni and its by-products Cu and Co.

Nickel by-products are obtained together with nickel at the last step, in the amounts indicated in Table 5.11. Two issues are shown in Fig. 5.15. First, at mining and beneficiation step ($j = 1$), an input of 1.505 MJ/kg of fuel oil is required. Accordingly, the ERC of minerals involved in this operation are depicted, and the exergy cost allocation factor is calculated (taken into account the mass output of each mineral). This way, the input can be distributed to each mineral in an objective way. Second, the following steps ($j = 2$, $j = 3$, $j = 4$) show all inputs of natural gas, electricity and fuel oil for each stage. Considering the exergy cost allocation, calculated previously in stage 1, these input are alloted to each mineral. This will be the general procedure to analyze any metallurgical system, where main product and by-products are obtained.

Table 5.11 shows the variables considered to obtain the exergy cost allocation of each commodity, such as: the output product, the exergy cost allocation factor obtained from exergy replacement cost and the amount of mineral mined, the exergy cost calculated from a thermoeconomic input-output analysis and the unit price provided by *U. S. Geological Survey* (USGS) in the year 2011.

Table 5.11: Allocation factors of nickel and its by-products Cu and Co.

Commodity	Output product [kg]	Exergy cost a.f. [%]	Exergy Cost [MJ/kg]	Unit price [$/kg]	Ton. a.f. [%]	Price a.f. [%]	b_{ch} a.f. [%]
Nickel	1	82	1,534	23	65.57	82.2	67.3
Copper	0.515	6	53	9	33.77	16.5	32.2
Cobalt	0.01	12	1,906	36	0.66	1.3	0.4

Figure 5.16 depicts the exergy cost calculated through the thermoeconomic input-output analysis vs. unit price of metal. It can be observed that exergy cost based on ERC and unit price, gives the same appreciation for the three commodities. In first place cobalt is highlighted by price and by exergy content, in second place is nickel and in third place copper.

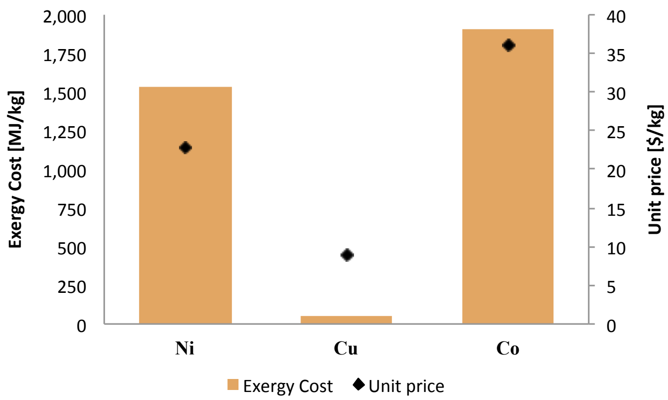


Figure 5.16: Cost allocation of Ni by-products, based on price and exergy

5.7.3 Exergy Cost Allocation of Lead and its by-products

The allocation of the subprocesses lead-silver production is not clear, because the only available data are the final commodity prices. Besides the share of the products in total costs is not easy to estimate. In Ecoinvent, Classen et al. (2007) the by-product allocation problem (the join production of silver and lead) is undertake by a subdivision of the sub-processes. The starting point for the estimation depends on the general profit expectations of the company, considering an arbitrary performance value of 10%. Hence, the allocation factors are based on revenue but these values are corrected by mass in order to keep up with the resource balance in the final commodity. Metal prices are used as the allocation parameter for polymetallic mines in Classen et al. (2007).

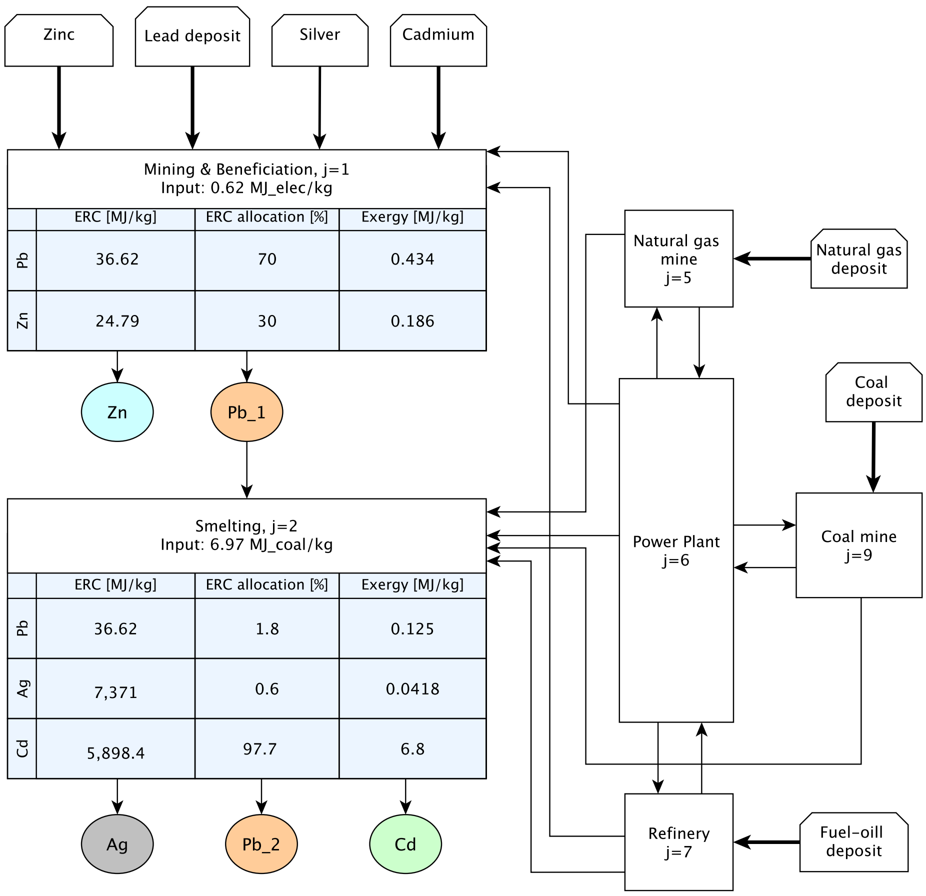


Figure 5.17: Exergy Cost allocation of Pb and its by-products Zn, Ag and Cd.

The exergy cost allocation to lead production and its by-products zinc, cadmium and silver, starts with the definition of the processing operations, which are grouped in two general stages: 1) Mining and Beneficiation and 2) Smelting. Figure 5.17 depicts the input-output of utilities (e.g. electricity, natural gas, fuel oil and coal) and raw materials (e.g. ores from which copper is produced), as well as the point in the process where the by-product are obtained. The same procedure (previously explained for copper and nickel, in Figs. 5.14 – 5.16, respectively) is followed to estimate the exergy cost allocation factor. In this manner, the inputs are shared out among the commodities obtained in each process.

Table 5.12 depicts the exergy cost allocation factor for each commodity, it can be observed that in the case of lead in the first stage the allocation factor is 70% whilst in the second stage is 1.8%. This situation is presented because in the first case, lead shares the energy inputs with zinc, which has a lower ERC. The opposite occurs in the last stage, where cadmium and silver have a very high ERC. This situation demonstrates that a general exergy cost allocation for a mineral processing operation cannot be established, but rather a detailed analysis of each process is required in order to allocate cost suitably.

Table 5.12: Allocation factors of lead and its by-product Zn, Ag and Cd

Commodity	Output product [kg]	Exergy cost a.f. [%]	Exergy Cost [MJ/kg]	Unit price [$/kg]	Ton. a.f. [%]	Price a.f. [%]	b_{ch} a.f. [%]
Lead_1		70	120		61.5	65	33.5
Lead_2	1	1.8	252	3	74.6	50	61.3
Zinc	0.626	30	59	2	38.5	35	66.5
Cadmium	0.339	97.7	4,595	3	25.29	17	38.4
Silver	0.00153	0.6	6,659	1,130	0.11	32	0.3

Figure 5.18 depicts the exergy cost calculated from a thermoeconomic input-output analysis and the unit price of commodities provided by *U. S. Geological Survey* (USGS) in the year 2011. It can be observed that silver is the only metal with high market price and high exergy cost. On the contrary, cadmium for instance, has a very low price considering its high exergy content.

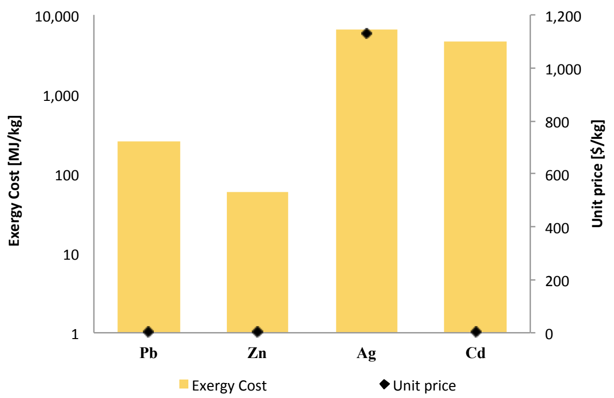


Figure 5.18: Cost allocation of Pb by-products, based on price and exergy.

5.7.4 Exergy Cost Allocation of REE

The rare earth elements (REE) are a group of seventeen chemically similar elements. Nonetheless in this analysis only six will be taken into account: lanthanum, cerium, praseodymium, neodymium, gadolinium and yttrium. REE are generally obtained from monazite or bastnaesite. This study is focused on the former ore. The production structure of REE processing depicted in Fig. 5.19 is divided into three general steps: 1) Mining and Beneficiation, 2) REO (Rare Earth Oxides) separation and 3) Reduction. Stages 2 and 3 are separated for light, medium or heavy REE. (See Chapter 2, section 2.12). In order to perform the exergy analysis, the production process was separated in two stages: oxide production (mining and beneficiation and REO separation) and metal production (separation and reduction of LRE, MRE and HRE). The energy required during these processes are presented in Table 2.13. The oxide production is considered as the concentration step. In fact, with such energy values, the ERC [MJ/kg] were calculated and presented previously in Table 5.2. All data used in this analysis was taken from the study developed by Koltun & Tharumarajah (2008).

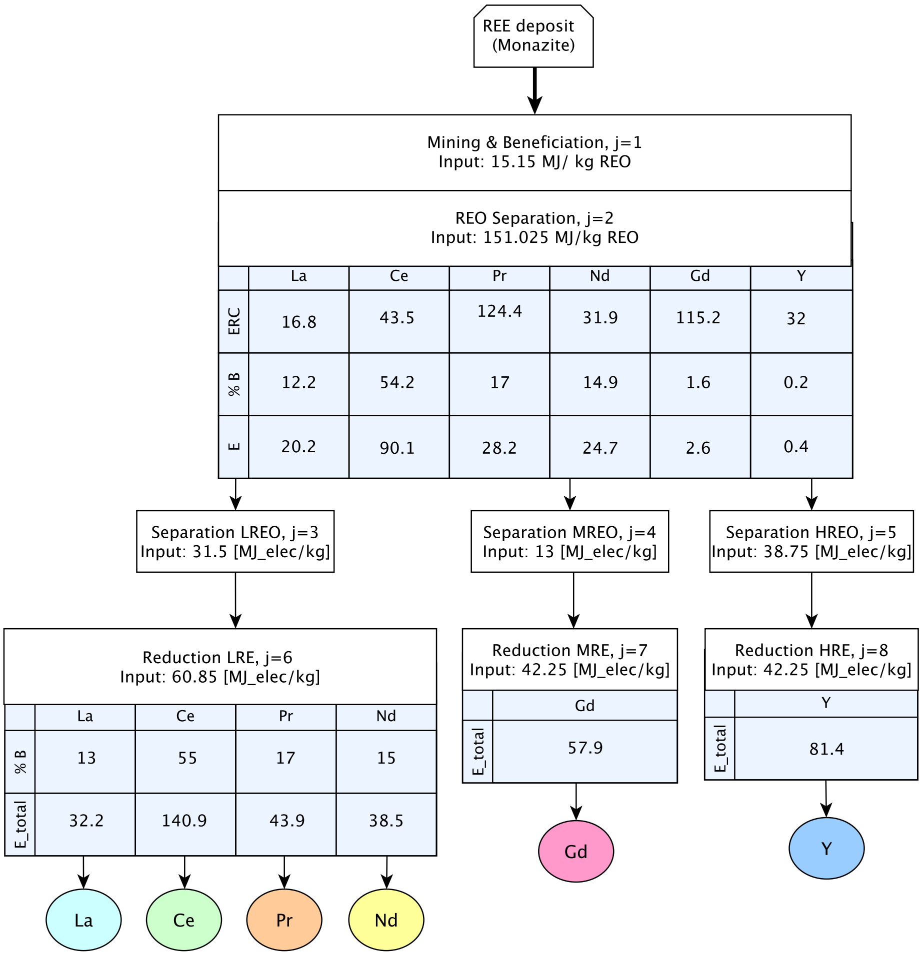


Figure 5.19: Exergy Cost allocation of REE.

Figure 5.19 shows the general scheme to produce REE. Once, the ERC have been calculated, it is possible to calculate the exergy cost allocation factors (% B), for the oxide production processes. Then, the total energy input of 166.175 MJ during the oxide production of 1 kg of a mixture of REO ($j = 1$ and $j = 2$) was considered and allocated to each REE as shown in Fig. 5.19. The subsequent stage of metal production has a total energy input of 92.35 MJ/kg of light REE, 55 MJ/kg of medium REE and 81 MJ/kg of heavy REE. The exergy allocation was performed in the same way than for oxide production. Accordingly, the total energy consumption (E_{total}) which includes the oxide and metal production was calculated for each REE and depicted in Fig. 5.19.

Table 5.13 shows the output amount of each REE, the exergy cost allocation factor, the unit price provided by *U. S. Geological Survey* (USGS) in the year 2011, the price allocation factor and the tonnage allocation factor. It can be observed that although the numbers are quite different for the three allocation factors (ERC, price and tonnage), the order to appraise the REE is similar. The REE with the greatest allocation factors is cerium, whereas yttrium and gadolinium are those with the lowest ones. This is because cerium is the most abundant REE in monazite whilst yttrium and gadolinium are the least abundant. It is important to highlight that the exergy cost allocation factors are based on ERC (which in turn are independent on the mass output product or metal prices) this is why exergy cost allocation factors provide more objective values to perform any distribution of resources among the different products obtained from the same process.

Table 5.13: Exergy Cost Allocation of REE.

Commodity	Output product [kg]	Exergy Cost a.f. [%]	Unit Price [$/kg]	Price a.f. [%]	Ton. a.f. [%]
Lanthanum	0.228	12.2	38	26.2	27.9
Cerium	0.392	54.2	30	35.6	48
Praseodymium	0.043	17.0	60	7.8	5.3
Neodymium	0.147	14.9	63	27.9	18
Gadolinium	0.004	1.6	165	2.2	0.5
Yttrium	0.002	0.2	50	0.3	0.3

5.8 Summary

In this chapter, the tools described in the Ch. 4 have been improved, so as to adapt the methodologies to the analysis of mining and metallurgical systems. Accordingly, an analysis of the energy used in mining as function of ore grade, the exergy replacement cost and the unit exergy costs of different minerals have been performed. Results obtained were published in Domínguez et al. (2013). The general observed trend is that as the ore grade declines, the energy and the exergy replacement costs increase exponentially. A mineral has a high exergy replacement cost when 1) the concentration of the mineral in the crepuscular crust (in Thanatia) is low and the difference between the ore grade of the current mines (x_m) is high and/or 2) when the energy required to extract the mineral and beneficiate it is significant.

The obtained values are an intermediate step for assessing in a physical way, the free exergy provided by Nature that man is rapidly destroying through the depletion of high-grade ores. This should serve as an assessment tool for decision-makers in the mineral industry. It should be stated that the values obtained are first assessments. Important assumptions have been made, such as assuming that the same technology is applied for the whole range of grades analyzed, including the crepuscular ore grade. One of the major limitations found is the lack of real data over time. So estimation of future trends of this issue without real and reliable information becomes subjective. Therefore, the results and data provided are an attempt to afford indicators for identifying challenges and opportunities in the mining sector and should not be taken as final and closed.

An additional activity undertaken in this chapter was to propose a new allocation method. Since the mining and metallurgical industry commonly produces two or more commodities simultaneously and bearing in mind that the use of LCA in these processes will continue to increase, the necessity to look for suitable by-product cost allocation procedures, was presented. In this chapter, three cost allocation approaches through tonnage, price and exergy replacement cost were analyzed and applied to 33 different mineral deposits. The exergy replacement cost allocation procedure was further applied to four metallurgical processes (copper, nickel, lead and REE), using an extended thermoeconomic approach. It was demonstrated that cost allocation through tonnage is not always a suitable option because minor by-products appearing at very low concentrations can be even more valuable than the major product. With market prices used to perform cost allocations, the problem is associated with their high volatility, which in turn depends on macroeconomic variables that commonly do not reflect the physical conditions of non-fuel mineral resources in Nature and the fact Man is destroying the mineral wealth on Earth, which will be unavailable for future generations. The exergy cost allocation using exergy replacement cost provides in turn, objective values to dispersion and offers a "natural" cost of minerals extracted. Furthermore, it measures mineral endowment depletion on a grave to cradle basis.

Once the general basis to perform a complete exergy analysis of mineral resources and the metallurgical processes have been presented, in the next chapter a more detailed exergy analysis of the processing of seven metals is carried out.

Chapter 6

Exergy analysis of metal processing

In this chapter, the exergy analysis is applied to seven metals through three different methodologies. Firstly, the exergy accounting for the case of nickel processing is performed by applying the methodology used first by Ayres et al. (2006). However, the scope of this methodology is extended in the "cradle to market" path through the use of the Thermo-ecological Cost (TEC). Accordingly, in second place, an exergy analysis through the TEC methodology is accomplished in order to extend the scope of the mineral processing from a specific mining operation to a general mineral production system. Finally, the same analysis is carried out through a combination of the TEC and the ERC. The result is an improved TEC methodology (denoted here as TERC) with which an absolute exergy life cycle analysis can be accomplished (including also the grave-cradle approach), thereby allowing for a complete and deeper assessment of non-fuel mineral processing. The resulting "TERC" analysis has been further applied to seven mineral processing chains: aluminium, copper, chromium, gold, iron, nickel and manganese.

6.1 Exergy accounting applied to mineral processing

As was explained throughout this thesis, exergy analysis can be used to assess energy and material inputs and outputs in metallurgical systems whilst also helping to identify opportunities for improving the efficiency of processes and help to achieve a more sustainable mining sector. Some commodities related to nickel production, like iron and steel, have already been the subject of exergy analyzes. For instance, Michaelis et al. (1998) applied the exergy analysis to the steel life cycle concluding that electricity use is one of the largest exergy consumers in its production. Costa et al. (2001) likewise undertook exergy accounting of energy and material flows for various steel production processes, coming to the conclusion that overall exergy losses are highly dependent on the efficiency of electricity generation. Ostrovski & Zhang (2005) focused on identifying exergy losses of specific processes such as direct iron smelting. They found that the overall fuel efficiency depends on the utilisation of gases emitted as by-products.

Other investigations, such as the exergy assessment of natural resources accomplished by Finnveden & Ostland (1997) demonstrated that chemical exergies along with specific system boundaries may be used as a characterisation method in life cycle assessments as well as other applications of exergy analysis.

This section undertakes an exergy analysis of the two main routes for nickel production, namely from laterites and sulphides. Exergy inputs and outputs as well as exergy efficiencies for both, including their disaggregated steps, are presented and discussed.

6.1.1 The case of nickel processing

The exergy accounting for the case of nickel processing is performed by applying the methodology used first by Ayres et al. (2006) who accomplished exergy analyzes of five metal industries: steel, aluminium, cooper, lead and zinc. Ayres et al. consider that although exergy can be divided into four components: kinetic, potential, physical and chemical, only the last one should be taken into account. Considering that the systems under analysis are chemical and metallurgical processes, the first three components are disregarded, and only the chemical exergy component is used to assess and analyze mining operations. Hence, the methodology is based on the assumption that chemical exergy is the main and only component taken into account.

It is however important to point out that physical exergy b_{ph}[1] is relevant for analysing thermal and mechanical processes such as power plants, yet not so important when chemical and metallurgical processes are surveyed. Consequently, the exergy associated with pressure or temperature should be considered in those processes where these properties show a significant differentiation relative to the environment (e.g., steam production). In this regard, an exergy analysis applied to the life cycle of steel performed by Michaelis et al. (1998) suggest that both, the physical and chemical exergies, must be considered in order to take into account the pressure or temperature differences relative to environmental conditions. However, one of the conclusions of this study was that steel production is primarily a chemical process and therefore, physical exergy can be disregarded.

As already explained in Chapter 4, the chemical exergy b_{ch} is the work that can be obtained by a substance having the parameters T_0 and P_0 to a state of thermodynamic equilibrium with the datum level components of the environment[2] and thus is closely related to the energy required in the metallurgy of the mineral.

In this particular case study, the chemical exergies for each mass flow in the process of nickel production are obtained through Eq. 4.27. The chemical exergy content of fuels meanwhile, has been determined by multiplying an exergy coefficient by its net heating value, as performed in Szargut et al. (1988*b*).

A list of several substances involved in nickel production from laterites and sulphide ores, their chemical exergy and exergy coefficients of fossil fuels is presented in Table 6.1.

[1]Physical exergy is the work obtainable by taking a substance through reversible physical processes from its initial state (temperature T, pressure p) to the state determined by the temperature T_0 and the pressure P_0 of the environment, (Szargut et al. 1988*b*).

[2]The reference environment used in this work is that proposed by Szargut et al. (1988*b*) and is commonly used to calculate standard chemical exergies for a number of chemical compounds and pure elements.

Table 6.1: Chemical exergies of substances involved in nickel production. The values are obtained from Ayres et al. (2006), Szargut et al. (1988*b*), Valero, Valero & Gomez (2011).

Description		Exergy (GJ/t)
Ammonium sulphate	$(NH_4)_2SO_4$	4.98
Cement	Ca_3SiO_5	1.19
Carbon dioxide	CO_2	0.44
Copper	Cu	2.11
Cu ground	$CuFeS_2$	8.38
Cyanide	CN	9.15
Flotation agent	CuS	7.19
Hydrogen	H	116.88
Leaching agents		1.64
Lime	$CaCO_3$	0.18
Ni ground		8.85
Silica	SiO_2	0.014
Slag		0.014
Steam	$H_2O_{(g)}$	0.52
Sulphur dioxide	SO_2	4.85
Sulphuric acid	H_2SO_4	1.64
Water	$H_2O_{(l)}$	0.0416
Coal		23587.84
Coke		29998
Fuel oil		42383.5
Natural gas		45760
Diesel fuel		42265

Afterwards, an exergy accounting is applied to the overall chain of nickel production, not only to single process stages. Information regarding raw materials and utilities for each step was obtained from Ecoinvent (Classen et al. 2007), the data base of metal life cycle inventories. The assumptions considered in performing both a mass and exergy analysis are:

1. H_2SO_4 is obtained in sulphuric acid production plants, where 200% of by-product off-gases are recovered from previous sintering, roasting and smelting processes, (Ayres et al. 2006).

2. H_2SO_4 is the leaching agent.

3. The composition of dross, slag and anode slime is the same as sulphide acid tailings.

4. Losses are not taken into consideration.

The exergy balance for each step of the production process can be calculated according to Eq. 4.2. In order to calculate exergy efficiency, it is important to define inputs and products. A further analysis not carried out in this study, should take into account that nickel production involves processes where some by-products such as slags, tailings, sulphur acid, etc., are obtained.

The stages in each process chain are characterised by inputs such as raw materials (RM) and utilities (carbon, natural gas, fuel oil, diesel, coke and electricity); outputs such as tailings, slags, steam, dross, slimes among other wastes; and energy losses in form of heat. Heat released by the system into the surroundings is by convention, a negative quantity, whilst the energy transferred to the system as heat from its surroundings is a positive quantity. In the flow diagrams shown in Figures [6.1-6.3] as well as in the Tables [6.2 - 6.4], values are expressed in mass units for raw materials and in energy units for fuels and heat.

Table 6.2: Main mass and energy flows for the production of 1 kg of nickel from laterites.

Process		Mining	Drying	Roasting	Refining	Other	Melting
Inputs	[kg]						
	Ni ground	1.74					
	Explosive	0.001					
	Lime						0.47
Utilities	[MJ]						
	Diesel	1.91					
	Electricity	0.11	2.34	2.88	24.48	1.08	1.8
	Natural gas		28.8				1
	Fuel oil				3.75		
	Coal			40			
Outputs	[kg]						
	Overburden	18					
	Slag						12.4
	Dust						0.3
	Carbon dioxide						0.21
Wastes	[kg]						
	Dust	0.01					
Waste heat	[MJ]		32.29	46.4	24.34	33.4	2.62

Table 6.2 displays the main mass and energy consumption of each production step when the starting material is nickel laterites. The simplified mass flow diagram of the production of 1 kg of nickel from these sources is presented in Fig. 6.1, including the associated exergy flows entering or leaving the system.

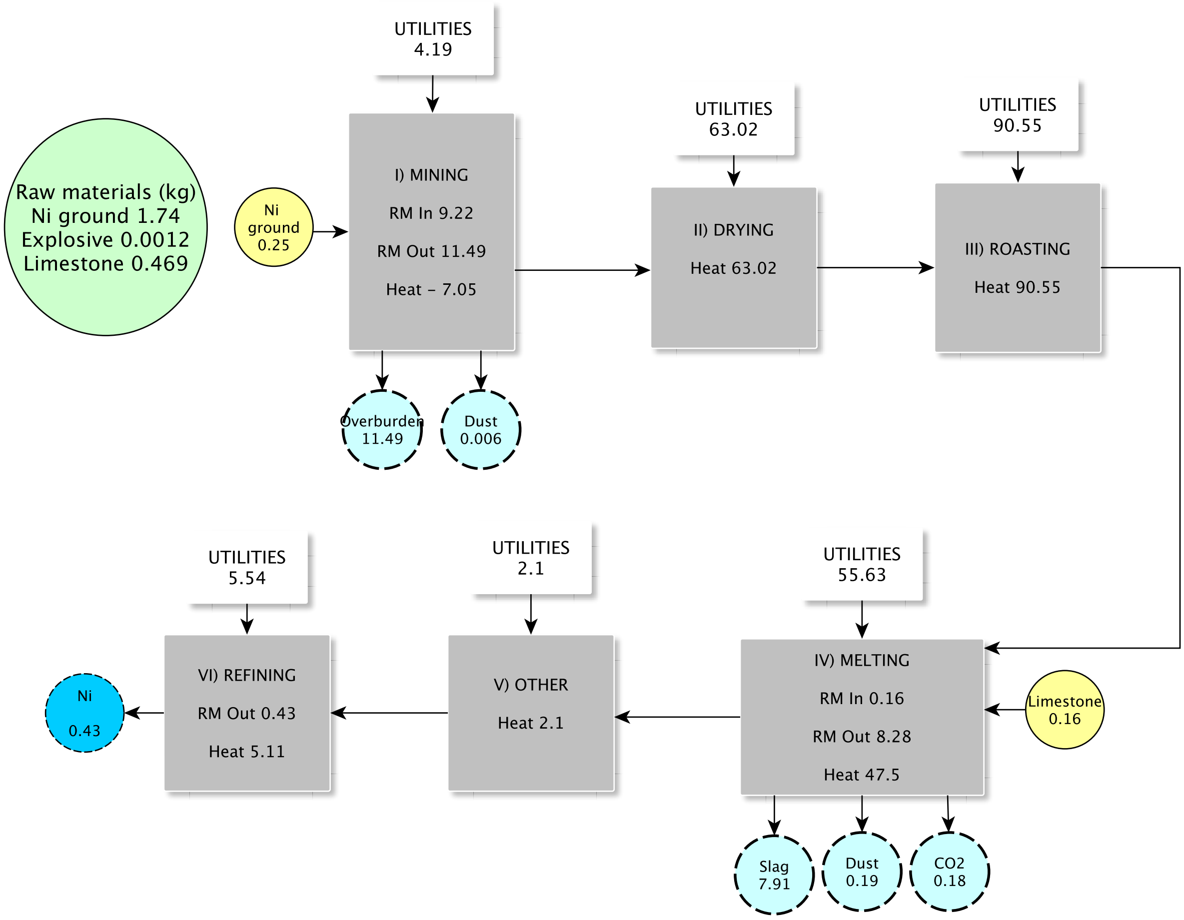


Figure 6.1: Exergy flows (MJ) in the production of 1 kg of nickel from laterites.

The most energy-intensive processes are the pyrometallurgical treatments: drying, roasting and refining. The first one has a high consumption of natural gas, the second one consumes a large amount of coal, and the third one consumes mainly electricity. In regards to waste heat, the drying, roasting and refining processes have once again the highest values. On the other hand, outputs such as overburden are presented mostly in the initial mining step and slags in the last melting step.

Figure 6.2 shows the simplified mass and exergy flow diagram for the production of 1 kg of nickel with a sulphide origin, whereas Table 6.3 displays the main mass and energy consumption of each production step.

It is shown that the mass input is considerably larger for sulphides than for laterites due to the great amount of water used during mining and beneficiation operations. The process with the highest energy consumption is the smelting stage, which uses fuel oil. Mining operation also shows a significant consumption of electricity. Thence, both processes show the largest values corresponding to waste heat. Mining and beneficiation stages produce large amounts of tailings and overburden. Overburden is disposed close to the mine whilst tailings usually are left to tailing heaps or ponds.

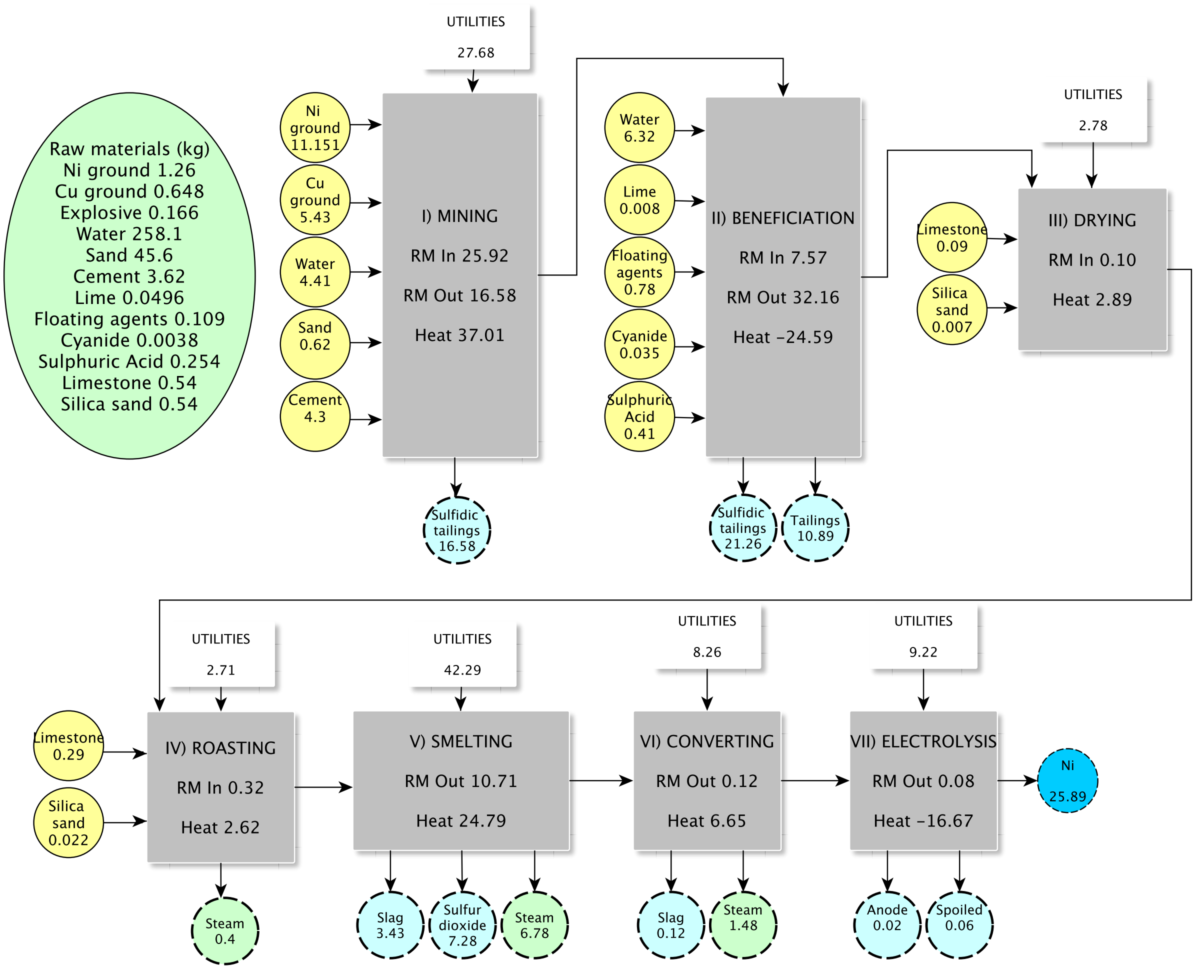


Figure 6.2: Exergy flows (MJ) in the production of 1 kg of nickel from sulphides - option A.

As aforementioned, there are sundry routes to produce nickel from sulphide ores. Figure 6.3 shows the mass and exergy flows associated with an alternative production route. Table 6.4 displays the main mass and energy consumption of each production step shown in Figure 6.3 from which exergies are obtained.

Table 6.4 depicts that leaching technologies are those that have the higher utilities consumptions in the form of electricity. Leaching processes performed with sulphidic acid involve the use of off-gas and shows a high value of waste heat. Till heap leaching operation presents different kinds of wastes or even copper as a by-product.

Broadly, it can be observed, that exergy wastes in form of heat are considerably higher during production of nickel from laterite ores than those of the sulphide ores due to their complex metallurgy. Therefore, as expected exergy efficiency values are lower than for sulphides.

Table 6.5 shows results of exergy and exergy efficiency obtained for eleven different routes of nickel production. It is noticeable that exergy consumption during mining and beneficiation steps for laterites is smaller than for sulphides, due to the fact that laterite ores are mostly mined open cut and beneficiation is carried out by easy and economic techniques. Otherwise, exergy required during the refining process of laterites is larger than for any sulphide option because laterites cannot be significantly upgraded or concentrated before the smelting and refining steps, hence almost all laterite ore mined must be treated in the entire process.

Table 6.3: Main mass and energy flows for the production of 1 kg of nickel from sulphides - option A.

Process		Mining	Beneficiation	Drying	Roasting	Smelting	Converting	Electrolysis
Inputs	[kg]							
	Ni ground	1.26						
	Cu ground	0.65						
	Explosive	0.17						
	Water	106.1	152					
	Sand	45.6		0.54	1.66			
	Cement	3.62						
	Lime		0.16	0.54	1.66			
	Cyanide		0.004					
	Sulphuric Acid		0.25					
Utilities	[MJ]							
	Diesel	11.2						
	Electricity	15.7		0.25	0.78	10.44	5.09	5.1
	Natural gas			2.44		2.8	3.05	3.97
	Fuel oil				1.8	24.8		
	Coke					2.2		
Outputs	[kg]							
	Sulphidic tailings	50.7	65					
	Tailings	33.3						
	Slag					10.5	0.39	
	Sulphur dioxide					1.5		
Wastes	[kg]							
	Steam				0.78	13.1	2.86	
	Anode slime							0.07
	Spoiled anodes							0.18
Waste heat	[MJ]	37.01		2.89	2.628	24.79	6.65	9.14

Table 6.4: Main mass and energy flows for several processes in the production of 1 kg of nickel from sulphides .

Process		Sulphuric acid	Leaching	Reduction	Carbonyl	Purification of leaching	Hydrogen reduction
Inputs	[kg]						
	Off gas	22.6					
	Leaching agents		0.08				
	Hydrogen						0.005
Utilities	[MJ]						
	Electricity	4.49	2.62	0.06	0.82	0.06	0.06
	Natural gas		1.76				
	Fuel oil				1.21		
Wastes	[kg]						
	Ammonium sulphat		0.3				
	Precipitates		0.17				
	Dross		0.03			0.001	
	Copper		0.51				
	Steam			0.24			
Waste heat	[MJ]	22.98	1.95			0.06	2.35

The exergy values presented in Table 6.5, show the same tendency as energy consumption for nickel production presented in Table 2.10 in Chapter 2, since in both cases, energy and exergy analysis, it can be observed that greater values are presented for nickel production coming from laterites than from sulphides, although the chemical exergy of laterites (0.0788 GJ/t) is smaller than for sulphides (8.85 GJ/t).

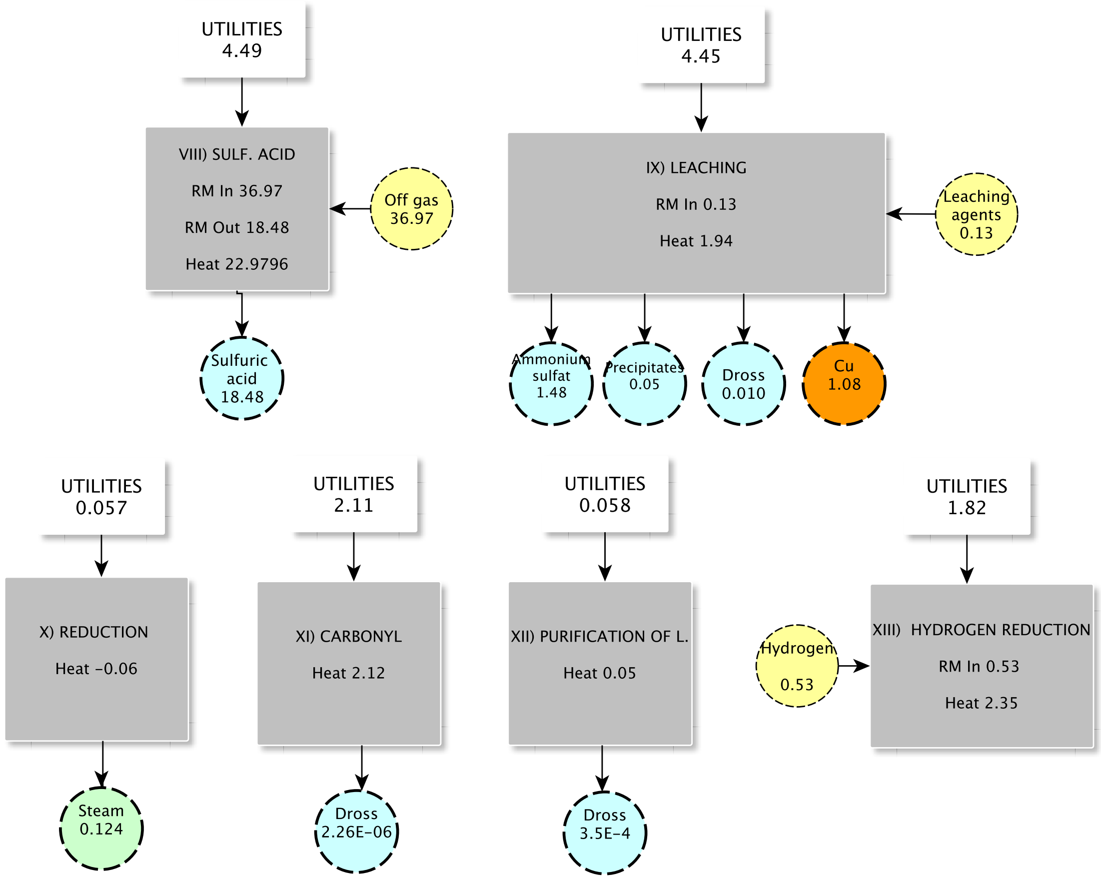


Figure 6.3: Exergy flows (MJ) for several processes in the production of 1 kg of nickel from sulphides.

Exergy required to obtain 1 kg of nickel from laterites or sulphide ores is 221 GJ/t and 127 GJ/t, respectively, as depicted in Table 6.5. However, different values can be obtained depending on: the system boundary selected (for instance, if direct electricity or the primary energy sources extracted from the environment used to produce electricity, are considered as inputs), the accurate composition of ores (based on information from specific mines), the multi-output allocation problem (which usually takes place in mining and metal production where several metals are produced from the same raw material) and the way in which it is solved. Sulphide ore processing has efficiencies fluctuating from 0.67 to 0.79, depending on the specific technologies utilised. The higher efficiencies are reached when leaching technologies are used. On the contrary if nickel is produced from laterites, the efficiencies achieved are lower on average (0.38) due to the cost-intensive processing.

Table 6.5: Exergy and exergy efficiency in nickel production. Values expressed in GJ/ton of Ni.

Process	Mining and beneficiation	Smelting and refining	Total	Exergy Efficiency ε
Laterites	4.45	217.02	221.46	0.39
Sulphides				
A	61.17	65.71	126.88	0.67
B	61.17	58.60	119.77	0.71
C	61.17	61.07	122.25	0.69
D	61.17	52.68	113.85	0.75
E	61.17	59.79	120.96	0.71
F	61.17	55.01	116.18	0.73
G	61.17	56.83	118	0.72
H	61.17	46.88	108.06	0.79
I	61.17	51.52	112.7	0.76

The obtained results allow to have a unified picture of the overall processes involved in nickel production. The use of the same units for all inputs and outputs facilitates a direct comparison among production routes, the establishment of efficiency ratios including not only energy (in form of electricity, diesel, natural gas or coal), but also water and raw material consumptions and the identification of improvement possibilities. This way for instance, it has been stated that when leaching technology is used to produce nickel, higher efficiencies are obtained than when electrolysis processes are utilised.

Nevertheless, there are some aspects in this methodology that are not taken into account. One of the most limiting shortcomings of the exergy analysis is its *complexity* of calculation and in the understanding of it for non-exergy practitioners, including plant engineers or decision makers. This means that the advantages of using exergy as an accounting tool need to be perfectly justified and in this regard, exergy analysis should provide information and solutions that other more conventional analyzes are unable to do.

The total exergy associated with the production of nickel is lower for sulphides than for laterites. But the same conclusion can be drawn if the analysis is carried out regarding only energy values (as revealed by Table 2.10), since the use of other substances is not very relevant. Hence, the use of exergy as it was implemented here is not justified. The same thing happens with many other metals where the dominant factor in the production chain is the consumption of energy and not of water, chemicals, etc.

Furthermore, awkward results can be obtained when using only the chemical exergy of substances as an accounting tool. For instance, a common chemical used in the metallurgy sector, sulphuric acid, has a chemical exergy value of 161 kJ/mol, whereas scarce and precious gold has only 60 kJ/mol. Here it can be seen clearly that the chemical exergy component is not always a good accounting tool and should not be used in isolation. In the case study, laterites have an almost negligible chemical exergy, although the energy requirements and exergy accounting results are greater than those obtained for sulphides, which in turn have a greater chemical exergy.

There is an important factor missing from the methodology, namely the concentration exergy. As explained previously, laterites are more abundant than sulphides. If only chemical exergy is taken into account, then it is clear that the best way to produce nickel is from sulphides. In the same way, from a chemical exergy point of view, gold is of little value. Therefore, the way in which the minerals are found on the crust is completely ignored with the methodology suggested by Ayres et al. (2006). This shortcoming is solved by integrating the Exergy replacement cost into the calculations, as performed in the next sections. The latter approach implies that the scarcity factor of mineral resources should be accounted for when assessing the sustainability of mining and metallurgical processes. If this is indeed carried out, the advantage of using sulphides over laterites is not so evident.

Additional and detailed information in regards to mining processing can be obtained if the boundaries of the analyzed system are expanded. For instance, the analysis of a specific mining operation can be enlarged if the system of energy production (power and refinery plants) required to produce minerals is included. The latter can be performed through the Thermo-Ecological Cost methodology, which also will be complemented with the Exergy replacement cost, as depicted in next sections.

6.2 Thermo-Ecological Cost applied to metallurgical systems

The Thermo-Ecological Cost (TEC) expresses the cumulative consumption of non-renewable exergy per unit of the considered useful product (Szargut 1986, 1989, 2005) and provides a *cradle to market* approach. In this section, the analysis of nickel processing is extended with the TEC methodology, broadening the scope from a mineral processing operation to a more complex metallurgical system where the power and refinery plants (required to satisfy the energy consumption of minerals production) are included into the exergy analysis.

6.2.1 TEC analysis: the case of nickel production

The first step to calculate the TEC of a process is to identify the inlet and outlet flows of raw materials, semi-finished products and products for each stage. In order to exemplify the methodology, the case of nickel production is analyzed first.

In Chapter 2 – section 2.2.13, the general route to produce nickel from sulphide ores has been explained. It includes several steps, namely: ore mining, beneficiation, drying, roasting, smelting, converting, sulphuric acid, leaching, reduction, electrolysis, purification of leachate and carbonyl. There are assorted processes used to produce nickel. These variations depend on factors such as the grade or the concentrate and the presence of other metals in the material mined. The options for nickel production from sulphide concentrates are classified in Table 2.11. Nevertheless, Fig. 6.4 depicts the nickel processing route A: mining, beneficiation, drying, roasting, smelting, converting and electrolysis.

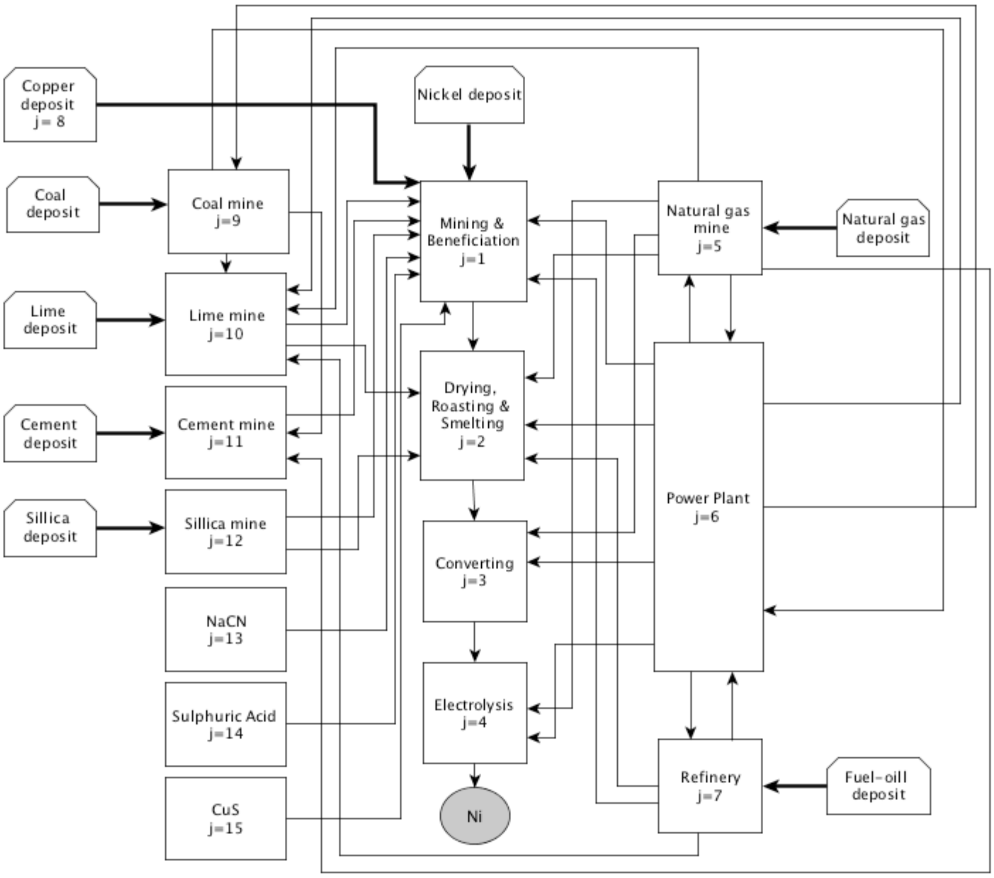


Figure 6.4: Nickel production system for sulphide ores.

Whilst, the way to produce nickel from laterite ores, described in Chapter 2 – section 2.2.12, consists mainly of five linked operations: ore mining, drying, roasting, melting and refining, as depicts Fig.6.5. Accordingly, Tables 6.6 and 6.7 contain data of sulphide and laterite ores, respectively.

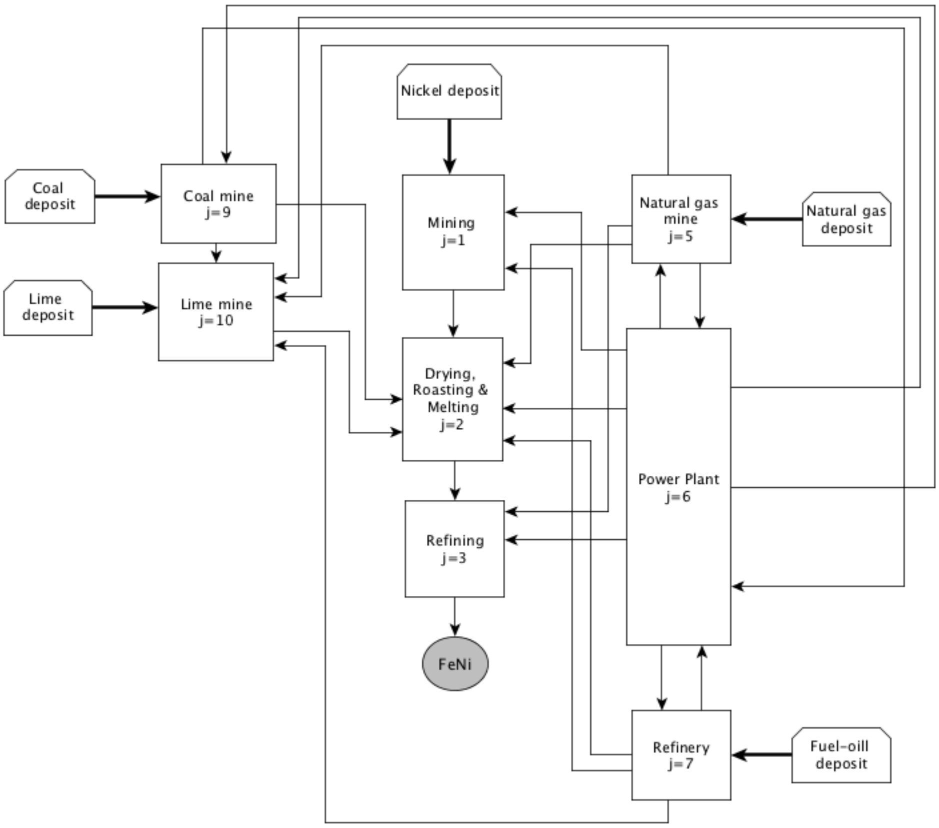


Figure 6.5: Nickel production system for laterite ores.

Data for estimation of coefficients of consumption a_{ij} were obtained from several sources such as CFE (2013), Classen et al. (2007), Domínguez et al. (2013), ITP (2002), Stanek (2009), Szargut & Stanek (2012), Valero et al. (2013). For instance, assumptions taken into account to perform the calculations include that production of fuels such as natural gas or coal, requires 0.26 and 0.24 MJ of electricity per kilogram of fuel, respectively, in accordance with Szargut & Stanek (2012). Production of electricity meanwhile, requires 2.48 MJ of natural gas, 2.87 MJ of fuel oil and 2.816 MJ of coal per MJ of electricity produced CFE (2013). It was considered a low heating value of 39.5 MJ/kg of fuel oil, 44 MJ/kg of natural gas and 21.68 MJ/kg of coal. Whilst, the efficiencies to produce energy from fuel oil was assumed as 35 %, from natural gas 36.5 % and from coal 28.5 %.

Table 6.6: Consumed products during Ni production from sulphide ore - option A.

			Considered j_{th} process										
			1	2	3	4	5	6	7	8	9	10	11
			kg_Ni	kg_Ni	kg_Ni	kg_Ni	kg_NG	MJ_pp	kg_R	kg_Cu	kg_coal	kg_lime	kg_cem
	1	kg_Ni		2.80									
	2	kg_Ni			1.143								
	3	kg_Ni				1.246							
	4	kg_Ni											
	5	MJ_NG		1.871	2.669	3.178		2.480				0.005	0.005
	6	MJ_PP	2.110	4.096	4.454	4.091	0.260		0.080		0.240	0.014	0.450
Consumed	7	MJ_R	1.505	10.290				2.870				0.022	
i_{th} product	8	kg_Cu	0.087										
a_{ij} [i]/[j]	9	MJ_coal						2.816				0.001	0.151
	10	kg_lime	0.021	0.786									
	11	kg_cem	0.487										
	12	kg_sil	6.129	0.786									
	13	kg_NaCN	0.001										
	14	kg_sulph	0.034										
	15	kg_CuS	0.01472										
Chemical Exergy	b_j MJ/[j]		8.85				45.76		42.265	8.34	23.58	0.2	0.24
Concent. Exergy	b_j MJ/[j]		260.27							38.22		1.47	

It is important to note that Tables 6.6 and 6.7 are related to a physical structure which depicts the overall connections between each branch as shown in Fig. 6.4 for sulphides ores or in Fig.6.5 for laterites ores.

Table 6.7: Consumed products during Ni production from laterite ore.

			Considered j_{th} process							
			1	2	3	4	5	6	7	8
			kg_Ni	kg_Ni	kg_Ni	kg_NG	MJ_pp	kg_R	kg_coal	kg_lime
	1	kg_Ni		3.5						
	2	kg_Ni			1.286					
Consumed	3	kg_Ni								
i_{th} product	4	MJ_NG		8.229	0.777		2.48			0.005
a_{ij} [i]/[j]	5	MJ_PP	0.028	8.486	2.24	0.260		0.08	0.24	0.014
	6	MJ_R	0.503	1.071			2.87			0.022
	7	MJ_coal		11.43			2.816			0.001
	8	kg_lime		0.134						
Chemical Exergy	b_j MJ/[j]		0.07			45.76		42.265	23.58	0.2
Concent. Exergy	b_j MJ/[j]		56.84							1.47

Subsequently, the TEC balance through Eqs.4.23–4.24 is applied individually for each process j^{th} of nickel production from sulphide ores, in order to obtain two equations for each branch. Hence, it is necessary to define the value for each coefficient a and f, which are related with the real production process shown in Fig. 6.4. The utilities used during the nickel production process through the different stages are gathered in the Ecoinvent database (Classen et al. 2007). Nickel production from sulphide ore using leaching (option B - Table 6.9) leads to obtain copper as a by-product. Thence, the coefficient f is the amount of copper as by-product in the mining step and represents the avoided cost of mine copper because it is mined together with nickel ore.

There are three types of equations that can be formulated depending if the process under analysis corresponds to the production of:

1. *Mineral.* When an ore is mined frequently different minerals are obtained. For this reason, a mineral can be acquired as a main product or as by-product. Hence, both cases have different TEC equations.

    - Production of a *mineral as a main product* includes electricity from power plant, fuels, raw minerals, other minerals presented in the same ore where the desired mineral is mined and the exergy of the mineral. For instance, the following Eqs. 6.1–6.2 relate all links between the different processes needed during the first step of nickel production: mining and beneficiation ($j = 1$), shown in Fig. 6.4. It should be noticed that exergy of the mineral appears only in Eq. 6.1, because Eq. 6.2 represents the TEC part due to fuel consumption.

$$\rho_1 = a_{6,1} \cdot \rho_6 + a_{7,1} \cdot \rho_7 + \cdots + b_{Ni} \tag{6.1}$$

$$z_1 \cdot \rho_1 = a_{6,1} \cdot \rho_6 \cdot z_6 + a_{7,1} \cdot \rho_7 \cdot z_7 + \ldots \tag{6.2}$$

- Production of a *mineral as by-product* includes the same inputs as production of a *mineral as a main product*, but additionally the by-product term must be included. For example, in this study copper is produced as a by-product during the electrolysis process of nickel production from sulphide ore depicted in Fig. 6.4. Then, Eqs. 6.3–6.4 are obtained:

$$\rho_4 = a_{3,4} \cdot \rho_3 + a_{5,4} \cdot \rho_5 + \cdots - f_{4,8} \cdot \rho_8 \tag{6.3}$$

$$z_4 \cdot \rho_4 = a_{3,4} \cdot \rho_3 \cdot z_3 + a_{5,4} \cdot \rho_5 \cdot z_5 + \cdots - f_{4,8} \cdot \rho_8 \cdot z_8 \tag{6.4}$$

Fuel. In general when a fuel is produced, for instance natural gas, coal or fuel oil, the main contribution to its TEC is electricity and its chemical exergy. For production of natural gas ($j = 5$) shown in Fig. 6.4, Eqs. 6.5–6.6 are obtained. It is important to mention that the fuel exergy is included in both equations and not only in the first one as in the case of mineral production (Eqs. 6.1–6.2).

$$\rho_5 = a_{6,5} \cdot \rho_6 + b_{NG} \tag{6.5}$$

$$z_5 \cdot \rho_5 = a_{6,5} \cdot \rho_6 \cdot z_6 + b_{NG} \tag{6.6}$$

Products which are not obtained directly from nature e.g. electricity. The main inputs for the electricity production in a power plant ($j = 6$) are fuels such as natural gas, oil and coal, as Fig. 6.4 depicts and Eqs. 6.7–6.8 express:

$$\rho_6 = a_{5,6} \cdot \rho_5 + a_{7,6} \cdot \rho_7 + a_{9,6} \cdot \rho_9 \tag{6.7}$$

$$z_6 \cdot \rho_6 = a_{5,6} \cdot \rho_5 \cdot z_5 + a_{7,6} \cdot \rho_7 \cdot z_7 + a_{9,6} \cdot \rho_9 \cdot z_9 \tag{6.8}$$

Once the TEC methodology has been applied, the ERC are introduced in the set of equations listed previously. This way, the exergy of the mineral denoted by b_{Ni} in Eq. 6.1 is substituted by the ERC. The same procedure is performed to those equations which involve mineral resources. The Exergy Replacement Cost of the commodities analyzed in this chapter are presented in Table 5.2, in Chapter 5. The aforementioned fusion of TEC and ERC is explained in the next section.

6.3 Integration of the Thermo-Ecological Cost and Exergy Replacement Cost to assess mineral processing

The motivation to join both indicators, Thermo-Ecological Cost and Exergy Replacement Cost, starts when I was in a 3-month research stay at the Institute of Thermal Technology of the Silesian University of Technology in Poland. Professor Stanek explained me their *Thermo-Ecological Cost* methodology. He had applied the TEC method to a simplified steel work (Szargut & Stanek (2012)) and results showed that the mineral part of TEC was always smaller when compared to the fuel part, due to the fact that in TEC analysis, the mineral part was obtained taken into account only the chemical exergy of mineral resources. However, this assumption is not always sufficient when mineral resources are assessed, as explained in Chapter 5. The value of a mineral is very much associated with its scarcity degree. This is why the concentration exergy component, accounted for through the *Exergy Replacement Cost*, is very relevant when non-fuel minerals come into play.

The original TEC approach leads to results implying that mainly exergy coming from fuel consumption influences the Thermo-Ecological Cost of a particular good. Therefore, it suggests that non-fuel mineral consumption is of minor relevance from the Thermo-Ecological Cost Theory point of view. As this is not necessarily true, the TEC methodology is complemented with ERC, so as to account for the impacts associated with mineral consumption and dispersion. Details of both methodologies can be consulted in chapter 5.

As aforementioned, the TEC provides a *cradle to market* approach. The ERC, meanwhile, enhances the TEC because it assesses the concentration exergy that would be expended in recovering a mineral deposit from the material dispersed in the Earth's crust with the available technology through a *grave to cradle* approach developed by Valero & Valero (2010*a*). Results show that when Exergy Replacement Costs are embedded into the TEC infrastructure, the impacts associated with mineral consumption are significantly greater. Accordingly, the inclusion of ERC into TEC allows for a more comprehensive and fairer weight to the consumption of non-fuel mineral resources, thereby providing better indications as to the achievement of a more sustainable production.

TERC methodology proposed in this chapter, means that the Thermo-ecological cost is complemented with the Exergy Replacement Cost, with the main objective to integrate concentration exergy of mineral resources into the cumulative exergy account associated with the production of a particular commodity performed through the TEC method.

The Thermo-Ecological and Exergy Replacement Costs of mineral processing are very variable, depending on raw material sources, production process and final products obtained. Both methodologies have been applied to seven different cases of metal production. In order to explain the procedure that integrates the ERC into TEC analysis, the results from the case of nickel processing will be analyzed first.

6.3.1 TERC analysis of nickel production

Both methodologies have been applied to three different cases of nickel production: nickel from sulphide ore using electrolysis (option A - Table 6.8), nickel from sulphide ore using leaching obtaining copper as a by-product (option B - Table 6.9), and ferronickel from laterite ore (Tables 6.10 and 6.11). Ni_1, Ni_2, Ni_3, Ni_4 represent Ni obtained at each of the processes involved in the nickel production chain, which are shown in Figs. 6.4 and Fig.6.5. Results of the exergy analysis of nickel production are presented in four sections, as follows: 1) TEC methodology, 2) TEC complemented with ERC, and 3) sensitivity analysis.

TEC methodology

In order to explain the results of TEC analysis, results of nickel production from sulphide ores (option A) and shown in Table 6.8 will be explained. TEC increase through the first step of mining and beneficiation (27.29 MJ/kg_Ni) until the last electrolysis step (179.2 MJ/kg_Ni), because in this final step the highest amount of energy consumption (as electricity and natural gas) takes place as Table 6.6 depicts. The opposite occurs with z_m values which decrease from mining and beneficiation operations (63.87 %) to electrolysis process (39.64 %) because the main impact in regards to mineral part is presented during the initial step which is directly connected with nickel deposit, as can be observed in Fig. 6.4. Besides, Table 6.8 shows that smelting and refining processes consume most of the energy required to produce nickel, whilst mining and beneficiation steps consume around 7-35%, as reported by Eckelman (2010). Processes where the Thermo-Ecological Cost mineral part is zero are those in which all of the burden is due to the consumption of fossil fuels like in the natural gas plant, the power plant, the refinery and the coal mine.

Table 6.8: Thermo-Ecological and Exergy Replacement Costs for Ni production from sulphide ore - option A.

	Process	TEC			TEC+ERC		
		ρ_j MJ/[j]	z_m [%]	r_j	ρ_j MJ/[j]	z_m [%]	r_j
1	Ni Mining–Beneficiation	27.29	63.87	3.005	278.6	96.37	31.4
2	Ni Drying–Roasting–Smelting	104.8	48.39		809.75	93.37	
3	Ni Converting	131.5	42.52		937.13	91.78	
4	Ni Electrolysis	179.2	39.64		1183.22	90.7	
5	Natural gas	1.07	0	1.017	1.07	0	1.017
6	Power Plant	3.98	0		3.98	0	
7	Refinery	1.08	0	1.006	1.08	0	1.006
8	Copper ore	8.34	100	1	38.22	100	4.583
9	Coal	1.121	0	1.03	1.133	0	1.03
10	Lime	0.279	73.93	1.353	1.549	95.42	7.703
11	Cement	1.76	13.82		1.736	13.82	
12	Silica	1.5	95		1.84	95	
13	NaCN	9.15	1		29.42	1	
14	Sulphuric acid	14.53	1		14.53	1	
15	CuS	7.19	1		32.59	1	

Analyzing option B, when leaching technology takes place during nickel production from sulphide ores, by-products such as copper can be obtained. In this case copper is gained when the electrolysis operation of Fig. 6.4 is replaced by a leaching operation. Hence, a new product is obtained in the process and values for TEC are shown in Table 6.9. It can be observed that the mineral part of TEC has a greater influence in nickel and copper ore than in nickel and copper as a final product.

One of the challenges of the mining industry is the multi-output allocation problem, analyzed in Chapter 5.3. The nickel production has this hitch, due to the nickel and copper content of sulphide ores. Depending on the process utilized, copper can be obtained as a by-product. It is important to highlight that in this study, copper is mined together with nickel sulphide ore. Accordingly, it is necessary to perform an assignment of resources required during its mining. Nevertheless, until today there is not an agreement if this must be done based on tonnage, market price or energy (exergy) values. In TEC methodology, all fuel inputs required during nickel and copper mining and beneficiation processes are assigned directly to nickel. Whilst copper is included in the analysis through Eqs. 6.3 and 6.4. Then the mineral part of copper always will be 100 %. Obviously, this is not a reasonable allocation method because all burden is allotted to nickel. Therefore, in Chapter 5.3 an objective allocation method based on ERC of commodities was applied.

Table 6.9: Thermo-Ecological and Exergy Replacement Costs of mineral inputs in Nickel production with Copper as by-product - option B.

			Ni ore	Ni	Lime	Cu ore	Cu
	ρ_j	MJ/[j]	27.29	138.31	0.279	8.344	82.634
TEC	z_m	[%]	63.87	42.15	73.93	100	33.28
	ρ_j	MJ/[j]	278.6	991.52	1.549	38.224	447.6
TEC+ERC	z_m	[%]	96.37	91.77	95.42	100	87.53

Results of the approach used to solve the multi-output allocation problem are shown in Table 6.9, for nickel as a main product and copper as a by-product. These results are the proposal of TEC methodology to solve this problem, because the overall process has been evaluated through the balance equations involving copper production and finally a Thermo-Ecological Cost for copper as by-product is obtained. Therefore, the total TEC value for this case is not only 138.31 GJ/t of nickel, because it must be added the amount of 82.634 GJ/t of copper. The mineral part of TEC has the greater values in the process connected directly with nickel, lime and copper ore deposits.

Results shown in Tables 6.10 and 6.11 display a TEC increment through the overall process until nickel is acquired. It can be observed that TEC values for sulphide ores in the first step of the mining and beneficiation are lower for laterite ores, because sulphide ores are generally mined underground whilst laterite ones are mostly mined open cut and less energy is required. TEC at the last step of nickel production from laterite ores (75.6 MJ/kg_Ni) is smaller than TEC of nickel produced from sulphide ores (179.12 MJ/kg_Ni), because from laterite ore, ferronickel is obtained as final product, whilst from sulphide ore nickel class I is obtained. Results are similar to those presented by Eckelman (2010). However, the energy required to produce nickel from laterite ores is significantly higher than from sulphide ores, as reported by Domínguez et al. (2013), Eckelman (2010), Mudd (2010), Norgate & Haque (2010).

Table 6.10: TEC and ERC of Ni production processes. Units: GJ/t_Ni

Process	Ni_1		Ni_2		Ni_3		Ni_4	
	TEC	TEC+ERC	TEC	TEC+ERC	TEC	TEC+ERC	TEC	TEC+ERC
Laterites	1.39	57.46	53.90	248.9	75.60	327.4		
Sulphides								
A	27.28	277.9	104.75	805.9	131.43	936.9	179.12	1183
B	27.28	277.9	104.75	805.9	131.43	936.9	138.32	991.3

The results presented in Table 6.10 show that in the case of the electrolysis, TEC values are higher than in the case of leaching technology. A high mineral part of TEC values for leaching technology results from the additional TEC value of copper which is obtained as by-product, as Table 6.11 depicts.

TEC complemented with ERC

In general, if Exergy Replacement Costs (ERC) are added to the TEC methodology, TEC values increase in branches connected to mineral deposits, due to the additional exergy required to produce minerals from a completely dispersed state to the original conditions in which they were originally found in Nature. This is the case of the mining and beneficiation operations which are directly connected with nickel and copper deposits, as shown in Fig. 6.4. Hence, percentages of TEC mineral part (z_m) increases as depicted in Table 6.8, as well as the index of

Table 6.11: Mineral part of TEC and ERC of Ni production processes.

Process		Ni_1 z[%]	Ni_2 z[%]	Ni_3 z[%]	Ni_4 z[%]
Laterites	TEC	10.08	0.543	0.487	
(Ferronickel)	TEC+ERC	98.91	80	78.19	
Sulphides					
A	TEC	63.87	48.39	42.52	39.64
	TEC+ERC	96.37	93.37	91.78	90.7
B	TEC	63.87	48.39	42.52	42.15
	TEC+ERC	96.37	93.37	91.78	91.77

sustainability. For instance, nickel ore has a value of $r_1 = 3.005$ and if the ERC are considered, the value is increased to $r_1 = 31.4$, as Table 6.8 shows. It means that if ERC are taken into account, the mining industry would be far from sustainable development, because concentration exergy granted by Nature in mining deposits, which has been ignored with TEC approach, will play a major role in energy consumption in the mining sector.

Sensitivity analysis

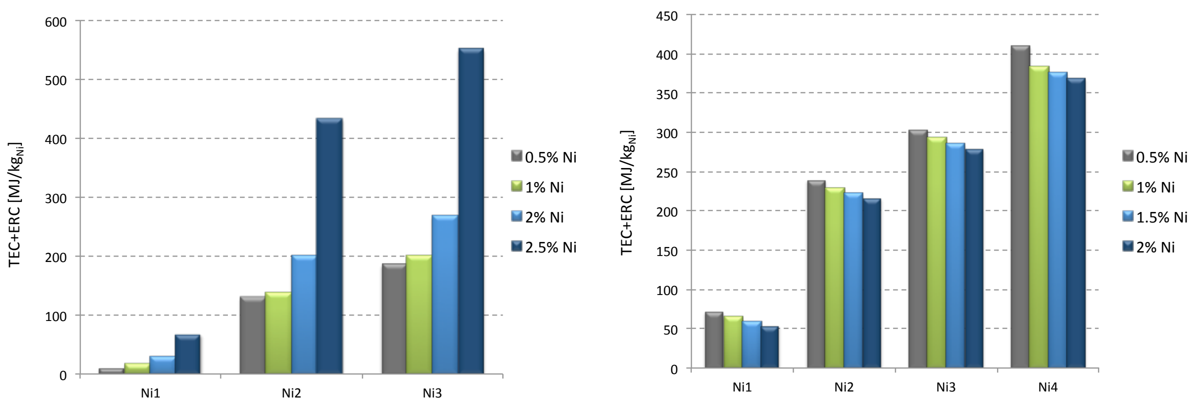
As previously mentioned, the mining industry has very large energy requirements. In this section, assumptions in regards to the kind and amount of fuels consumed through the different steps in nickel production were done using information from the Ecoinvent database (Classen et al. 2007). Since the reliability of the data is not always ideal and the amount of energy is presumably going to increase as ore grades decline, it is important to perform a sensitivity analysis in regards to the electricity and fossil fuels consumed during the different processes in nickel production, so as to identify the impact on the Thermo-Ecological Cost analysis when these inputs are changed. Accordingly, the effect of TEC and ERC of nickel production has been analyzed when electricity, fuel oil and natural gas consumptions are increased or decreased by $\pm 10\%$. The obtained results are shown in Table 6.12, where it can be observed that electricity is the variable with the highest influence. For laterites, the electricity requirement during the processes of drying, roasting and melting will increase or decrease the Thermo-Ecological Cost in a most significant manner than natural gas or fuel oil consumption. Sulphides are meanwhile more susceptible to Thermo-Ecological Cost fluctuations caused by changes in electricity than in fuel oil consumption, during the first step of mining and beneficiation.

In general, Table 6.12 allows to identify the process and the kind of resource that can have a great effect on the TEC of nickel production. If the objective is to diminish the TEC of nickel production in a particular process, electricity input plays a major role. For instance, a decrement of 10% in electricity will lead to a 0.22% decrease of the TEC in mining and beneficiation of nickel sulphides, whilst a decrement of 10% in fuel oil will lead to a 0.07% decrease of the TEC in the same process. Accordingly, it can be inferred that in order to reduce the TEC of mining and beneficiation of nickel sulphides, it would be preferable to reduce the electricity or to make an effort to produce it from renewable sources than to reduce the use of fuels or to include bio-fuels in the processes, because of the greatest impact on the TEC will be associated with electricity consumption.

Table 6.12: Effect of energy consumption in TEC and ERC of Ni production [%].

Processes	Electricity ±10[%]	Fuel oil ±10[%]	Natural gas ±10[%]
Laterites			
Ni Mining	±0.02	±0.1	-
Ni Drying-Roasting-Melting	±1	±0.04	±0.08
Ni Refining	±0.2	-	-
Sulphides			
Ni Mining-Beneficiation	±0.22	±0.07	-
Ni Drying-Roasting-Smelting	±0.15	±0.14	±0.02
Ni Converting	±0.14	-	±0.03
Ni Electrolysis	±0.08	-	-

Moreover, Exergy Replacement Costs are very dependent on ore grade and therefore changes in TEC including ERC for laterite and sulphide ores are presented in Fig. 6.6. Sensitivity analysis disclosed that ore grade variation had a greater effect on laterites than on sulphides. This is mostly due to the high-energy intensity of nickel production from lateritic ores.



(a) Laterite ore (b) Sulphide ore

Figure 6.6: Effect of ore grade in TEC including ERC.

Ore grade variation was done according to values reported by the mining industry. Nowadays, laterite ore has a maximum nickel content of 3 % whilst nickel content in the sulphide ore range from 0.4% to 2%. For sulphides, the results show that TEC including ERC at this commercial nickel content are closer to the values presented in Table 6.10 than for laterites. This means that lateritic ores are more susceptible to ore grade variation, therefore declining in ore grade will result in a significant energy consumption increase. In summary, nickel produced from lateritic ore will need much more exergy than nickel produced from sulphidic ore.

6.3.2 TERC analysis of aluminium production

An overview of the processes for the aluminium production system is presented in Fig. 6.7. It was grouped into six processes to perform the exergy analysis: mining, production of aluminium hydroxide, aluminium oxide, electrolysis anode, electrolysis cathode and aluminium liquide, to finally obtain aluminium. These processes were explained in Chapter 2, section 2.2.1.

Figure 6.7 is the a physical structure which displays the overall connections between each stage, in order to obtain the balance equations of TEC analysis.

Bauxite, is the mineral from which aluminium is gained, the mining and beneficiation step requires electricity and diesel to produce 1.4 kg of bauxite, which will be the input to the production of aluminium hydroxide, then 1.53 kg of aluminium hydroxide will be feed to produce aluminium oxide. Finally, 1.92 kg of aluminium oxide will be needed to produce 1 kg of aluminium liquide. The step which the highest energy consumption is the electrolysis to produce aluminium cathode ($j = 5$).

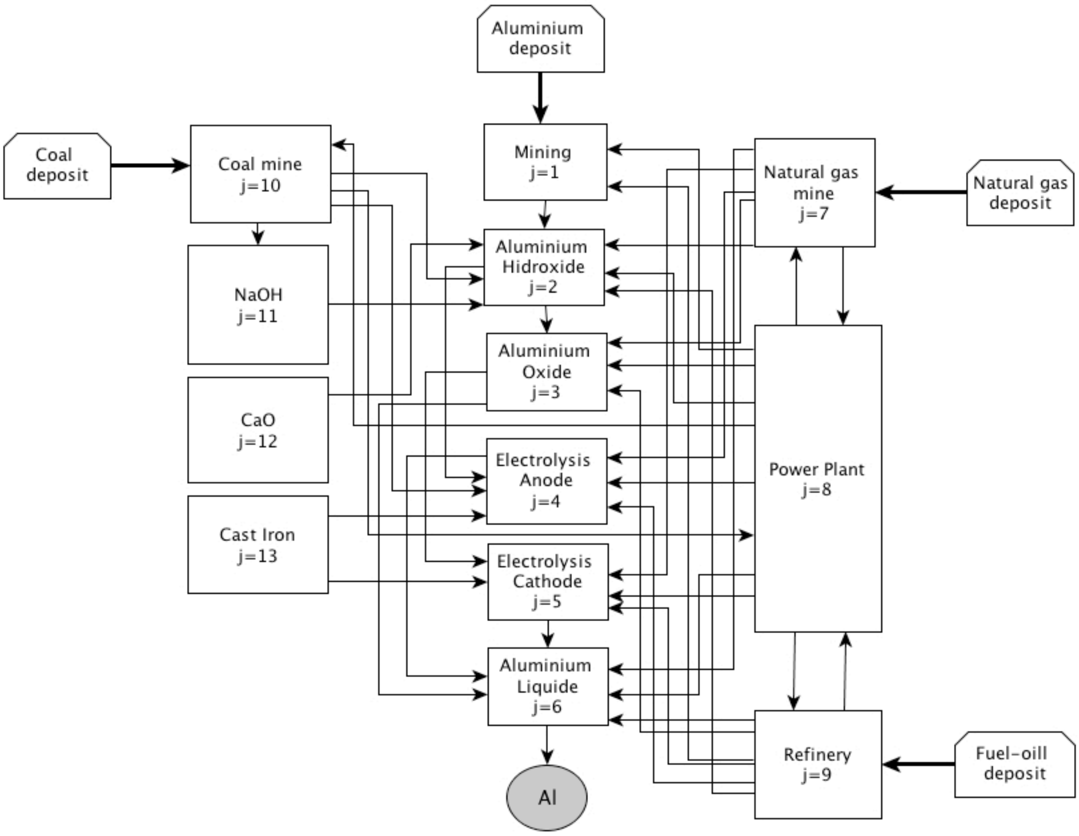


Figure 6.7: Aluminium production system.

A brief description of the production processes follows.

1. Mining: Includes mechanical grinding and separation of the ore from the gangue material and drying process. Electricity and diesel are inputs in this step.
2. Aluminium hydroxide production: This stage is done through the Bayer-Process. This process includes operations such as: grinding, digestion, precipitation and calcination. Sodium hydroxide (NaOH), also known as caustic soda as well as calcium oxide is used in this process. Besides electricity, heat from coal, natural gas and oil is required.
3. Aluminium oxide production: This operation is based on the Bayer-Process. After filtration, the aluminium is calcined to aluminium oxide. In this step, electricity and heat from coal, natural gas and oil is needed. According to Dutta & Mukherjee (2010), this method

is advantageous because it is capable of handling various categories of bauxite and can produce wide variety of alumina.

4. Electrolysis to produce anodes: This step is done in Hall-Héroult cells. For this operation electricity and heat from natural gas and oil is required. In addition, cast iron is needed.

5. Electrolysis to produce cathodes: This step is performed in Hall-Héroult cells. Electricity and heat from natural gas and oil is required. Additionally, cast iron and aluminium oxide is required.

6. Aluminium liquid production: This stage requires electricity and heat from natural gas and oil, as well as aluminium oxide, anodes and cathodes for aluminium electrolysis.

7. Aluminium production: This final step use the aluminium liquid together with electricity and heat from oil and natural gas to produce aluminium.

The production system presented is to obtain primary aluminium. However, it is important to highlight that aluminium has a relatively large global recycling rate, as stated by Sohn (2006). Recycling is a decisive element of the aluminium industry due to its economic advantages and its contribution to the environment. Through the recycling of scrap aluminium industry has been accomplished greatest energy savings. Currently, aluminium is one of the most commonly recycled metals in the world.

6.3.3 TERC analysis of chromium production

The physical structure of the three processes for the chromium production system considered for this study, is presented in Fig. 6.8. These processes are grouped in three stages: mining and beneficiation, production of ferrochromium and chromium. These process were explained in Chapter 2, section 2.2.3.

Chromite is the ore from which chromium is obtained. The electrolytic process of chromium ($j = 3$) where ferrochrome is used as the feed material, is the most energy-intensive branch. These process consumes 156 MJ of electricity and 103 MJ of natural gas per kg of chromium produced. These energy requirements are those reported in 1994 for a world-wide production average, taken from Classen et al. (2007).

A brief description of the production processes follows.

1. Mining and Beneficiation: Chromite ores are usually mined underground. This stage includes operations such as: crushing, mills and gravity concentration. Diesel and electricity are utilities used in this step. Also, a small amount of steel is used for abrasion in milling.

2. Ferrochromium: It is a master alloy of iron and chromium (45 – 95 %) and various amounts of iron, carbon, and other elements. High-carbon ferrochromium is produced by direct reduction of chromite ore with carbon. Electric arc furnace used for this operation works with an input of chromite, silica, bauxite and aluminium anodes, electricity and coke.

3. Chromium: The metal can be made from chromite ore and metallo-thermic reduction by carbon. A reducing agent used is aluminium powder. In the electrolytic process, ferrochrome is used as the feed material. In this step, electricity and natural gas are required.

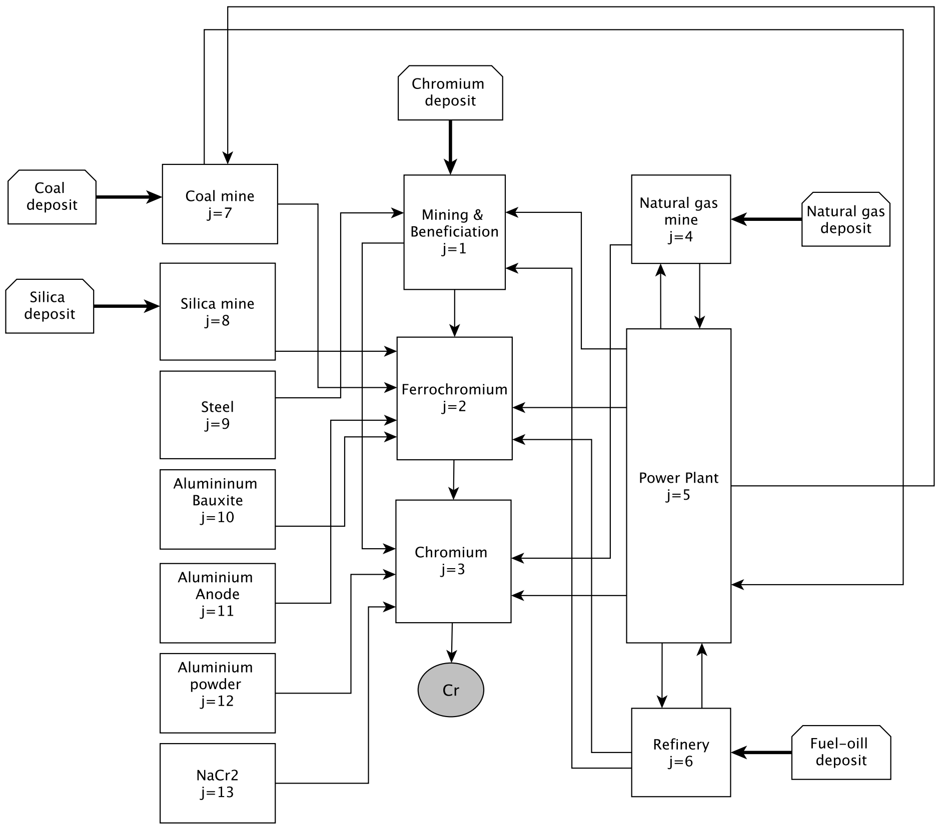


Figure 6.8: Chromium production system.

6.3.4 TERC analysis of copper production

Copper is always associated with other metals, mainly nickel, molybdenum and platinium group metals. In this case, molybdenum is mined together with copper in stage. Molybdenum and copper are coexisting in prophry deposits of the copper-molybdenum type, as molybdenite (MoS_2) and chalcopyrite ($CuFeS_2$).

The production diagram of the three group of processes for the copper production system is presented in Fig. 6.9. These processes were explained in Chapter 2, section 2.2.5. The mining and beneficiation step ($j = 1$) is a multi-output process, yielding copper concentrate and molybdenite concentrate. 4.11 g of molybdenite concentrate is obtained per each kilogram of copper concentrate. The stage of solvent extraction and electrowinning (SX/EW) copper ($j = 3$) is the most energy-intensive. It requires 28 MJ per kilogram of copper produced.

A brief description of the production processes follows.

1. Mining and beneficiation: this step includes operations such as: mining, ground, gravity concentration, and flotation. Raw materials such as lime (for neutralisation), steel (for abrasion), sodium cyanide (as depressant), sulphuric acid (for pH adjustment and leaching) and floating agents are used. Also, electricity and diesel are required. Molybdenum is produced as co-product in this step.

2. Pre-treatment, reduction and refining: are the three types of unit operation in pyrometallurgical treatment of copper concentrates. Pre-treatment consists of drying and roasting,

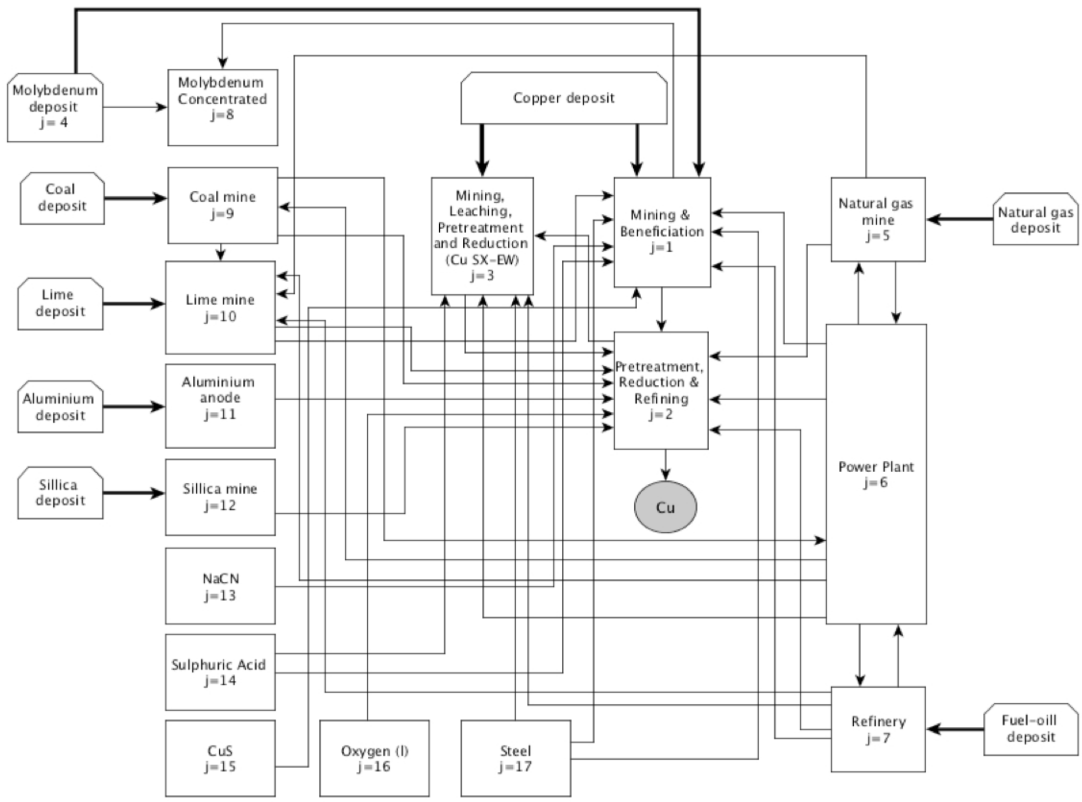


Figure 6.9: Copper production system.

this operation demand sillica and limestone. Reduction involves smelting and converting, these processes require electricity and fuels such as natural gas, oil and coal. Refining step uses copper from SX-EW.

3. Mining, leaching, pretreatment and reduction: this operations are the hydrometallurgical route to produce copper. Solvent extraction-electrowinning (SX-EW) is the main process. Sulphuric acid is required for leaching operations, steel for abrasion. Electricity and diesel are the utilities needed.

6.3.5 TERC analysis of gold production

The process extraction in open mining consist of three general steps: mining, processing and refining. A sketch of the raw materials and utilities required in gold production system is presented in Fig. 6.10. The processes required in gold mining were explained in Chapter 2, section 2.2.6. All mining processes needed in gold mining, were grouped in a single stage ($j = 1$), because there is not available information in regards to input and output flows of material and utilities. Then, the total energy consumption for this only stage was considered as 95,052 MJ per kilogram of gold.

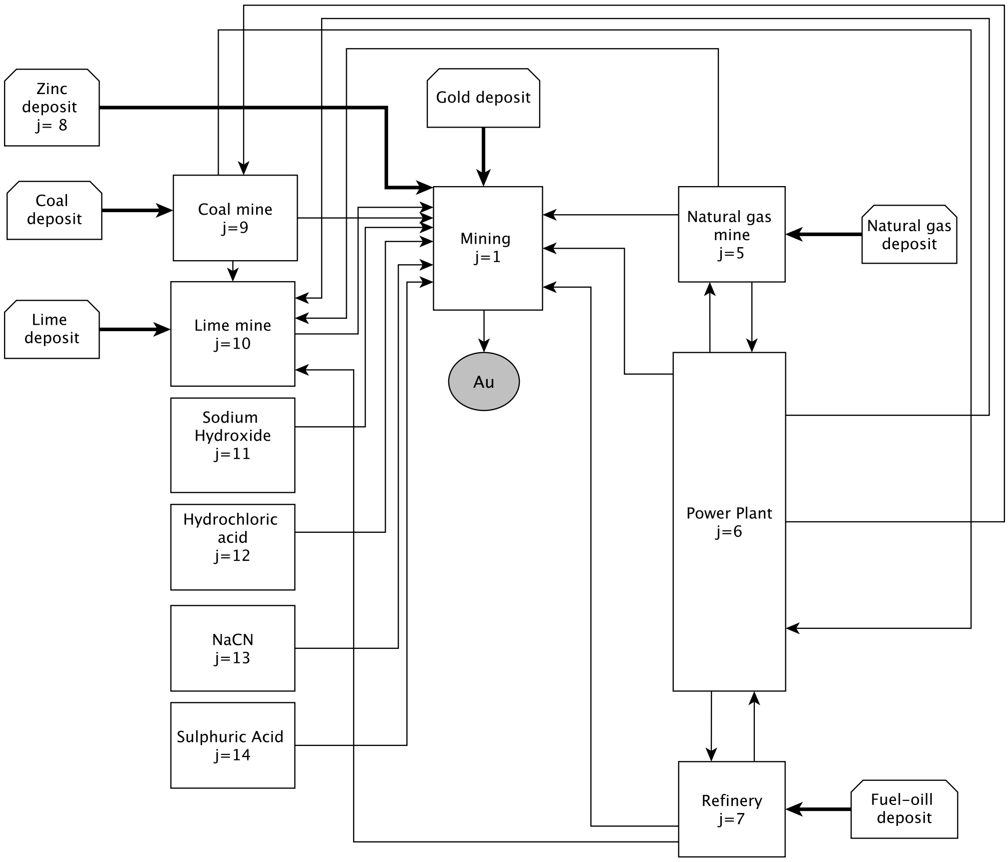


Figure 6.10: Gold production system.

6.3.6 TERC analysis of iron production

Iron ores are mixtures of up to 400 different minerals. The ore considered for this analysis is hematite. The production system includes six processes for the iron production: mining and recultivation, beneficiation, production of sinter, pellets, pig iron and cast iron, as Fig. 6.11 depicts. These processes were explained in Chapter 2, section 2.2.7. The pig iron production ($j = 5$), is the process with the highest energy requirement, 10.35 MJ per kilogram produced in the blast furnace.

A brief description of the production processes follows.

1. Mining and recultivation: the ore is won in stripes using hydraulic excavators and/or belt loaders. Electricity and diesel are required in this stage.
2. Beneficiation: this step includes milling and sorting of crude ore. Electricity is needed.
3. Sinter: this process agglomerates the unrefined iron particles. Coke is the main sinter plant energy input, with electricity and natural gas.
4. Pellets: this process agglomerates the refined iron ore particles under different temperature range in regards to sinter.

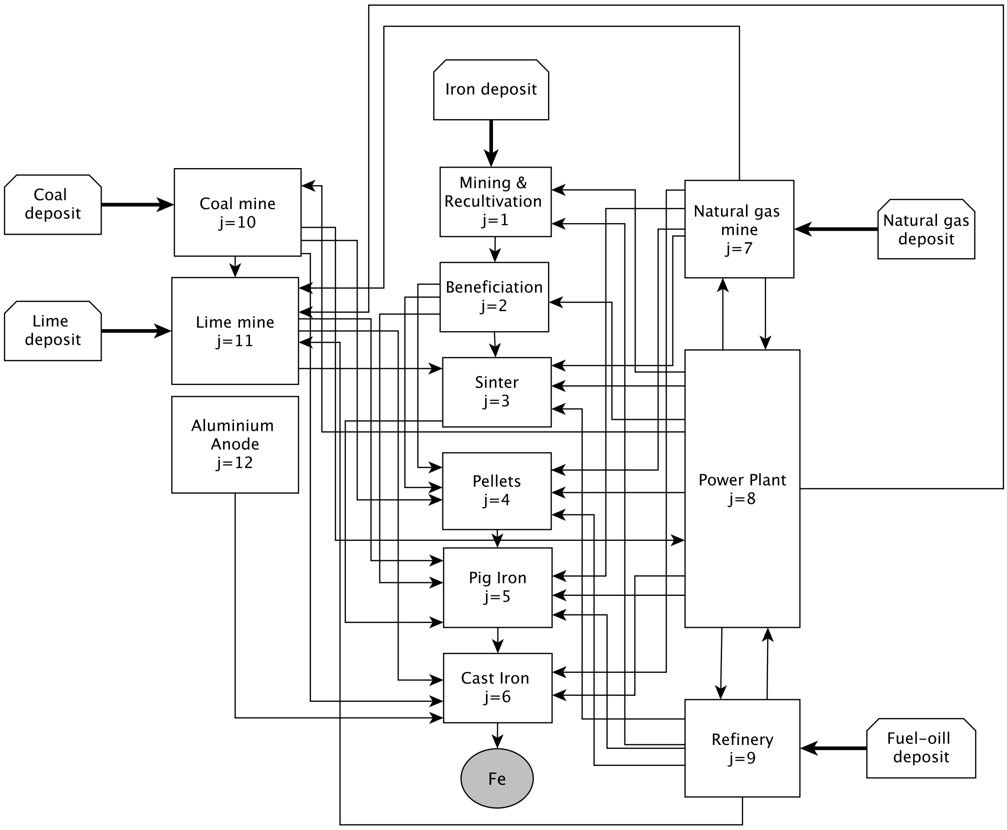


Figure 6.11: Iron production system.

5. Pig iron: the blast furnace is the most important process for the production of pig iron. This system requires additives (limestone) and reducing agents (coke). Uses sinter, pellets and iron ore as inputs.

6. Cast iron: is made by remelting pig iron in small furnaces.

6.3.7 TERC analysis of manganese production

Manganese is produced from pyrolusite ore. An overview of the three processes for the manganese production system is presented in Fig. 6.12. These processes are: mining and beneficiation, production of ferromanganese and manganese. These processes were explained in Chapter 2, section 2.2.9. The production of manganese as pure metal ($j = 3$), is the process which consumes the greatest electricity consumer, 9.5 MJ per kilogram of manganese.

A brief description of the production processes follows.

1. Mining and beneficiation: mining, crushing, milling and gravity concentration are the operations in this stage. Steel for abrasion in mill is required, as well as electricity and diesel.

2. Metallurgy-Ferromanganese: this stage includes the reduction to high-carbon ferromanganese. The ore is processed in blast furnaces (20%), electric arc furnaces without flux

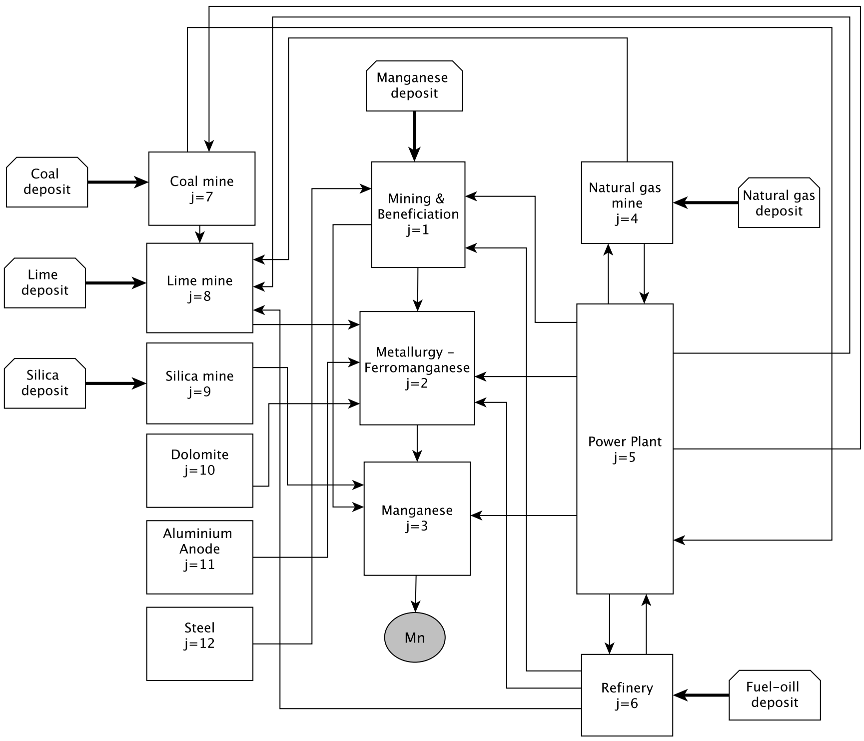


Figure 6.12: Manganese production system.

(27%) and electric arc furnaces with calcareous flux (53%). The raw materials required are manganese ores, limestone, dolomite or silica and reductants such as coke. Utilities like electricity, and heat from coke and coal are added.

3. Manganese: in this step manganese as a pure metal, is produced by electrolysis from ore (25%) and by electrothermic process from ferromanganese (75%). For both processes electricity is required and silica for the electrothermal process.

6.3.8 TERC analysis results of metals production

The TEC values for all commodities increase through the first stage where the ore is mined and processed until the last step where the smelted and refined metal is obtained, because in this finals steps is where the greater amount of energy is consumed, as Table 6.13 depicts. Otherwise, the mineral part of TEC z_m decreases from mining and beneficiation to smelting and refining operations, as Table 6.14 shows, because the mineral consumption is presented during the initial step which is directly connected with mineral deposits.

Table 6.13 shows TEC and TEC+ERC results for each commodity from the initial process (mining) through the final process (refining). TEC means without considering the concentration exergy whilst TEC+ERC shows values when it is considered. It is important to highlight that trend is the same for both approaches, an increment from the initial to the ending process. There are some exceptions as the case of iron where the output of a process is not the input to the follow process, then a decrease in TEC is presented in intermediate processes.

Table 6.13: Thermo-Ecological and Exergy Replacement Costs for different mineral production processes.

Commodities		Process_[1]	Process_[2]	Process_[3]	Process_[4]	Process_[5]	Process_[6]	Process_[7]
Aluminium	TEC	0.09	6.0	12.0	5.8	20.5	191.0	192.4
	TEC+ERC	217.10	309.8	476.7	16.1	30.8	1088.0	1090.0
Chromium	TEC	1.37	49.7	206.7				
	TEC+ERC	4.87	114.8	231.9				
Copper	TEC	19.03	118.7	13.3				
	TEC+ERC	53.01	226.0	13.3				
Gold	TEC	154873.00						
	TEC+ERC	1113000.00						
Iron	TEC	0.16	0.5	3.2	1.2	16.2	17.2	
	TEC+ERC	17.80	29.8	34.1	32.0	65.3	52.5	
Manganese	TEC	0.45	29.0	64.8				
	TEC+ERC	10.06	51.7	101.7				

If Exergy Replacement Cost (ERC) are added to the TEC methodology, TEC values increase due to the additional energy needed during the concentration process. As well as the index of sustainability, it means that if energy to obtain minerals from the crust Earth is considered, the mining industry would be far from sustainable development. For instance, aluminium has a value $r = 13.68$ and if the mineral bonus is considered the value is increased to $r = 21708$, as Table 6.14 shows.

Table 6.14 depicts values of the mineral part of TEC ($z_m[\%]$), it can be observed that values decrease from the initial to final processes, as expected, because mineral part has the greater contribution to TEC in the initial step. When concentration values are included, the trend is the same, the difference is that values are bigger because of that consideration.

The results show that cumulative mineral exergy has a greater significance than cumulative fuel exergy, as a result of include concentration exergy in the mineral part analysis. In this manner, the way in which the minerals are found on the crust is considered. If Exergy Replacement Cost (ERC) are added to the TEC methodology, TEC values increase due to the additional energy needed during the concentration process.

Table 6.14 depicts values of the mineral part of TEC ($z_m[\%]$), it can be observed that values decrease from the initial to final processes, as expected, because mineral part has the greater contribution to TEC in the initial step. When concentration values are included, the trend is the same, the difference is that values are bigger because of that consideration. The main advantage of consider the Exergy Replacement Cost (exergy concentration) can be observed when the sustainability index is calculated, because TEC methodology only consider the chemical exergy then r values are higher than if both exergies (named chemical and concentration) are included. For instance, gold which has a very low chemical exergy has a very high index of sustainability if TEC is applying but if Exergy Replacement Cost is included the value decrease to expected values.

The results show that cumulative mineral exergy has a greater significance than cumulative fuel exergy, as a result of include concentration exergy in the mineral part analysis. In this manner, the way in which the minerals are found on the crust is considered, and better index of sustainability are reached.

As opposed to fossil fuels, minerals are not lost when they are used. On the contrary they usually end up in landfills and become eventually dispersed. In the limit, when all mineral deposits are completely exhausted, Man will need to extract minerals from those dispersed landfills, i.e. from the grave. Having an order of magnitude of how much would it cost to replace such valuable minerals from the grave, would allow to manage scarce materials more appropriately.

Table 6.14: Mineral part of Thermo-ecological and Exergy Replacement Costs for different mineral production processes.

Commodities	z_m	Process_[1]	Process_[2]	Process_[3]	Process_[4]	Process_[5]	Process_[6]	Process_[7]	Sustainability
	[%]								index (r)
Aluminium	TEC	7.31	0.73	0.57	0.02	0.01	0.06	0.06	13.68
	TEC+ERC	99.96	98.08	97.52	54.28	33.53	82.44	82.34	21708
Chromium	TEC	63.69	4.39	1.39					1.57
	TEC+ERC	89.81	58.59	12.08					5593
Copper	TEC	44.25	23.41	8.62					2.28
	TEC+ERC	79.99	59.78	8.62					6356
Gold	TEC	0.35							595666.00
	TEC+ERC	86.13							4280000
Iron	TEC	66.92	38.80	6.09	15.36	1.93	1.34		1.49
	TEC+ERC	99.69	99.03	91.07	96.70	75.64	67.65		161.9
Manganese	TEC	60.04	2.26	3.76					1.67
	TEC+ERC	98.21	45.21	38.71					37.26

6.4 Summary

In this chapter an exergy analysis of metal processing was performed. In first place, an exergy accounting of energy and material flows for the two main routes of nickel production (from laterites and sulphides ores) was performed under the assumption that chemical exergy is the main and only component taken into account. Accordingly, the chemical exergy of the different raw materials and utilities involved in the production of nickel was calculated. Exergy inputs and outputs as well as exergy efficiencies for both, including their disaggregated steps, were presented and discussed. The results showed that nickel processing has higher efficiencies when it is produced from sulphides than from laterites. The strengths and weakness of the methodology applied were discussed. Moreover, the scope of this methodology was extended in the "cradle to market" path through the use of the Thermo-ecological Cost (TEC) and in the "grave to cradle" tack with the Exergoecology approach through the Exergy Replacement Costs (ERC).

Accordingly, an extended assessment of resources consumption in metal processing, has been performed integrating two methodologies based on exergy, leading to the improved TERC methodology. In this way a global exergy life cycle assessment of metal processing was accomplished. It was demonstrated that the Thermo-Ecological Cost associated with mineral consumption increases significantly when Exergy Replacement Costs are included in the TEC methodology. This is because TEC values increase in those processes connected to mineral deposits, due to the additional exergy needed during the concentration process of commodities in the grave-cradle approach. If concentration exergy (through the ERC) is taken into account, the Thermo-Ecological Cost associated with the mineral part becomes even more significant than the fuel one. Consequently, the combined methodology enhances the importance of mineral consumption, which is increasingly becoming an issue due to the criticality of raw materials.

Additionally, this methodology integration has shown that when ERC are included in TEC methodology, higher index of sustainability are obtained. This would then mean that if ERC are taken into account, the considered energy required in mining and metallurgical processes would be even more far removed from sustainable development, because concentration exergy granted by Nature in mining deposits, which was traditionally ignored with the TEC approach, will play a major role.

Finally, a sensitivity analysis allows to identify the metal production route (e.g. among nickel ores) more susceptible to ore grade changes or energy consumption variations. For the nickel processing, it has been shown that laterite ores are more sensitive to changes in ore grade and that both nickel ores are very dependant especially on electricity consumption.

Chapter 7

Conclusions

This chapter of conclusions provides a synthesis of this PhD. The main contributions and the scientific publications derived from this research work are then listed. Finally, the perspectives that have arisen as a result of the development of this thesis are commented and proposed for further research.

7.1 Synthesis

The accessibility of mineral resources has become a crucial matter for technological progress. Many resources that are considered critical, are determinant for the development of renewable energies, ICTs or agriculture. Consequently, to ensure their availability has become an imperative task. An initial and mandatory step towards this endeavour is to account properly for the resources used and to analyze and optimize with objective and rigorous tools the mining and metallurgical industry.

Accordingly, the main objective of this PhD thesis was to apply thermoeconomic methodologies so as to undertake "absolute Life Cycle Assessment" of mineral resources. This way, not only the conventional approach is accounted for, namely, the cradle to grave path, but also the complementary one, the grave to cradle one. This has been performed by complementing the thermoeconomic analysis with the exergoecological approach through the exergy replacement cost (ERC). The ERC account for the exergy that would be required for recovering back to their initial composition, concentration and cohesion conditions with current technology, the minerals that have been extracted. Consequently, the combined methodology not only takes into account the effort required to produce a given metal, but also the loss of mineral wealth associated with the depletion of the natural deposits.

The aim of the starting Chapter 1 was to provide an overview of mineral resources and the mining industry. Since this PhD is focused on the assessment of global mining, issues like sustainable development and life cycle assessment for abiotic resource depletion have been reviewed. Additionally, a general overview of world mineral supply, market price evolution and current situation of mineral resources was outlined.

Chapter 2 provided a general outlook of the production chains of several metals. Accordingly, a description of the main physical processes applied in the mining and metallurgical industry was presented. Subsequently, a detailed analysis of the particular metallurgical processes of selected commodities analyzed and applied in different case studies in this thesis was performed. It was stated that energy requirements data for metal processing varies greatly, and the associated energy increases substantially due to different factors such as: lower ore grades, deeper mines, complex ores and more waste rock produced. The chapter ended with a compilation of energy requirements for 33 mineral commodities, dividing the information into 1) the mining and beneficiation and 2) smelting and refining stages.

Technical changes have historically played a crucial role in the progress of the mining and metallurgical industry. Accordingly, Chapter 3 displayed the historic evolution of technological innovation in the mining industry, which were supposed to offset the increase of costs associated with several operational handicaps throughout history.

Yet the mining activity in addition to the problems that are common for other industries, needs to face an additional issue: decline in ore grades. Hence, future availability of mineral resources is influenced by two opposed facts. On the one hand, general trends suggest a long-term decline in ore grade, which increases energy consumption in the mining industry, but on the other hand there have been technological transitions that might avert rises in energy consumption. The aim of Chapter 3 was therefore to become acquainted if technological breakthroughs that have occurred can preclude the rising energy demand for the gold mining industry as an example.

As experience is acquired, material and energy efficiency increase and technical changes can be expressed through the so called learning curves. Accordingly, the learning curves theory was applied to several mines in different countries. Average progress ratios obtained between different operation and recovery processes ranged from + 20% to – 22%. This survey allowed us to have a more suitable understanding of the mining sector and the outcomes of technology evolution together with ore grade declining. In this way, mines in which mining operations have proved to be successful when the goal was to save energy were identified. Therefore, these estimates can be used to point out best mining practices and can serve as a reference for other worldwide mines with similar conditions. That said, general results suggest that although progress in technology has been made, in most cases energy requirements are increasing, because the main variable is the ore grade. Therefore, it can be asserted that technology, in general cannot avert the rising energy demand at least for the case of gold mining in the future if no major changes are performed around the world.

After having reviewed the main aspects related to the minerals industry, the thesis entered with Chapter 4 into the thermodynamic dimension for the assessment of mining and metallurgical processes. It thus presented the fundamentals of the exergy, thermoeconomic, thermoecological and exergoecological analysis. Particularly, it was shown that thermoeconomics is a general theory for energy saving, which integrates thermodynamics (exergy analysis) and economics (exergy cost) by means of the Second Law. The thermoecological cost theory meanwhile, is defined as the cumulative consumption of non-renewable exergy connected with the fabrication of a particular product with additional inclusion of the consumption resulting from the necessity of compensation of environmental losses caused by rejection of harmful substances to the environment. Both methodologies are closely linked and the similarities and differences between both approaches have been explained. Furthermore, both theories can be improved for the analysis of metallurgical systems in the same way, namely, through the exergoecology approach using the exergy replacement costs of minerals. The exergy replacement costs are the point of reference in order to evaluate in a single variable, characteristics such as composition, concentration (ore grade), cohesion and the state of technology of mineral resources. Contrary to fossil fuels, non-fuel minerals are not lost when they have been used but they usually end up scattered in landfills. Having an order of magnitude of how much it will cost to replace these dispersed minerals, will allow to manage resources more appropriately. The importance of the exergy replacement costs lies thus in their ability to establish a scarcity factor of mineral resources which should be accounted for, when assessing the sustainability of mining and metallurgical processes.

The fundamentals of the exergoecological approach were developed in a previous PhD thesis, but a set of unresolved issues still remained such as the influence of the long-term decline in ore grades on the exergy replacement costs. This thesis has thus tried to improve the methodology and calculate more accurate ERC of substances. The basic ingredient to obtain them is assessing the so called unit exergy costs, which are the ratio between the real energy required for mining and concentrating a substance and the minimum thermodynamic energy (exergy) required to achieve the same process. Hence, it provides a measure for the irreversibility (or technological ignorance) of the process. Since the energy required in mining depends on the ore grade as well as on the technology utilized, both factors influence the unit exergy replacement costs. Taking into account empirical data of energy requirements in mining as a function of ore grade, the exergy replacement costs for several minerals were obtained in Chapter 5. Additionally, a general expression of mining energy vs. ore grade was derived for those mineral commodities where no empirical data was available. The general observed trend was that as the ore grade declines, the energy and the exergy replacement costs increased exponentially. The obtained values are an intermediate step for assessing in a physical way the free exergy provided by Nature that man is rapidly destroying through the depletion of high-grade ores. This should serve as an assessment tool for decision-makers in the mineral industry.

Another issue that has addressed this thesis is the allocation problem of mining and metallurgical processes. As is well known, in the mining industry, with each metal extracted, main products, by-products and wastes are obtained. A strategy of sustainable development in mining industry is to implement a zero waste policy, changing to polymetallic mining, in which all mineral resources are deployed and many by-products are recovered. Accordingly, the mining industry must be considered as a system which produces by-products. These by-products need objective cost allocation methods, like the one proposed in Chapter 5 of this thesis.

Metals produced as by-products generally have highly complex demand/supply, technology and investments requirements. By-products production depends on the availability and technical feasibility to recover those metals during or next processing of main metals, as well as on the economic profit of by-product metal recovery. The final energy used in obtaining such by-products is difficult to ascertain as current cost allocation procedures are at least debatable.

Nowadays, allocations among products when one or more by-products come about in a mining or metallurgical process are based either on tonnage or on commercial prices. Both ways of allocating environmental costs entail many disadvantages, such as subjectivity with price or underestimating charges for certain by-products when the tonnage is low. Since mineral extraction and processing constitutes the first stage of any given process, using conventional LCA software, which allocates cost in regards to tonnage or revenue, can lead to incorrect results. In Chapter 5, a rigorous way to allocate costs among non-fuel minerals through the exergy replacement costs was proposed. This approach allows to allocate costs according to the physical quality of minerals. Cost allocation approaches based on tonnage, market price and exergy replacement cost, were applied to different mineral deposits. In this way, it was demonstrated that cost allocation through tonnage is not always a suitable option because minor by-products appearing at very low concentrations can be even more valuable than the major product. With market prices used to perform cost allocations, the problem is associated with their high volatility, which in turn depends on macroeconomic variables that commonly do not reflect the physical conditions of non-fuel mineral resources in Nature. If by way of contrast, exergy replacement cost is applied, the results are similar to those obtained via the price indicator. This supports the idea that the exergy replacement cost indicator is very close to the value society places on minerals. Nevertheless, contrarily to prices, exergy replacement cost does not fluctuate with external factors linked to market mechanisms but remains constant.

Having demonstrated the power and reliability of the new allocation procedure in the extraction stage, the methodology was subsequently applied to four metallurgical processes used to produce nickel, copper, lead and rare earth elements, as well as their corresponding by-products. The aim was to allocate to each by-product, their respective inputs of raw materials and fossil fuels using an extended thermoeconomic approach. Accordingly, the physical cost of the production of different commodities was calculated. The results showed that in general, prices do not adequately refer natural costs because they do not take into account the depletion factor of minerals and the fact Man is destroying the mineral wealth on Earth, which will be unavailable for future generations.

In Chapter 6 of this thesis, exergy analyzes of different processes for obtaining various minerals were performed. The case of nickel processing, was studied in detail. Particularly, an exergy analysis of energy and material flows to produce nickel from two types of ore (laterite and sulphide) was performed to identify the main losses occurring in the disaggregated process. Firstly, an exergy analysis based only on the chemical component was performed. Results showed that nickel processing has greater efficiencies when nickel is produced from sulphides than from laterites. Sulphide ore processing has efficiencies fluctuating from 67% to 79%, depending on the specific technologies utilised. The higher efficiencies are reached when leaching technologies are used and on the contrary if nickel is produced from laterites, the efficiencies achieved are lower on average 38% due to the cost-intensive processing. This first analysis allowed us to conclude that exergy analysis based on chemical exergies is not enough to assess properly mineral resources. For instance, laterites have an almost negligible chemical exergy, although the energy requirements and exergy accounting results are greater than those obtained for sulphides, which in turn have a greater chemical exergy. Hence, it can be stated that using chemical exergy alone leads to unreliable results, because there is an important factor missing, namely the concentration exergy because the "value" of minerals is rather associated with its depletion degree and not with its particular chemical exergy. This is the main reason why concentration exergy, calculated through the exergy replacement cost, is more convenient when mineral resources come into play.

A more complex analysis of the nickel production was subsequently performed through the thermo-ecological cost methodology, thereby extending the scope of the analysis through a "cradle to market" approach. TEC assesses the cumulative consumption of non-renewable exergy required to produce a unit of useful product from raw materials contained in mineral deposits. TEC results can be separated into those associated with consumption of fossil fuels and with consumption of mineral resources in each process stage, thereby identifying the types of resources that are being consumed in each step of the overall production process. This differentiation is important due to the fact that fossil fuels could be substituted by renewable sources, whereas minerals cannot be easily replaced by other kinds of resources. A problem detected with the TEC was that the exergy associated with the mineral component was small compared to the fuel component. This is because the TEC traditionally uses the chemical exergy of substances in their assessment and fossil fuels eclipse any other raw material. In order to overcome such issue, exergy replacement costs were embedded into the TEC infrastructure,including also the grave-cradle approach. Results showed that the impacts associated with mineral consumption are significantly greater. Accordingly, the inclusion of ERC into TEC allows for a more comprehensive and fairer weight to the consumption of non-fuel mineral resources, thereby providing better indications to assess mineral resources consumption, which could be even more critical than fossil fuel depletion.

Finally, it can be concluded that exergy analysis carried out through methodologies such as TEC and ERC allows to: (1) analyse inputs-outputs of materials and energy resources, (2) analyse the transformation efficiency of resources, (3) perform an objective cost allocation among products and by-products, (4) assess environmental impacts and (5) identify the opportunity areas to reach a sustainable development in the mining sector.

7.2 Contributions

The general contribution of this PhD was to improve and adapt current methodologies based on the exergy analysis and used to optimize industrial processes to the specific case of the mining and metallurgical industry. Particularly, Thermoeconomics and the Thermo-Ecological Cost methodology have been complemented with the Exergoecological approach, allowing for a better assessment of non-fuel mineral resources. The specific contributions of this PhD thesis are outlined next.

1. The main contribution made in Chapter 3 is the use of learning curves from an exergoecology approach. This analysis allows to become acquainted if research and technological breakthroughs that have occurred in the production processes of mining industry can preclude the rising energy demand.

2. The first contribution made in Chapter 5 is a more accurate calculation of the exergy replacement costs of minerals, taking into account time through variable unit exergy costs, which in turn depend on the energy requirements. Additionally, a general expression of mining energy vs. ore grade has been derived for those mineral commodities where no empirical data was available. This should serve as an assessment tool for decision-makers in the mineral industry.

3. The second contribution of Chapter 5 is the development of a new methodology for cost allocation among by-products based on exergy replacement costs. This method allows to allocate costs according to the quality of the products obtained, which is directly related to their ore grade and depletion state. The final aim is to estimate in a reliable way energy consumptions related to each mineral produced.

4. The main contribution made in Chapter 6 is the proof that the use of chemical exergy to assess mineral resources leads to unreliable results, because there is an important factor missing, namely the concentration exergy. The value of minerals is more associated to its scarcity degree than to its inherent chemical exergy. This is the reason why concentration exergy, calculated through the exergy replacement cost, is a more convenient unit of measure when mineral resources are analyzed.

5. An additional contribution of Chapter 6 is the integration of the exergy replacement cost into thermo-ecological cost methodology. This allows to perform an integral assessment of mineral resources: a grave-cradle-market analysis.

7.3 Scientific publications

The development of this PhD dissertation has led to some scientific publications, which have been presented in different scientific conferences and published in journals.

Al. Valero, A. Valero, A. Domínguez. Influence of technical development and declining ore grades on the availability of gold resources. In SDEWES 2011: Proceedings of the 6th Dubrovnik Conference on Sustainable Development of Energy, Water and Environment Systems, September 25 - 29, 2011, Dubrovnik, Croatia.

Al. Valero, A. Valero, A. Domínguez. Trends of exergy costs and ore grade in global mining. In SDIMI 2011: Proceedings of Sustainable Development in the Minerals Industry, June 14 - 17, 2011, Aachen, Germany.

A. Domínguez, Al. Valero. Global gold mining: is technological learning overcoming the declining in ore grades?. In ECOS, 2012: Proceedings of 25st International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, June 26 - 29, 2012. Perugia, Italy.

A. Domínguez, Al. Valero, A. Valero. Exergy accounting applied to metallurgical systems: The case of nickel processing. In CPOTE, 2012: Proceedings of 3rd International Conference Contemporary Problems of Thermal Engineering, September 18 - 20, 2012, Gliwice, Poland.

A. Domínguez, Al. Valero. Global Gold Mining: Is Technological Learning Overcoming the Declining in Ore grades? Journal of Environmental Accounting and Management, 2013 (1) 85 - 101.

Al. Valero, A. Valero, A. Domínguez. Exergy Replacement Cost of Mineral Resources. Journal of Environmental Accounting and Management, 2013 (2) 147 - 158.

A. Domínguez, Al. Valero, A. Valero. Exergy accounting applied to metallurgical systems: The case of nickel processing. Energy 2013 (62) 37 - 45.
http://dx.doi.org/10.1016/j.energy.2013.03.089

A. Domínguez, L. Czarnowska, Al. Valero, S. Wojciech, A. Valero. Thermo-Ecological and Exergy Replacement Costs of Nickel Processing. (Under review in Energy Journal, submitted in April 2, 2014)

Al. Valero, A. Valero, A. Domínguez. Exergy Cost Allocation of by-products in the mining and metallurgical industry. (Accepted in ECOS 2014, 25st International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems. Finland, June 15-19, 2014.)

7.4 Perspectives

Throughout the length and breadth of this thesis, further research opportunities have been identified. The main problem encountered in the writing of the results of this PhD was the lack of reliable information sources. When transparency in the mining and metallurgical sector becomes the norm, the methodology and the numbers obtained could be refined and extended to more case studies. Some of the identified open questions are listed as follows.

1. Due to lack of data, the learning curve methodology was only applied to the case study of gold. Consequently, even if gold is an important commodity, it cannot be representative

for all minerals produced in the world. Therefore, the analysis should be extended to other commodities and to countries from all over the world such as China, which holds currently a strategic position in the mining industry. With the help of a neural network model, the question of whether technological improvement can offset the declining in ore grades could be better solved.

2. In addition, the learning curves methodology used in this thesis is subject of improvements by adding a factor related with research and technological development in the mining industry. The extended methodology is known as learning curve of two factors, although there is also the multi-factors learning curve which can include additional independent variables to analyze the mining sector.

3. In this thesis, the ERC of 23 substances was obtained, from which only 6 commodities were derived from empirical information regarding energy consumption vs. ore grade. The remaining were obtained assuming a general behaviour based on observations where data was available. Hence, it becomes important to improve the obtained values when more information appears. But not only that, the calculation of ERC should be extended to all produced commodities. Major efforts should be especially devoted to those minerals considered as critical, including substances such as In, Ge, Ga, REE from the lanthanide group or P.

It is important to highlight that exergy replacement cost values as well as the exergy analysis of systems and process, are dependant on the data used, therefore their objectivity rely on the quality of such data. Hence, it is imperative the use of reliable information sources in regards to energy and raw materials correspondent to each mineral deposit and used technology.

Appendix A

Background of commodities

A.1 Metal processing and energy requirements of minerals

Antimony

This material is one of the critical raw materials for EU due to several factors such as: no effective substitute for its major application (flame retardant), low recycling due to dissipative nature of major usage and metal supply risk because China has the largest reserves of antimony ore worldwide according to the ad-hoc Working Group (2010) and Butterman & Carlin (2004).

The most important ore mineral of antimony is the sulfide stibnite and the method used to extract antimony from it is the sulphide ore flotation which has an energy consumption of 90 MJ per ton of treated material (Kihlstedt 1975), considering that sulfide ore contain an average of 13.25 % antimony, the energy during the concentrating process is 0.95 GJ/t. Once the concentrate ore is obtained the next step is roasting to produce oxide followed by smelting in blast furnace to produce crude metal, this metallurgic process is similar for sulphide ores such as molybdenum, thence the energy consumption is 12 GJ/t.

The energy requirement for the concentrating process of antimony was 1.4 GJ/t and for refining the energetic consumption was 12 GJ/t (Botero 2000).

Table A.1: Energy consumption in the antimony production. Values expressed in GJ/ton of Sb.

	E_{mining}	E_{refining}	E_{total}
Kihlstedt (1975)	0.95	12	12.95
Botero (2000)	1.4	12	13.4

Arsenic

Arsenic is a byproduct of mining nonferrous metals, being the copper processing industry the major source. Most arsenic was produced as the trioxide (As_2O_3) from the smelting process of cooper, lead, gold and silver ores. The most common commercial source of arsenic is the arsenopyrite ($FeAsS$) containing 46 % of arsenic.

The energy requirement for the concentrating process starting from sulphide ore is 9 GJ/t (without considering mining process) and the refining process consumes 19 GJ/t (Chapman &

Roberts 1983) considering that this process is similar to lead refining (Botero 2000).

Beryllium

There are several beryllium containing minerals on the Earth's crust, but only two beryllium minerals, bertrandite and beryl, are important commercially. The mining and beneficiation processes to obtain beryllium sulfate solution from beryl includes crushing, leaching with sulfuric acid and heating operations, then the solution undergoes solvent extraction and hydrolysis, which results in the formation of beryllium hydroxide from which can be obtained beryllium as metal by dissolving it in an ammonium bifluoride solution, followed by a concentrating operation in an evaporator, finally the beryllium fluoride is reacted with magnesium in induction furnaces to produce metallic beryllium (Cunningham 2000).

According to Kihlstedt, the energy consumptions of the operations mentioned above for concentrating beryllium from beryl which contains about 4 % Be, is 10.8 GJ/t (Kihlstedt 1975). The energy consumption for refining process is 450 GJ/t (Botero 2000).

The fact that 99% of world production originates in US and China, along with low recycling rate and difficult to substitute, makes this material critical for EU, as reported by the ad-hoc Working Group (2010).

Bismuth

Bismuth is mainly produced as a byproduct of lead ore refining, although it may occur in nature as a sulfide (bismuthinite, Bi_2S_3) or as a oxide (bismite, Bi_2O_3).

The energy consumptions of the sulphide or oxide ores flotation for concentrating bismuth and a content about 5 % Bi, is 3.54 GJ/t (Kihlstedt 1975). The energy consumption for refining process is 52.8 GJ/t (Botero 2000).

Fluor

Fluorine occurs mainly in the minerals fluorspar (CaF_2) and cryolite (Na_3AlF_6). There is not a unique route to obtain fluorine, but industrial production of fluorine entails the electrolysis of hydrogen fluoride in the presence of potassium fluoride. The energy consumption in the concentrating process is 1.45 GJ/t and no energy is required for refining process (Botero 2000).

Fluorspar is listed as critical material for EU because just 25% of the fluorspar consumption of the EU is overcast by domestic production, the remaining was imported mainly from China which applies export quota and export taxes. Besides, recycling rate is estimated underneath 1% in the EU and substitution possibilities appear to be scanty, as stated by the ad-hoc Working Group (2010).

Gallium

Gallium has many characteristics similar to aluminium, e.g. conductivity of heat and electricity. Hence, it is used in optoelectronics, telecommunication, aerospace and commercial items like alloys, computers and DVDs (Classen et al. 2007). It can be extracted from bauxite ore. The three process used to extract gallium is extraction with chelating agents, electrolytic processes and fractional precipitation.

China is the major producer of gallium with 75% of worldwide production, then trade restrictions have been imposed in this country as well as in South Africa and Russia. Nowadays, gallium is not being recycled from old scrap and just some applications have substitutes. The latter places gallium into the list of critical materials for EU (ad-hoc Working Group 2010).

Germanium

Germanium ores are imported in order to be refined in EU for further export. Hence there is a high dependency on imports from China, which accounts for more than 70% of world production. The recycling rate is about 30% in accordance to the ad-hoc Working Group (2010).

Indium

Indium is obtained as by-product during zinc, lead, tin and copper mining. The general process to obtain indium from hydrometallurgical zinc extraction are: leaching and solvent extraction (SX), cementation and anode casting, electrorefining and vacuum refining in order to reduce the level of volatile impurities (Classen et al. 2007). Indium is produced mainly by recovering from by-products of zinc smelting, which contain small amounts of indium together with other elements such as arsenic, zinc and cadmium. The main challenge is to remove contaminants that have negative effect on the properties of the semiconductor made from indium. Hence, a complex hydrometallurgical process is required to separate indium from impurities. These processes are highly dependent on the composition given by the specific deposit.

The fact that more than 81% of the EU's imports of indium comes from China, joint with limited recycling possibilities from manufacturing residues as well as shorty substitution for specific applications, arouse indium to be considered as critical material for EU, according to ad-hoc Working Group (2010).

Lithium

Lithium occur in nature combined with all igneous rocks such as spodumene ($LiAsSi_2O_6$), lepidolite, petalite and amblydonite also it is found in the waters of many mineral springs thence it is recovered from brines. Lithium metal is produced by electrolysis of a molten mixture of lithium chloride and potassium chloride.

The energy requirements for the hydroxide production of lithium is 12.5 GJ/t for the concentrating process and 420 GJ/t for the refining process (Botero 2000).

Magnesium

Magnesium can be extracted from seawater, from minerals (dolomite, magnesite and brucite) or can be earned through recycling. The metal magnesium is gaining more importance as a construction material.

The main production process are electrolysis of magnesium chloride melts (made from resources such as seawater and dolomite) and the metallothermic reduction of magnesium oxide.

Energy is used for the preparation of dolomite lime, making $MgCl\_2$ cell feed from seawater and acid generation. Different methodologies show energy requirements and large differences exist. Considering the higher energy efficiency, the cumulative energy use of 144 MJ/kg is considered (Classen et al. 2007).

China is by far the largest producer of magnesium over the world (93%), whilst EU imports almost 47% of world's production of magnesium. Taking into account that China, Russia and South Africa impose trade restrictions and that recycling rates are small, magnesium is considered a critical material for the EU, in accordande to the ad-hoc Working Group (2010).

Mercury

The energy requirement for mining and concentrating ore to produce mercury is 157 GJ/t, whilst the smelting and refining processes require 252 GJ/t (Chapman & Roberts 1983).

Niobium

Production of niobium takes places mainly in Brazil (92%) and in Canada (7%). Its recycling rate is around 20%. In spite of niobium substitution possibilities, it may entail higher costs and/or loss in performance, as stated by the ad-hoc Working Group (2010).

The consumption of energy for the smelting and refining of niobium in an electron beam furnace is 37.8 GJ/t (IPPC 2009*a*).

Platinum Group Metals (PGM)

The six platinium group metals are Ruthenium (Ru), Rhodium (Rh), Palladium (Pd), Osmium (Os), Iridium (Ir) and Platinum (Pt). These metals are associated with other metals, then their production always delivers other metals than PGM, mainly nickel and copper. Therefore, the process of primary production is a multioutput-process.

PGM are highly valuable because thier occurrence is scarce. PGM-containing ores are mined only in few sites such as Russia and South Africa. In the main, production of PGMs depends on their market price and the accompanying metals like Ni or Cu (Classen et al. 2007). Due to the low concentration and often difficult mining conditions PGM production is very energy intensive (Glaister & Mudd 2010).

Recycling is a further source of PGM metals. Automotive catalysts use large amounts of PGMs, which are recovered depending on the market price of the metals.

Mining ore is mined underground and transferred to beneficiation where operations such as gravity concentration, flotation, neutralisation are applied. Afterward, the ore is processed in the pyrometallurgical step which is divided in three substeps (roasting, smelting and converting).

The main metals that occur with PGM winning are nickel and copper, which are separated through hydrometallurgical process such as leaching. The remaining leach residue is composed of all PGM, which are extracted in the refining step (selective precipitation or solvent extraction).

The most important sources for PGM are Russia and South Africa. The recovery of PGMs from consumer products is still limited. For instance, in Europe the recovery rate of PGMs from automotive catalysts remains below 50%, whilst from electronic applications is around 10%. The challenge in PGMs consumer applications is the collection through a recycling chain of metal recovery processes. Although some PGMs such as platinum and palladium can be replacement for each other, the fact that both metals are mined together and in the same magnitude does not solve the problem, in accordance to the ad-hoc Working Group (2010).

Platinum

The platinum is mined from underground ore and transferred to a concentration step that includes flotation, tailing, roasting, smelting and converting processes and consumes 191,000 GJ/t. The refining process has two main steps, selective precipitation and solvent extraction, although this individual processes may have to be repeated to achieve the required purity, which makes the refining process complex, the energy consumption is around 2,430 GJ/t (Classen et al. 2007).

Potassium

Potassium is content in minerals such as sylvite, carnallite, langbeinite and polyhalite which are found in ancientlake and sea beds.

Potassium metal is produced on an industrial scale only by the reduction of potassium chloride with sodium metal.In the continuous production, a fractional distillation is incorporated into a reaction column packed with molten potassium chloride. By feeding sodium into the columns, a vapour mixture of sodium and potassium is fractionated. Potassium metal is then obtained by distillation of the vapour mixture (IPPC 2009*a*).

The energy consumption for the concentrating process is 3.7 GJ/t and no energy requirement is reported for refining step Botero (2000). The energy requirement to produce potassium chloride from sylvinite ore is 5.84 GJ/t (Chapman & Roberts 1983).

Silicon

Silicon occurs in nature as oxide (sand, quartz, rock crystal, etc.) or silicates (granite, feldspar, clay, etc.) minerals. Silicon is commercially produced by the reaction of silica in an electric arc furnace. Silica (SiO_2) is the most abundant mineral in the Earth's crust and is commonly found in nature as sand or quartz.

The energy required to produce silica from silicious rock was 0.79 GJ/t (Chapman & Roberts 1983). Energy consumption for mining and concentrating sand to obtain metallurgical silica is 0.72 GJ/ton (Hagedorn & Hellriegel 1992). The consumption energy for the production of silicon metal from silica was 231.49 GJ/t (Chapman & Roberts 1983), also the amount of 83 GJ/t using an electric furnace was reported (Classen et al. 2007).

According to Botero, the energy requirement outlined for concentrating and refining processes was 34 GJ/t and 76 GJ/t, respectively (Botero 2000). Finally, the energy considered for mining and concentrating process has an energy consumption of 0.72 GJ/t and 82.28 GJ/t for the refining process.

Sodium

The most common compound of sodium is sodium chloride (salt) which occurs in extensive amounts dissolved in seawater, as well as in solid deposits (halite).

Sodium metal is commonly produced by the electrolysis of fused sodium chloride through the Downs Cell, this process reported an energy requirement of 165.21 GJ/t and the energy consumption for concentrating sodium chloride in rock salt from mineral in the ground was 1.65 GJ/t, considering the content of sodium, the energy is 4.2 GJ/t of sodium (Chapman & Roberts 1983).

The energy requirement for mining and concentrating sodium from rock salt was reported as 3.28 GJ/t whilst the energy required for refining sodium through electrolysis of sodium chloride was 39.63 GJ/t (Botero 2000).

Tantalum

Tantalum is mainly gained from Tantalite and it is currently mined in open pits. A lot of tin deposits occurs with niobium.

The energy needed for mining and concentrating tantalum is 1,375 GJ/t and it was calculated assuming that the process takes place in an open pit mine by means of sulphide acid leaching process. The energy consumption for refining is 380 GJ/t considering that the process is equal as the vanadium refining process by means of direct reduction (Botero 2000).

The energy required during the mining and beneficiation processes is 1,693.16 GJ/t according to Ecoinvent database. The reduction stage is effectuated by means of magnesium vapor in a rotatory kiln or multiple hearth furnace, the resulting tantalum has an average concentration of 99.8 percent, this process consumes 2.59 GJ/t (Classen et al. 2007). The consumption of energy for the smelting and refining of tantalum in an electron beam furnace is 37.8 GJ/t (IPPC 2009*a*).

Recycling for tantalum is limited and substitution when possible involves loss of performance, as the ad-hoc Working Group (2010) states.

Tin

The most important tin ore is cassiterite (SnO_2). 20% of tin is extracted from underground mines and 40 % each from open pit mines and from offshore deposits. Underground mining includes processes like drilling, blasting, sorting (flotation) and thermal ore beneficiation.

The tin production has four main processes: mining, beneficiating, smelting and refining. The refining process of tin from ore concentrate by means of electric furnace and assuming a 70 % tin in concentrate, the energy requirement was 19.17 GJ/t (Boustead & Hancock 1979).

The energy requirement for mining and concentrating ore to produce Tin from alluvial ores is 187.5 GJ/t, which have an average percentage of recovery in the mining and concentrating process of 80 %, whilst the smelting and refining processes requires around 19.6 GJ/t using either electric arc or blast furnace. Otherwise if the tin is mining from hard-rock ores which have a typical recovery of 55 %, the energy consumption for concentrating is 157.3 GJ/t, while the energy for refining reaches 127 GJ/t (Chapman & Roberts 1983).

The energy consumption for mining and beneficiating processes in underground mining is

252.32 GJ/t due to the additional operations of drilling, blasting and thermal ore beneficiation in regard to open pit mining. Considering the beneficiated ores with the average tin content of 68 % the smelting and refining steps have an energy demand of 2.48 GJ/t (Classen et al. 2007).

Table A.2: Energy consumption in the tin production. Values expressed in GJ/ton of Sn.

	E_{mining}	E_{refining}	E_{total}
Boustead & Hancock (1979)		19.17	
Chapman & Roberts (1983)	187.5	19.6	207.1
Classen et al. (2007)	252.32	2.48	254.8

Titanium

Assuming that titanium is mined from rutile ore, the energy requirement for mining and concentrating is 2.8 GJ/t, whilst the smelting and refining processes require 575 GJ/t. If the mined ore is ilmenite the energy consumptions are 23 GJ/t and 687 GJ/t for concentrating and refining processes, respectively (Chapman & Roberts 1983).

The energy requirement for refining titanium is 406.8 GJ/t, this stage is the most energy intensive for several metals (Yoshiki & Toguri 1993). The consumption of energy for the smelting and refining of titanium in an electron beam furnace is 3.6 GJ/t (IPPC 2009*a*).

Using a Life Cycle Assessment (LCA) methodology was calculated the gross energy requirement in the titanium production process as 361 GJ/t of primary energy consumed in overall production life cycle from ilmenite, considering a generation efficiency of 50 % due to the utilization of thermoelectric and hydroelectric power plants, the energy requirement is 722 GJ/t (Norgate et al. 2007).

Table A.3: Energy consumption in the titanium production. Values expressed in GJ/ton of Ti.

	E_{mining}	E_{refining}	E_{total}
Rutile – Chapman & Roberts (1983)	2.8	575	577.8
Ilmenite – Chapman & Roberts (1983)	23	687	710
Yoshiki & Toguri (1993)		406.8	
Norgate et al. (2007)			722

Vanadium

Vanadium is found in nature in several minerals such as patronite, carnotite, roscoelite and vanadinite, although it is also present in phosphate rock, some iron ores, bauxite and fossil fuels.

The majority of vanadium metal is produced from vanadium slag, which is obtained from a pre-reducing process of titanomagnetite ore in an electric arc furnace. The electric arc furnace produces pig iron that is oxidised further in an oxygen blown converter in order to transfer the vanadium into the slag. The slag that contains vanadium is then used as the world's major raw material source to produce vanadium oxide, which can further be transformed by reduction to vanadium metal, especially alloys that contain vanadium (Classen et al. 2007).

The energy requirement for mining and concentrating ore to produce vanadium is 136 GJ/t, whilst the smelting and refining processes require 381 GJ/t (Botero 2000).

Wolfram (Tungsten)

China has the largest reserves of tungsten ore worldwide and is the principal supplier of raw material. Issues such as cost of alternative materials/technologies, performance decrement, and slight environmental alternatives are the substitution limiting, according to the ad-hoc Working Group (2010).

The energy requirement for mining and concentrating ore to produce tungsten is 213 GJ/t, whilst the smelting and refining processes require 144 GJ/t (Chapman & Roberts 1983).

Zirconium

The main economic source of zirconium is the zircon sillicate mineral, zircon ($ZrSiO_4$) which is a coproduct or byproduct of the mining and processing of heavy-minerals sands of titanium or tin minerals. The concentrating of zirconium is done through a magnesium-reduction process (Kroll process) with a energy requirement of 633 GJ/t and 738.5 GJ/t is consumed during refining stage (Botero 2000).

Table A.4: Uses of commodities

Commodity	Producing countries	Uses
Al	Australia, China, Brazil	Aircraft, automotive parts, railroads cars, seagoing vessels, packaging, building construction, electrical applications, pharmaceutical, water treatment
Ag	Peru, China, Mexico, United States, Canada	Industrial application, photography, jewellery, electrical applications, batteries
As	China, Chile, Morocco	
Au	China, Australia, United States, South Africa, Russia	Jewellery, electronics, official coin, dentistry, decoration
Be	United States, China, Mozambique	
Bi		Coolant for nuclear reactors, bi-metal polymer bullets, high-T superconductors, computer chips
Cd	China, Korea, Kazakhstan	Batteries, pigments, stabilisers, coatings, alloys
Ce		Catalyst, metal alloys, radiation shielding, phosphors for flat screen TVs
Co	Congo, Australia, China	Superalloy manufacture (gas turbines and jet engines), hybrid and electric car batteries, storage of solar energy, catalysts, cell phones, tire adhesives, magnetic recording media, hard materials, chemical uses

Commodity	Producing countries	Uses
Cr	South Africa, India, Kazakhstan, United States	Non-ferrous alloys, aerospace industry (superalloys), electroplated, protective coating, catalyst, pigments
Cu	Chile, Peru, United States, Australia, Canada, China	Building wire, tube, alloy rod, telecommunication wire
Eu		Liquid crystal displays, fluorescent lighting, LEDs, red and blue phosphors for flat screen TVs, portable electronics and small motors
Fe	China, Brazil, Australia	Steel production, automobile industry, mechanical engineering, building industry (e.g. radiators, boilers, sanitary ware and pipes), chemical plant, shipbuilding, mining
Ga	China, Germany, Kazakhstan, Australia, Russia	Optoelectronics, telecommunication, aerospace and commercial items like alloys, computers and DVDs
Ge	China, Russia, United States	Fibre optic cable, optical technologies
Gd		Magnetic resonance imaging contrast agent, memory chips
He	United States, Algeria, Qatar	
In	China, Korea, Japan, Canada, Russia	Coatings, alloys, electronics, semiconductors, displays, thin layer photovoltaics
La		Batteries, optical glass, camera lenses, catalysts for petroleum refining, catalytic converters
Li	Chile, Australia, China	Lubricants, glass and ceramics, lithium carbonate (used for aluminium reduction, batteries, pharmaceuticals), high-performance alloys for aircraft, carbon dioxide absorber in spacecrafts, nuclear applications
Mg	China, Turkey, Russia	Aluminium alloy, die castings, steel, iron
Mn	China, Australia, South Africa, Soviet Union	Steel industry, batteries, alloys, colourants and pigments, ferrites, welding fluxes, agriculture, water treatment, hydrometallurgy, fuel additives, oxidizing agents, odour control, catalysts, metal coating
Mo	China, United States, Chile	Alloys and superalloys, lamp and light industries, electronic and semiconductor, glass and ceramic industry, nuclear technology, medicine
Nb	Brazil, Canada	High-T superalloys, next generation capacitors, superconducting resonators

Commodity	Producing countries	Uses
Nd		Hard disk drives, medical applications, portable electronics and small motors, high-strength permanent magnets, laser technology
Ni – laterites	Australia, Brazil, Cuba	Stainless steel, battery manufacture, coin production, welding products, fuel filters, paints, electronics
Ni – sulphide	Russia, Indonesia, Canada, South Africa, Australia	
Pb	China, Australia, United States, Canada	Batteries, pigments, alloys, cable sheathing, lead crystal, solder and radiation protection
Pd	Russia, South Africa, United States	Catalysts, seawater desalination
PGM	Russia, South Africa	Automotive catalysts, electronics, hydrogen fuel cells, industrial applications, jewellery, coins, glass, dentistry, petroleum, laboratory equipment, medical implants
Pr		Flat screen TVs, portable electronics and small motors, hard disk drives, magnets, lasers, pigments, cryogenic refrigerant
Pt	South Africa, Russia, Zimbabwe	Hydrogen fuel cells, chemical sensors, cancer drugs, flat-panel displays, electronics, catalysts, jewellery
REE	China, India, Brazil, United States, Australia	Optics, magnetics, electronics, ceramics, glass, metallurgy, catalyst
Re	Chile, United States, Kazakhstan	
Se	Japan, Belgium, Canada	
Sc		Super alloys, light aerospace components, X-ray tubes, catalysts
Sn	China, Indonesia, Peru	
Sb	China, Bolivia, Russia, South Africa	Micro capacitors
Ta	China,Thailand, Malaysia, Indonesia	Electronic components (capacitors), superalloys, medical technology, lining for chemical and nuclear reactors, wires, cameras
Tb		Green phosphor for flat screen TVs, lasers, fluorescent lamps, optical computer memories, medical applications
Te	Chile, United States, Peru, Canada, Japan	Photovoltaic solar cells, thermoelectric devices, steel alloy

Commodity	Producing countries	Uses
Ti	Malaysia, Indonesia and Thailand	Food packaging, electronics, chemicals, aircraft and automotive components, lightweight alloys, joint replacement, paints, watches, chemical processing equipment, marine equipment, pulp and paper processing equipment, pipes, jewellery
U	Canada, Kazakhstan, Australia	nuclear fuel, nuclear weapons, X-ray targets, photographic toner
V	China, South Africa, Russia	Alloys (especially steel), catalysts, pigments for ceramics and glass, batteries, medical, pharmaceutical, electronics
W	China, Russia, Canada	Negative thermal expansion devices, high-T superalloys, X-ray photo imaging, alloys (electric lamp filaments, electron and television tube, metal evaporation work), ammunition, chemical and tanning industry, paints
Y		Compact fluorescent lamps, LEDs, flat-screen TVs, medical applications, ceramics
Zn	China, Peru, Australia, Canada	Construction, automotive equipment, agriculture, electrical components, galvanizing, alloys, brass, batteries, roofing, water purification, coins, zinc oxide (widely used in manufactured goods), zinc sulfide (luminous dials, X–ray and TV screens, paints, fluorescent lights)
Zr		Ceramics, refractories, foundry sands, glass, chemical piping in corrosive environments, nuclear power reactors, hardening agent in alloys, heat exchangers, photographic flashbulbs, surgical instruments

Appendix B

Input-Output Analysis

The input-output was developed by Wassily Leontief from 1930s to the 1950s. It consists of a qualitative and quantitative analysis of the relations that link the flows of goods and services between the components of an economic unit, in order to study its structural characteristics. It describes how industries are interrelated through producing and consuming intermediate industry outputs.

Assuming that the economy is divided into n industries. The total output of industry i is denoted as x_i, the final demand for industry products as y_i, and the intermediate input sales from industry i to industry j as x_{ij}. Then, the I–O system of equations can be expressed as:

$$\begin{array}{lcccc} x_1 = x_{11} + x_{12} + & \cdots & +x_{1j} + & \cdots & +x_{1n} + y_1 \\ x_2 = x_{21} + x_{22} + & \cdots & +x_{2j} + & \cdots & +x_{2n} + y_2 \\ \quad\vdots & \vdots & & & \vdots \\ x_i = x_{i1} + x_{i2} + & \cdots & +x_{ij} + & \cdots & +x_{in} + y_i \\ \quad\vdots & \vdots & & & \vdots \\ x_n = x_{n1} + x_{n2} + & \cdots & +x_{nj} + & \cdots & +x_{nn} + y_n \end{array} \tag{B.1}$$

To aid further analysis, it is defined the technical coefficient which express the value of intermediate inputs that are required by industry j from industry i to produce a unit of product in industry j:

$$a_{ij} = \frac{x_{ij}}{x_j} \tag{B.2}$$

Using these technical coefficients, the I–O system of equations can be re-write in matrix form:

$$\mathbf{X} = \mathbf{AX} + \mathbf{Y} \tag{B.3}$$

where $\mathbf{X} = \begin{vmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{vmatrix}$

and $\mathbf{Y} = \begin{vmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{vmatrix}$

are n x 1 vectors, and

$\mathbf{A}= \begin{vmatrix} a_{1,1} & a_{1,2} & \dots & a_{1,j} & \dots & a_{1,n} \\ a_{2,1} & a_{2,2} & \dots & a_{2,j} & \dots & a_{2,n} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ a_{i,1} & a_{i,2} & \dots & a_{i,j} & \dots & a_{1,n} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ a_{n,1} & a_{n,2} & \dots & a_{n,j} & \dots & a_{n,n} \end{vmatrix}$

is the n x n matrix of technical coefficients. **A** is usually referred to as the technology matrix.

The later notation allows to calculate the production of each component as a function of final demand and the technical coefficients:

$$\mathbf{X} = (\mathbf{U} - \mathbf{A})^{-1} \cdot \mathbf{y} \tag{B.4}$$

Where **U** denotes the m x m identity matrix.

The Leontief inverse matrix $\mathbf{L} \equiv (\mathbf{U} - \mathbf{A})^{-1}$

shows output rises in each sector i due to the unit increase in final demand.

B.1 Cost Model

The cost model of the input-output analysis is a powerful tool to estimate the system cost as well as the individual processes cost.

Production cost of a system have the follow properties:

P1: The external resources costs are known, then the productions costs are calculated in regards to.

P2: The output costs in each process are proportional to the measured quantity of the flow.

$$c_{i1} = \ldots = c_{in} = c_i \tag{B.5}$$

P3: The production cost of each process is equal to the sum of the inputs costs.

$$c_i x_i = c_i x_{1i} + \ldots + c_n x_{ni} + v_i \tag{B.6}$$

Then, the production unit costs of the systems meets the expression:

$$c_i = c_1 a_{1i} + \ldots + c_n a_{ni} + b_i \tag{B.7}$$

Where x_{ni} and a_{ni} are the production and technical coefficients, respectively, and b_i represents the unit costs of the external resources.

The cost model equations can be re-writed in matrix form:

$$\left|\begin{array}{c} c_1 \\ \vdots \\ c_n \end{array}\right| = \left|\begin{array}{ccc} a_{i,1} & \dots & a_{1,n} \\ \vdots & \ddots & \vdots \\ a_{n,1} & \dots & a_{n,n} \end{array}\right| \cdot \left|\begin{array}{c} c_1 \\ \vdots \\ c_n \end{array}\right| + \left|\begin{array}{c} b_1 \\ \vdots \\ b_n \end{array}\right|$$

Or,

$$c = A^T \cdot c + b \tag{B.8}$$

Where A^T is the transposed matrix of A. Then, it is possible to calculate the unit costs of each process as function of the unit costs of the external resources and the technical coefficients or local consumptions, as follows:

$$c = \left(U - A^T\right)^{-1} \cdot b \tag{B.9}$$

Appendix C

Exergy Cost Allocation for deposit models

Allocation factors of several mineral deposits depicted in following Tables and its corresponding Figures, are based on tonnage, price and exergy replacement cost. See Chapter 5.

Table C.1: Cost allocation of Cu-Mn-P deposits as a function of tonnage, price and ERC.

Deposit	Replacement Mn			
type	Ton. [%]	Price [%]		ERC [%]
		1980	2006	
Copper	2.4	14.5	18.9	15.7
Manganese	89.3	85.1	80.8	84.1
Phosphorus	8.2	0.4	0.3	0.2

Table C.2: Cost allocation of Mn-P deposits as a function of tonnage, price and ERC.

Deposit	Volcanogenic Mn			
type	Ton. [%]	Price [%]		ERC [%]
		1980	2006	
Manganese	99.8	99.99	99.99	99.99
Phosphorus	0.2	0.01	0.01	0.01

Table C.3: Cost allocation of Fe-P deposits as a function of tonnage, price and ERC.

Deposit	Algoma and Sup. Fe				Volcan.-hosted magnetite			
type	Ton. [%]	Price [%]		ERC [%]	Ton. [%]	Price [%]		ERC [%]
		1980	2006			1980	2006	
Iron	99.9	99.9	99.9	99.997	99.3	99.6	99.6	99.98
Phosphorus	0.1	0.1	0.1	0.003	0.7	0.4	0.4	0.02

Table C.4: Cost allocation of Sb-Au-Ag deposits as a function of tonnage, price and ERC.

Deposit type	Sb venis Ton. [%]	Price [%] 1980	Price [%] 2006	ERC [%]	Disseminated Sb Ton. [%]	Price [%] 1980	Price [%] 2006	ERC [%]
Antimony	99.99	90.2	94.1	98.1	99.996	94.6	96.7	98.9
Gold	0.001	7.9	5.2	1.8	0.001	4.7	3	1.0
Silver	0.01	1.9	0.7	0.2	0.003	0.6	0.2	0.1

Table C.5: Cost allocation of Co-Cu deposits as a function of tonnage, price and ERC.

Deposit type	Sedim.-hosted Cu Ton. [%]	Price [%] 1980	Price [%] 2006	ERC [%]
Cobalt	10	72.1	33.1	91.7
Copper	90	27.9	66.9	8.3

Table C.6: Cost allocation of Cu-Pb-Ag-Zn deposits as a function of tonnage, price and ERC.

Deposit type	Sedim. Exhal Zn-Pb Ton. [%]	Price [%] 1980	Price [%] 2006	ERC [%]
Copper	2.2	4	4.8	7.1
Lead	32.2	24.7	17.3	34.5
Silver	0.1	27.2	5.9	10.8
Zinc	65.51	44.1	72	47.5

Table C.7: Cost allocation of Co-Ni deposits as a function of tonnage, price and ERC.

Deposit type	Laterite Ni Ton. [%]	Price [%] 1980	Price [%] 2006	ERC [%]
Cobalt	4.9	29.9	6.1	42.4
Nickel	95.1	70.1	93.9	57.6

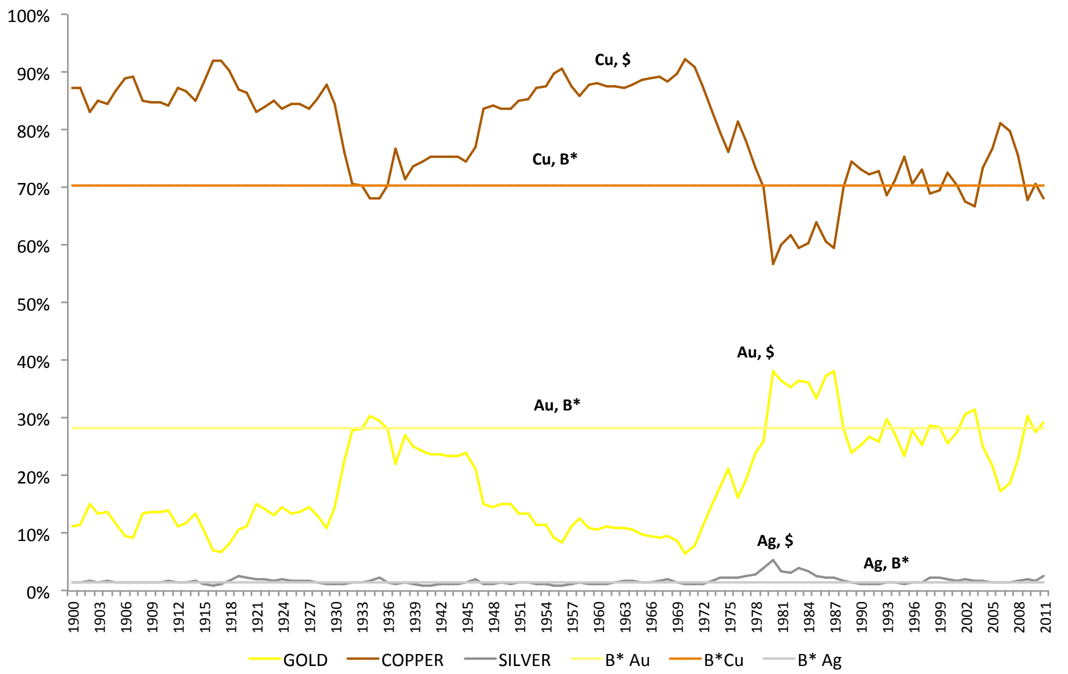


Figure C.1: Cost allocation of Cu-Au-Ag deposits as a function of price and ERC.

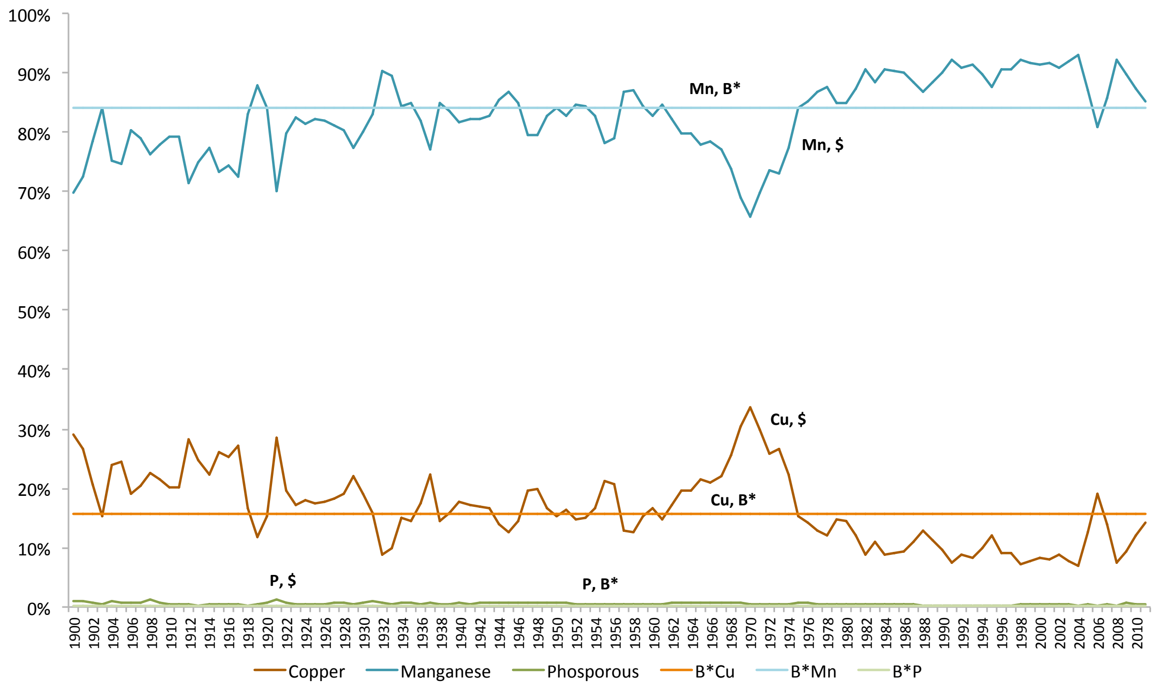


Figure C.2: Cost allocation of Cu-Mn-P deposits as a function of price and ERC.

Figure C.3: Cost allocation of Co-Cu deposits as a function of price and ERC.

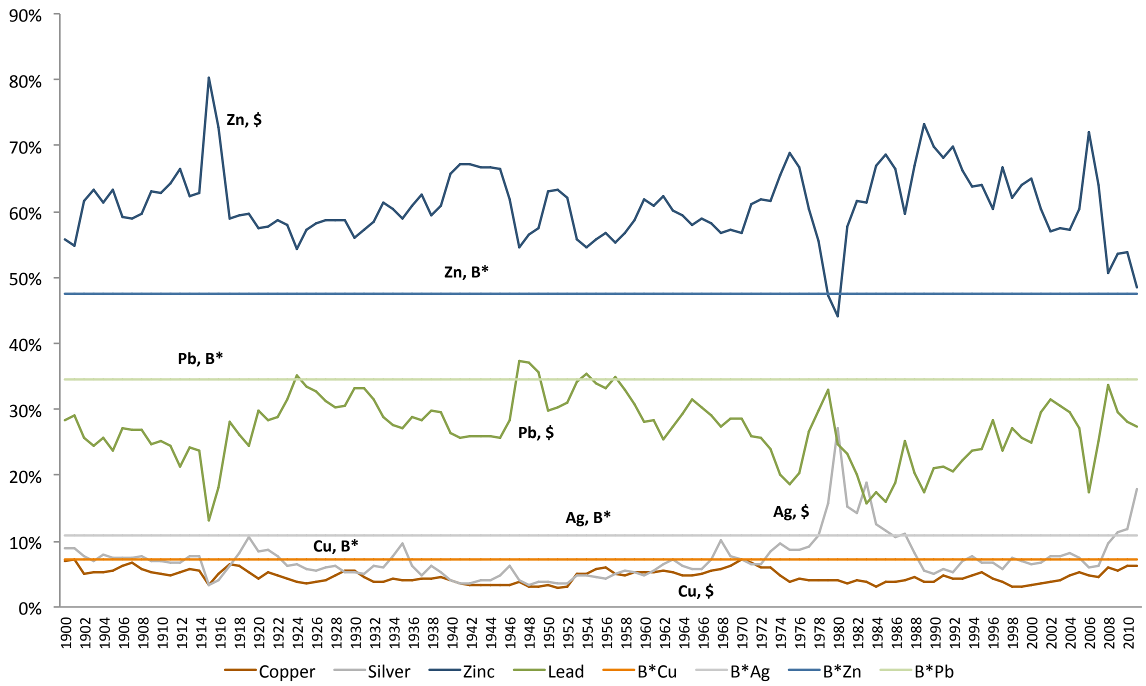


Figure C.4: Cost allocation of Cu-Pb-Ag-Zn deposits as a function of price and ERC.

Figure C.5: Cost allocation of Co-Ni deposits as a function of price and ERC.

Table C.8: Cost Allocation of Ni and Cu based on Exergy Replacement Costs.

	kg_Ni	kg_GN	MJpp	kg_R	kg_Cu	kg_coal	kg_lime	kg_cem	kg_sil	kg_NaCN	kg_sulph	kg_CuS
kg_Ni	1.26	0	0	0	0	0	0	0	0	0	0	0
kg_GN	11.393	0	0.905	0	0.858	0	0.0047	0.0048	0	0	0	0
MJ_pp	34.736	0.006	0	0.002	2.615	0.011	0.0138	0.45	0	0	0	0
kg_R	26.784	0	1.0045	0	2.016	0	0.0222	0	0	0	0	0
kg_Cu	0.648	0	0	0	0	0	0	0	0	0	0	0
kg_coal	0	0	0.802	0	0	0	0.001	0.151	0	0	0	0
kg_lime	2.194	0	0	0	0.165	0	0	0	0	0	0	0
kg_cem	3.36	0	0	0	0.253	0	0	0	0	0	0	0
kg_sil	44.45	0	0	0	3.346	0	0	0	0	0	0	0
kg_NaCN	0.0036	0	0	0	3E-04	0	0	0	0	0	0	0
kg_sulph	0.236	0	0	0	0.018	0	0	0	0	0	0	0
kg_CuS	0.102	0	0	0	0.008	0	0	0	0	0	0	0

Table C.9: Cost Allocation of Ni-Cu-Co based on Exergy Replacement Costs.

	kg_Ni	kg_GN	MJ_pp	kg_R	kg_Cu	kg_coal	kg_lime	kg_cem	kg_sil	kg_NaCN	kg_sulph	kg_CuS	kg_Co
kg_Ni	1.260	0	0	0	0	0	0	0	0	0	0	0	0
kg_GN	10.045	0	0.905	0	0.735	0	0.005	0.005	0	0	0	0	1.470
MJ_pp	30.627	0.0059	0	0.002	2.241	0.011	0.014	0.450	0	0	0	0	4.482
kg_R	23.616	0	1.005	0	1.728	0	0.022	0	0	0	0	0	3.456
kg_Cu	0.648	0	0	0	0	0	0	0	0	0	0	0	0
kg_coal	0	0	0.803	0	0	0	0.001	0.151	0	0	0	0	0
kg_lime	1.934	0	0	0	0.142	0	0	0	0	0	0	0	0.283
kg_cem	2.968	0	0	0	0.217	0	0	0	0	0	0	0	0.434
kg_sil	39.196	0	0	0	2.868	0	0	0	0	0	0	0	5.736
kg_NaCN	0.003	0	0	0	0.000	0	0	0	0	0	0	0	0.000
kg_sulph	0.208	0	0	0	0.015	0	0	0	0	0	0	0	0.030
kg_CuS	0.090	0	0	0	0.007	0	0	0	0	0	0	0	0.013
kg_Co	0.013	0	0	0	0	0	0	0	0	0	0	0	0

Table C.10: Cost Allocation of Cu-Mo-Ag-Te based on Exergy Replacement Costs.

	kg_Cu$_1$	kg_Cu_2	kg_Mo	kg_Te	kg_Ag	kg_Cu_3	kg_GN	MJ_pp	kg_R	kg_coal	kg_lime	kg_Al	kg_sil	kg_NaCN	kg_sulph	kg_CuS	kg_O	kg_steel
kg_Cu_1	0	3.150	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
kg_Cu_2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
kg_Mo	0.008	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
kg_Te	0	0.00005	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
kg_Ag	0	0.0003	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
kg_Cu_3	0	0.094	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
kg_GN	0	2.816	0	0.272	0.076	0	0	0.905	0	0	0.005	0	0	0	0	0	0	0
MJ_pp	2.553	1.577	0.087	0.152	0.042	2.910	0.006	0	0.002	0.011	0.014	5.526	0	0	0	0	0	0
kg_R	0.003	5.319	0.00009	0.513	0.143	0.783	0	1.005	0	0	0.022	0.189	0	0	0	0	0	0
kg_coal	0	0.023	0	0.002	0.001	0	0	0.803	0	0	0.001	0	0	0	0	0	0	0
kg_lime	0.041	0.201	0.001	0.019	0.005	0	0	0	0	0	0	0	0	0	0	0	0	0
kg_Al	0	0.001	0	0.000	0.00002	0	0	0	0	0	0	0	0	0	0	0	0	0
kg_sil	0	0.671	0	0.065	0.018	0	0	0	0	0	0	0	0	0	0	0	0	0
kg_NaCN	0.001	0	0.00004	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
kg_sulph	0.130	0	0.004	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
kg_CuS	0.035	0	0.001	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
kg_O	0	0.234	0	0.023	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0
kg_steel	0.026	0	0.0009	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Conclusiones

En este apartado de conclusiones se presenta una síntesis de esta tesis. Además, se mencionan las principales contribuciones así como las publicaciones científicas derivadas de este trabajo. Finalmente, se exponen las perspectivas que han surgido durante el desarrollo de esta tesis y se proponen para estudios posteriores.

Síntesis

La accesibilidad y disponibilidad de los recursos minerales se ha convertido en un tema crucial para el progreso tecnológico. Muchos de estos recursos son considerados estratégicos o críticos, puesto que son determinantes para el desarrollo de nuevas tecnologías, las energías renovables y las TICs. Por lo que asegurar su disponibilidad se ha convertido en una tarea imperativa. En este sentido, es necesario como primer paso contabilizar apropiadamente el uso de los recursos así como optimizar y analizar a través de métodos objetivos y rigurosos la industria minera y metalúrgica.

Por consiguiente, el objetivo principal de esta tesis doctoral consistió en la aplicación de metodologías termoeconómicas que permitieron realizar un "Análisis de Ciclo de Vida absoluto" de los recursos minerales. De esta manera, no sólo el enfoque convencional de "la cuna a la tumba" es considerado, sino también el complementario, de "la tumba a la cuna". Por lo tanto, se complementó el análisis termoeconómico con el enfoque exergoecológico a través de los costes exergéticos de reposición (ERC). Los ERC contabilizan la exergía necesaria para regresar un mineral que ha sido extraído a sus condiciones iniciales de composición, concentración y cohesión con la tecnología actual. De esta forma, la combinación de metodologías permite tener en cuenta no sólo el esfuerzo requerido para producir un metal sino también la pérdida de la riqueza mineral asociada al agotamiento de los depósitos naturales.

El objetivo del Capítulo 1 consistió en mostrar un perspectiva general de los recursos minerales y de la industria minera. Dado que esta tesis doctoral esta centrada en la evaluación de la minería global, temas como el desarrollo sostenible y el análisis de ciclo de vida aplicado al agotamiento de los recursos naturales han sido abordados. Adicionalmente, se ha presentado una perspectiva global de la producción, la evolución de los precios de mercado y la situación actual de los minerales.

En el Capítulo 2 se proporcionó una síntesis de la cadena productiva de varios minerales metálicos. Por lo que se describieron los principales procesos de extracción y metalúrgicos en la industria minera. Posteriormente, se realizó un análisis más detallado de los procesos metalúrgicos específicos para cada uno de los metales analizados, y aplicados en diferentes casos de estudio a lo largo del desarrollo de esta tesis. Se observó que los datos de los requerimientos energéticos para el procesado de metales varía notablemente, así como el hecho de que la energía asociada se incrementa sustancialmente debido a diferentes factores, tales como: bajas leyes minerales, profundidad de las minas, complejidad de la mena y el aumento de residuos. El Capítulo 2 finaliza con una recopilación de los requerimientos energéticos necesarios para la producción de 33 minerales, dividiendo la información en dos etapas: 1) minería y concentración y 2) fundición y refinado.

Los cambios tecnológicos han jugado un factor crucial en la evolución de los procesos de producción dentro del sector minero. De ahí que en el Capítulo 3 se mostró la evolución histórica de la innovación tecnológica en la industria minera, la cual debería compensar el incremento de los costos asociados a las dificultades operativas que se han presentado este sector a través del tiempo.

La industria minera, además de hacer frente a los problemas comunes a cualquier otra industria, debe enfrentar un problema adicional: la disminución de las leyes minerales. Entonces, se puede decir que la disponibilidad futura de los recursos minerales esta influenciada por dos factores opuestos. Por un lado, la tendencia general sugiere una disminución de la ley mineral, lo que ha incrementado el consumo energético en la industria minera. Y por otro lado, ha habido transiciones tecnológicas que podrían evitar el aumento del consumo energético. El objetivo del Capítulo 3 consistió en analizar si los avances tecnológicos que han tenido lugar en este sector, pueden evitar el aumento en la demanda de energía, tomando como ejemplo la minería del oro.

Conforme se adquiere experiencia, la eficiencia en el uso de materias y energía aumenta, estos cambios tecnológicos pueden expresarse a través de las curvas de aprendizaje. Por consiguiente, la teoría de las curvas de aprendizaje se aplicó a varias minas de oro en distintos países. Los porcentajes de progreso promedios obtenidos para diferentes países varían entre +20% y -22%. Este estudio permitió tener un mejor conocimiento del sector minero así como de las consecuencias de la evolución tecnológica aunada al decremento de la ley mineral. De tal forma que se pueden identificar las minas en las cuales las operaciones mineras y los procesos metalúrgicos han probado ser exitosos en lo que al ahorro de energía se refiere. De esta manera, es posible identificar las mejores prácticas en el sector minero, para que las innovaciones tecnológicas sirvan de referencia a otras minas con condiciones similares alrededor del mundo. Los resultados muestran que aunque ha habido avances tecnológicos, por lo general el consumo energético en el sector ha ido en aumento en la mayoría de los casos, debido a que estos dependen principalmente de la ley mineral. Por lo anterior, se puede decir que en general los avances tecnológicos no han sido ni serán capaces de mitigar el aumento de energía en la industria minera si no se presentan avances tecnológicos contundentes.

Una vez revisados los principales aspectos relacionados con la industria minera, en el Capítulo 4 se presentaron los fundamentos termodinámicos para evaluar los procesos mineros y metalúrgicos. Por lo que se presentaron las bases de los análisis exergético, termoeconómico, termoecológico y exergoecológico. Particularmente, se presentó la Termoeconomía, definida como una teoría general para el ahorro de energía, la cual integra la Termodinámica (análisis exergético) y la Economía (costo exergético) a través de la Segunda Ley de la Termodinámica. Mientras que la teoría del Costo Termo-Ecol?gico (TEC), define este último como el consumo acumulado de exergía no renovable requerida para producir una unidad de producto útil a partir de materias primas contenidas en los depósitos naturales, con la inclusión adicional del consumo resultante de la necesidad de compensar los daños ambientales debidos a la emisión de sustancias contaminantes al ambiente. Ambas metodologías están muy relacionadas, por lo que sus similitudes y diferencias fueron explicadas. Además, ambos métodos pueden ser mejorados en cuanto al análisis de la extracción de minerales y procesos metalúrgicos se refiere, a través de la Exergoecología, usando los costos exergéticos de reposición de los minerales.

Los costos exergéticos de reposición son el punto de referencia para evaluar la concentración, composición y el estado de la tecnología integrados en un sólo parámetro. Al contrario de los combustibles fósiles, los minerales no se pierden cuando son utilizados, puesto que generalmente terminan dispersos en vertederos. Contar con un orden de magnitud de cuanto costaría reponer estos minerales dispersos, permitirá una gestión más adecuada de los mismos. La importancia de los costos exergéticos de reposición radica en su habilidad para establecer un factor de escasez de los recursos minerales, los cuales deben ser contabilizados cuando se analiza la sostenibilidad de la industria minera.

Los fundamentos del enfoque exergoecológico fueron desarrollados en una tesis doctoral previa, sin embargo algunos aspectos quedaron sin resolver, como la influencia de la tendencia del decremento de la ley mineral en los costos exergéticos de reposición. Por lo tanto, esta tesis ha tratado de mejorar la metodología y se han calculado valores de ERC más precisos para cada sustancia. La variable principal para obtener dichos costos es el costo exergético unitario, el cual representa la proporción entre la energía acumulada real requerida para la extracción y concentración de una sustancia y la energía (exergía) mínima requerida para realizar el mismo proceso. Por lo tanto, proporcionan una medida de la irreversibilidad (ignorancia tecnológica) de un proceso. Dado que la energía requerida en la minería es función de la ley mineral y de la tecnología utilizada, ambos factores tienen influencia sobre los costos exergéticos de reposición unitarios. Teniendo en cuenta datos empíricos de los requerimientos energéticos en la minería en función de la ley mineral, los nuevos valores obtenidos de los costos exergéticos de reposición para diferentes minerales se presentaron en el Capítulo 5. Adicionalmente, se obtuvo una expresión general del consumo de energía vs. la ley mineral, para aquellos minerales de los que no se tenían datos empíricos disponibles. Se observó que la tendencia general es que conforme la ley mineral decrece, la energía y los costos exergéticos de reposición incrementan exponencialmente. Los valores obtenidos constituyen un paso intermedio para evaluar de una manera física, la exergía gratuita de la naturaleza que el hombre esta destruyendo rápidamente a través del agotamiento de las mayores leyes minerales. Estos valores deberían proporcionar una herramienta de valoración para los tomadores de decisiones en la industria minera.

Otro aspecto que se ha analizado en esta tesis, es el problema de asignación de costos en los procesos de la industria minera y metalúrgica. Se sabe que en la minería con cada mineral extraído, se obtienen subproductos y residuos. Una estrategia de desarrollo sostenible en la industria minera consiste en implementar una política de cero desechos, emigrando a la minería polimetálica, en la que se aprovechen todos los recursos minerales y se recuperen la mayor cantidad de subproductos. Por lo que la industria minera debe ser vista como un sistema que produce subproductos, mismos que necesitan métodos de asignación de costos objetivos, como el propuesto en el Capítulo 5 de esta tesis.

Los metales que se producen como subproductos generalmente tienen complicaciones en cuanto a la demanda y suministro, los requerimientos tecnológicos así como en temas de inversión. La producción de estos subproductos dependen de la disponibilidad y factibilidad tecnológica para recuperar estos metales durante o después del procesado de los metales principales, así como del beneficio económico de los subproductos recuperados. La energía final utilizada para obtener dichos subproductos es difícil de estimar puesto que hasta ahora no existe uniformidad en cuanto a los procedimientos para la asignación de costos.

Actualmente, la asignación de costos entre los productos y subproductos obtenidos en la industria minera y metalúrgica están basados en el tonelaje o en precios comerciales. Ambos métodos de asignación conllevan varias desventajas, tales como subjetividad con el precio o la subestimación de aquellos subproductos que presentan un bajo tonelaje. Si se tiene en cuenta que la extracción de minerales y el subsiguiente procesado de los mismos constituye la primer etapa de cualquier proceso, utilizar programas convencionales para el análisis de ciclo de vida, que asignan costos en función del tonelaje o los precios de mercado, puede conducir a resultados incorrectos. En el Capítulo 5 se propuso un método riguroso basado en exergía para asignar costos entre los subproductos mineros a través de los costos exergéticos de reposición. Este enfoque permitió asignar costos en función de la calidad física de los minerales. Los métodos de asignación de costos basados en tonelaje, precio y costos exergéticos de reposición, fueron aplicados a varios modelos de depósitos minerales. De esta manera se demostró que la asignación de costos teniendo en cuenta el tonelaje no siempre es una opción apropiada debido a las pequeñas cantidades de subproductos que pueden presentarse, pero que pueden ser tanto o más valiosas que el producto principal. Por otra parte, si se utiliza el precio de mercado para la asignación de costos, se presenta el problema asociado a su alta volatilidad, que a su vez depende de variables macroeconómicas que comúnmente no reflejan las condiciones físicas de los recursos minerales en la Naturaleza. Los resultados obtenidos sugieren que si los costos exergéticos de reposición son aplicados a la asignación de costos, se obtienen valores de asignación similares a los que se obtienen cuando se considera el precio como indicador. Lo anterior respalda la idea que los costos exergéticos de reposición son similares al valor que la sociedad asigna a los minerales. Con la ventaja de que los costos exergéticos de reposición no fluctúan con factores externos relacionados con los mecanismos de mercado, sino que permanecen constantes, caso contrario a lo que ocurre con los precios.

Una vez que se demostraron las ventajas del nuevo procedimiento de asignación de costos, se aplicó la metodología a cuatro casos de estudios donde se produce níquel, cobre, plomo y tierras raras, como metales principales y sus respectivos subproductos, con el objetivo de asignar a cada subproducto las entradas de materia prima y combustibles fósiles correspondientes. De esta manera, se calculó el costo físico de la producción de los diferentes metales obtenidos en una operación minera. Los resultados demuestran que en general los precios no están relacionados adecuadamente con los costos naturales, porque no se está tomando en cuenta el factor de agotamiento mineral y el hecho de que el hombre esta destruyendo la riqueza mineral de la tierra, que estará indisponible para las generaciones futuras.

En el Capítulo 6 de esta tesis, se realizó el análisis exergético del proceso de obtención de diversos minerales. El caso del procesamiento de níquel, se estudió exhaustivamente en esta tesis, se realizó un análisis exergético del flujo de energía y materiales para la producción de níquel a partir de dos tipos de mineral (lateritas y sulfuros). Los resultados muestran que el procesamiento de níquel presenta mayores eficiencias cuando se produce níquel a partir de sulfuros que de lateritas. El procesamiento de sulfuros presenta eficiencias que fluctúan entre 67% y 79%, dependiendo de la tecnología utilizada, las mayores eficiencias se alcanzan cuando se emplean procesos de lixiviación. Para el caso de lateritas, las eficiencias alcanzadas están alrededor de 38% debido al costo intensivo de procesamiento. Este análisis se realizó teniendo en cuenta la exergía química de los materiales, lo que permitió hacer comparaciones directas entre diversas rutas de producción. Los resultados fueron comparados con el método exergoecológico, que incluye no sólo la exergía química de los minerales, sino que involucra también la exergía de concentración. Se concluyó que el análisis a partir de la exergía química no es suficiente para valorar adecuadamente los minerales. Por ejemplo, las lateritas tienen una exergía química insignificante, sin embargo, sus requerimientos energéticos y contabilización exergética son mayores que los obtenidos para los sulfuros, los cuales tienen una mayor exergía química. Así pues, se puede concluir que la exergía química utilizada en los análisis exergéticos puede conducir a resultados poco fiables, porque esta faltando la exergía de concentración. Es importante destacar que el valor de los minerales está mucho más asociado con su grado de escasez. Ésta es la razón por la cual la exergía de concentración, calculada por los costos exergéticos de reposición, es mucho más relevante cuando se analizan recursos minerales.

Posteriormente, en este mismo Capítulo 6 se realizó un análisis exergético más complejo del procesamiento de varios minerales a través del costo termoecológico, ampliando así el análisis hasta un enfoque de "la cuna al mercado". El TEC evalúa el consumo acumulado de exergía no renovable requerida para producir una unidad de producto útil a partir de materias primas contenidas en los depósitos naturales. Con este método, es posible dividir los resultados en componentes asociadas al consumo de combustibles fósiles o consumo de minerales en cada etapa del proceso y de esta manera saber cuanto y que tipo de recurso se consume en cada operación. Esta diferenciación es importante porque los combustibles fósiles podrían ser sustituidos por combustibles de origen renovable, no así los minerales, que difícilmente pueden ser reemplazados por otro tipo de recursos. Un inconveniente de esta metodología es el uso de la exergía química para evaluar los recursos minerales, lo que conduce a obtener valores de exergía asociada a la parte mineral mucho menores que los obtenidos a partir de combustible fósiles. Por lo anterior el TEC se complementó con la introducción de los ERC, los cuales proporcionan un enfoque de "la tumba a la cuna". Los resultados muestran que cuando los ERC son incluidos en los TEC, los impactos asociados al consumo de minerales son significativamente mayores. De esta manera, se obtienen mejores indicadores para evaluar el consumo de recursos minerales. De tal forma que el consumo de minerales se vuelve una cuestión aún más crítica que el consumo de combustibles en la industria minera.

Finalmente, se puede concluir que los análisis exergéticos realizados a través de metodologías como el TEC y los ERC permiten: (1) analizar entradas y salidas de materiales y recursos energéticos, (2) analizar la eficiencia de la transformación de recursos, (3) realizar una asignación de costos objetiva entre productos y subproductos, (4) evaluar las consecuencias ambientales e (5) identificar áreas de oportunidad para alcanzar un desarrollo sostenible en el sector de la minería.

Contribuciones

La contribución general de esta tesis doctoral consistió en mejorar y adaptar las metodologías de análisis y optimización exergética al caso concreto de la industria minera y metalúrgica. Particularmente, la Termoeconomía y el Costo Termoecológico fueron complementados con el enfoque exergoecológico, lo que permitirá realizar un "Análisis de Ciclo de Vida absoluto" de los recursos minerales. A continuación se presentan las principales contribuciones de esta tesis doctoral.

1. La principal contribución del Capítulo 3 es el uso de las curvas de aprendizaje desde un enfoque exergético. Este análisis permite saber si la investigación e innovación tecnológica de los procesos de producción dentro del sector minero han podido o pueden evitar el aumento en la demanda de energía.

2. La primera contribución realizada en el Capítulo 5 consiste en una determinación más exacta de los costos exergéticos de reposición de los minerales, al integrar la variable del tiempo a través de los costos exergéticos unitarios variables que a su vez dependen de los

requerimientos energéticos. Adicionalmente, se obtuvo una expresión general del consumo de energía vs. la ley mineral, para aquellos minerales de los que no se tenían datos disponibles. Estos valores deberían proporcionar una herramienta de valoración para los tomadores de decisiones en la industria minera.

3. La segunda contribución del Capítulo 5 es el desarrollo de un nuevo método de asignación de costos basado en exergía para resolver el problema de asignación de costos entre los subproductos mineros a través de los costos exergéticos de reposición, los cuales tienen en cuenta el factor físico de agotamiento mineral. Contar con este tipo de indicadores objetivos de asignación de costos, permitirá estimar los consumos energéticos asociados a cada uno de los minerales producidos, de una forma objetiva.

4. La principal contribución del Capítulo 6 es la demostración de que el uso de la exergía química para evaluar los recursos minerales conduce a resultados poco fiables, puesto que es necesario introducir la exergía de concentración. El valor de los minerales está asociado a su grado de escasez. Y ésta es la razón principal por la que la exergía de concentración, calculada a través de los costos exergéticos de reposición, es mucho más sobresaliente cuando los recursos minerales son analizados.

5. Otra contribución del Capítulo 6 es la integración de los costos exergéticos de reposición en el análisis exergético realizado con la metodología del Costo Termoecológico, lo que permite evaluar los recursos minerales de una forma más completa, al incluir un enfoque de “la tumba – a la cuna – al mercado ”.

Publicaciones

El desarrollo de esta tesis doctoral ha permitido la elaboración de varias publicaciones científicas que han sido presentadas en diferentes congresos internacionales y publicados en revistas internacionales.

Al. Valero, A. Valero, A. Domínguez. Influence of technical development and declining ore grades on the availability of gold resources. In SDEWES 2011: Proceedings of the 6th Dubrovnik Conference on Sustainable Development of Energy, Water and Environment Systems, September 25 - 29, 2011, Dubrovnik, Croatia.

Al. Valero, A. Valero, A. Domínguez. Trends of exergy costs and ore grade in global mining. In SDIMI 2011: Proceedings of Sustainable Development in the Minerals Industry, June 14-17, 2011, Aachen, Germany.

A. Domínguez, Al. Valero. Global gold mining: is technological learning overcoming the declining in ore grades?. In ECOS, 2012: Proceedings of 25st International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, June 26 - 29, 2012. Perugia, Italy.

A. Domínguez, Al. Valero, A. Valero. Exergy accounting applied to metallurgical systems: The case of nickel processing. In CPOTE, 2012: Proceedings of 3rd. International Conference Contemporary Problems of Thermal Engineering, September 18-20, 2012, Gliwice, Poland.

A. Domínguez, Al. Valero. Global Gold Mining: Is Technological Learning Overcoming the Declining in Ore grades? Journal of Environmental Accounting and Management, 2013, 1, 85-101.

Al. Valero, A. Valero, A. Domínguez. Exergy Replacement Cost of Mineral Resources. Journal of Environmental Accounting and Management, 2013, 2, 147-158.

A. Domínguez, Al. Valero, A. Valero. Exergy accounting applied to metallurgical systems: The case of nickel processing. Energy 2013 (62) 37 - 45.
http://dx.doi.org/10.1016/j.energy.2013.03.089

A. Domínguez, L. Czarnowska, Al. Valero, S. Wojciech, A. Valero. Thermo-Ecological and Exergy Replacement Costs of Nickel Processing. (En revisión en la revista Energy, enviado el 2 de Abril del 2014.)

Al. Valero, A. Valero, A. Domínguez. Exergy Cost Allocation of by-products in the mining and metallurgical industry. (Aceptado en ECOS 2014, 25st International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems. Finland, June 15-19, 2014.)

Perspectivas

Durante el desarrollo de esta tesis, se han identificado varias areás de oportunidad para investigaciones futuras. El principal problema encontrado para obtener resultados de esta tesis ha sido la falta de fuentes de información fiables. Una vez que se establezca un sistema de información transparente en el sector minero y metalúrgico, tanto las metodologías como los resultados obtenidos podrán ser refinados y extendidos a más casos de estudio. Algunas de las interrogantes identificadas en esta tesis son enlistadas a continuación.

1. Debido a la falta de datos, la metodología de curvas de aprendizaje fue aplicada únicamente al oro. Aunque el oro es un mineral muy importante, los resultdos obtenidos a partir de su análisis no pueden ser representativos para todos los minerales producidos a escala global. Por lo tanto, el análsis debería ser extendido a otros minerales y a otros países alrededor del mundo, como por ejemplo China. Puesto que actualmente, China esta poscionado estratégicamente en la industria minera. Con la ayuda de un modelo de redes neuronales, la cuestión acerca de si la tecnología puede contrarrestar el decremento de la ley mineral podría ser mejor abordada.

2. Adicionalmente, la metodología de curvas de aprendizaje utilizada en esta tesis, puede ser mejorada al incorporar un factor relacionado con la investigación y desarrollo tecnológico en la industria minera. Esta fórmula extendida es conocida como curva de aprendizaje de dos factores, aunque también existen las curvas de aprendizaje de múltiples factores que podría incluir variables independientes adicionales que permitan analizar el sector minero.

3. En esta tesis, los ERC de 23 minerales fueron obtenidos, de los cuales sólo 6 fueron obtenidos a partir de información empírica que relaciona el consumo de energía con la ley mineral. Los restantes fueron obtenidos asumiendo un comportamiento general basado en observaciones de datos disponibles. Por lo tanto, resulta importante mejorar los valores obtenidos conforme vaya apareciendo más información. Sin embargo, también es importante extender el cálculo de los ERC a todos los minerales, prestando especial atención a aquellos minerales considerados como críticos o claves, ya que por sus propiedades físico-químicas están siendo ampliamente utilizados en aplicaciones relacionadas con

las nuevas tecnologías y el desarrollo del sector de las energías renovables. Por ejemplo: In, Ge, Ga, P y las REE del grupo de los lantánidos.

Es importante destacar que tanto los cálculos de los costos exergéticos de reposición como los análisis exergéticos de sistemas y procesos, están supedidatos a las bases de datos utilizadas y que la objetividad de los mismos depende de dichos datos. Por lo tanto, es imperativo el uso de fuentes de información fiables en cuanto a consumo de energía y materias primas, diferenciados por el tipo de depósito mineral y las tecnologías utilizadas.

List of Tables

List of Figures

Nomenclature

A	Matrix of direct requirement
a_{ij}	Coefficient of consumption of raw material and semi-finished product
b	Constant reflecting the rate energy decrease from year to year (learning index)
b_c	Concentration exergy
b_{ch}	Chemical exergy
b_{com}	Comminution exergy
b^*_{com}	Comminution exergy cost of a mineral in a mine
b_f	Fuel exergy
b_m	Mineral exergy
B	Exergy
B^*	Exergy cost
B^{CH}	Chemical exergy
B_i	Exergy of the i_{th} product stream
B^*_i	Exergy cost of the i_{th} product stream
B^K	Kinetic exergy
B^P	Potential exergy
B^{PH}	Physical exergy
c	Elasticity of learning by researching
$\Delta G_{mineral}$	Standard normal free energy of formation of the mineral (Gibbs free energy)
d_M	Geometrical mean size of the natural fragments found in the mine
d_θ	Size of the bare rock of the Crepuscular Earth model
E	Energy
ε	Efficiency
F	Fuel
f_{ij}	Coefficient of production of by-product
I	Irreversibilities
k	Unit exergy cost
k^*_i	Unit average exergy cost of the i_{th} product stream
KS	Knowledge stock
$\langle KP \rangle$	Matrix of marginal unit exergy consumptions (nxn)
L	Leontief inverse matrix
M	Tonnage

P	Product
R	Wastes
$\bar{R}$	Gas constant ($8.3145 J/molK$)
r_i	Index of sustainability
r_{ij}	Junction coefficients
ρ	Specific Thermo-Ecological Cost of a main product
S	Energy slope expressed as a decimal value (learning rate)
T_0	Reference Temperature ($298.15K$)
v_k	Number of moles of element k in the mineral
W_i	Bond work index [kWh/t][μm]$^{0.5}$
x	Sequential number of the unit for which the energy is to be computed
x_c	Ore grade (average concentration in the Earth's crust)
x_i	Concentration of the substance i
x_i	Molar concentration of substance i
x_m	Average mineral concentration in a mine
$\overline{x}_m$	Average grade of the mineral deposit
x_r	Refining grade
Y_0	Theoretical energy of the first production unit
y_{ij}	Distribution coefficients
Y_x	Energy required to produce the x_{th} unit
ζ_k	TEC of compensation of the deleterious impact of the rejected waste product
z_f	Fraction of the Thermo-Ecological Cost of a main product due to fuel consumption
z_m	Fraction of the Thermo-Ecological Cost of a main product due to mineral consumption

Abbreviations

CIP	Circuit in Pulp
CIL	Circuit in Leach
ERC	Exergy Replacement Cost
GDP	Gross Domestic Product
HL	Heap Leach
ISF	Imperial Smelting Furnace
LCA	Life Cycle Assessment
LHV	Lower heating value [kJ/kg]
MIX	Mixed (open pit and underground)
OP	Open Pit
PR	Progress ratio
R.E.	Reference Environment
REE	Rare Earth Elements
REM	Rare Earth Metals

REO	Rare Earth Oxides
S/X	Solvent extraction
TEC	Thermo-Ecological Cost
TFLC	Two factor learning curve
UG	Underground
UG_t	Underground tailings

Acronyms

CIM	Canadian Institute of Mining, Metallurgy and Petroleum
EU	Europe Union
OECD	Organisation for Economic Co-operation and Development
SAMREC	South African Code for Reporting of Exploration Results, Mineral Resources and Mineral Reserves
SEM	Society for Mining, Metallurgy, and Exploration

References

Achzet, B. & Helbig, C. (2013), 'How to evaluate raw material supply risks – an overview', *Resource Policy* **38**, 435 – 447.

ad-hoc Working Group (2010), Critical raw materials for the eu. report of the ad-hoc working group on defining critical raw materials, Technical report, European Commission.
URL: *http://ec.europa.eu/enterprise/policies/raw-materials/files/docs/report–b_en.pdf*

AditNow (2013).
URL: *http://www.aditnow.co.uk/*

Agudelo, A., Valero, A. & Torres, C. (2011), Allocation of wastes in thermoeconomic analyses, *in* '24st International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems (ECOS 2011)'.

Agudelo, A., Valero, A. & Uson, S. (2011), The fossil trace of co_2 emissions in energy systems., *in* '24st International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems (ECOS 2011)'.

Ahrendts, J. (1980), 'Reference states', *Energy* **5**, 667–677.

Alvarado, S., Maldonado, P. & Jaques, I. (1999), 'Energy and environmental implications of copper production', *Energy* **24**, 307–316.

AngloGold Ashanti (2013).
URL: *http://www.anglogold.co.za/Home*

Ausenco (2013).
URL: *http://www.ausenco.com/page/Our_Projects/Pierina_Gold_Mine/*

Ayres, R. (2008), 'Sustainability economics: Where do we stand?', *Ecological Economics* **67**, 281 – 310.

Ayres, R. & Ayres, L. (1996), *Industrial Ecology. Towards closing the material cycle*, Edward Elgar Publishing, Cheltenham U.K. and Northampton.

Ayres, R. & Ayres, L. (2002), *A Handbook of Industrial Ecology*, Edward Elgar.

Ayres, R., Ayres, L. & Masini, A. (2006), *Sustainable Metals Management*, Springer, chapter An application of exergy accounting to five basic metal industries, pp. 141–194.

Ayres, R., Ayres, L. & Rade, I. (2002), The life cycle of copper, its co-products and by-products, Technical report, International Institute for Environment and Development (IIED).
URL: *http://www.iied.org/pubs/pdfs/G00740.pdf*

Barrick Company (2013*a*).
URL: *http://www.barrick.com/GlobalOperations*

Barrick Company (2013*b*).
URL: *http://www.barrick.com/Theme/Barrick/files/docs_presentations/pr11_12_2003_weauau.pdf*

Botero, E. A. (2000), Valoración exergética de recursos naturales, minerales, agua y combustibles, PhD thesis, Universidad de Zaragoza.

Boustead, I. & Hancock, G. (1979), *Handbook of Industrial Energy Analysis*, Ellis Horwood Limited.

Bradley, R. L. (2007), 'Resourceship: An austrian theory of mineral resources', *The Review of Austrian Economics* **20**, 63–90.

Bravard, J., Flora, H. & Portal, C. (1972), Energy expeditures associated with the production and recycle of metals, Technical report, Oak Ridge National Laboratory.

Brentrup, F., Kiisters, J., Lammel, J. & Kuhlmann, H. (2002), 'Impact assessment of abiotic resource consumption conceptual considerations', *Int J LCA* **7 (5)**, 301–307.

Brobech, J. (1996), 'Sustainable metal resource management-the need for industrial development: efficiency improvement demands on metal resource management to enable a (sustainable) supply', *Journal of Cleaner Production* **4**, 97–104.

Brown, T., Idoine, N., Mills, A., Shaw, R., Hobbs, S. & Bide, T. (2012), European mineral statistics 2006-10. a product of the world mineral statistics database., Technical report, Britsh Geological Survey.

Brunetti, C. & Gilbert, C. (1995), 'Metals price volatility, 1972-95', *Resource Policy* **21**, 237 – 254.

Brunner, P. & Rechberger, H. (2004), *Practical Handbook of Material Flow Analysis*, Lewis Publishers, Boca Raton.

Butterman, W. & Carlin, J. (2004), Antimony. mineral commodity profiles, Technical report, U.S. Geological Survey.
URL: *http://pubs.usgs.gov/of/2003/of03-019/of03-019.pdf*

CFE (2013), 'Comisión federal de electricidad'.
URL: *www.cfe.gob.mx*

Chapman, P. & Roberts, F. (1983), *Metal Resources and Energy*, Butterworths.

Chen, M. (2010), 'Understanding world metals prices – returns, volatility and diversification', *Resource Policy* **35**, 127 – 140.

Classen, M., Althaus, H.-J., Blaser, S., Scharnhorts, W., Tuchschmid, M., Jungbluthm, N. & Faist, E. (2007), Life cycle invventories of metals. final report ecoinvent data v2.0., Technical report, Swiss Centre for Life Cycle Inventories.

Cleveland, C. & Ruth, M. (1997), 'When, where, and by how much do biophysical limits constrain the economic process? a survey of nicholas georgescu-roegen's contribution to ecological economics', *Ecological Economics* **22**, 203–223.

Cornelissen, R. L. & Hirs, G. G. (2002), ‘The value of the exergetic life cycle assessment besides the lca’, *Energy Conversion and Management* **43**, 1417–1424.

Costa, M., Schaeffer, R. & Worell, E. (2001), ‘Exergy accounting of energy and materials flows in steel production systems’, *Energy* **26**, 363–384.

Cox, D. & Singer, D. (1992), Mineral deposit models, Technical report, US Geological Survey.
URL: *http://pubs.usgs.gov/bul/b1693/*

Cunningham, L. D. (2000), Beryllium recycling in the united states in 2000, Technical report, U.S. Geological Survey.
URL: *http://pubs.usgs.gov/circ/c1196p/c1196p.pdf*

De Andrade, L. (2007), ‘Dynamic simulation of the carbon-in-pulp and carbon-in-leach processes’, *Brazilian Journal of Chemical Engineering* **24**, 623–635.
URL: *http://www.scielo.br/scielo.php*

Dewulf, J. & Van Langenhove, H. (2002), ‘Assessment of the sustainability of technology by means of a thermodynamically based life cycle analysis’, *ESPR Environ Sci & Pollut Res* **9**, 267–273.

Dewulf, J. & Van Langenhove, H. (2005), ‘Integrating industrial ecology principles into a set of environmental sustainability indicators for technology assessment’, *Resources, Conservation and Recycling* **43**, 419–432.

Dincer, I. (2002), ‘The role of exergy in energy policy making’, *Energy Policy* **30**, 137–149.

DOE (2007), U.s. energy requirements for aluminum production. historical perspective, theoretical limits and current practices, Technical report, U.S. Department of Energy.

Domínguez, A. & Valero, A. (2013), ‘Global gold mining: Is technological learning overcoming the declining in ore grades?’, *Journal of Environmental Accounting and Management* **1**, 85–101.

Domínguez, A., Valero, A. & Valero, A. (2013), ‘Exergy accounting applied to metallurgical systems: The case of nickel processing’, *Energy* pp. 1–9 1–9.

Dooley, G. & Lenihan, H. (2005), ‘An assessment of time series methods in metal price forecasting’, *Resource Policy* **30**, 208 – 217.

Dove, W. & Boustead, I. (1998), The effect of sulphur on primary zinc ecoprofile calculations, *in* ‘The 3rd International conference on EcoBalance, progress in LCA for a sustainable society’, pp. 413 – 416.
URL: *http://www.boustead-consulting.co.uk/download/tsukub98.pdf*

Durucan, S., Korre, A. & Munoz-Melendez, G. (2006), ‘Mining life cycle modelling: a cradle-to-gate approach to environmental management in the minerals industry’, *Journal of Cleaner Production* **14**, 1057–1070.

Dutta, M. & Mukherjee, S. (2010), ‘An outlook into energy consumption in large scale industries in india: The cases of steel, aluminium and cement’, *Energy Policy* **38**, 7286–7298.

EAA (2006), Sustainability of the european aluminium industry 2006, Technical report, European Aluminium Association.
URL: *http://www.eaa.net/upl/4/default/doc/SDI*$_brochure_nov06.pdf$

Eckelman, M. J. (2010), 'Facility-level energy and greenhouse gas life-cycle assessment of the global nickel industry', *Resources, Conservation and Recycling* **54**, 256–266.

EPA (2003), Tool for the reduction and assessment of chemical and other environmental impacts (traci): User's guide and system documentation, Technical report, National Risk Management Research Laboratory. US Environmental Protection Agency.

Espí, J. A. (2009), Recursos geológicos para el siglo xxi. the present of metals.

Faber, M. (1984), 'A byophysical approach to the economy entroypy, environment, and resources.', *Energy and time in economic and physical science* pp. 315–317.

Figuerola, I. & Gilbert, C. (2001), 'Price variability and marketing method in non-ferrous metals: Slade's analysis revisited', *Resource Policy* **27**, 169 – 177.

Finnveden, G. & Ostland, P. (1997), 'Exergies of natural resources in life-cycle assessment and other applications.', *Energy* **22**(9), 923–931.

Georgescu-Roegen, N. (1971), *The Entropy Law and the Economic Process*, Harvard University Press, Cambridge Massachussets, London England.

Ghosh, A. & Hem, R. (1984), *Principles of Extractive Metallurgy*, New Age International.

Giurco, D. & Cooper, C. (2012), 'Mining and sustainability: asking the right questions', *Minerals Engineering* **29**, 3–12.

Giurco, D., Prior, T., Mudd, G., Mason, L. & Behrisch, J. (2010), Peak minerals in australia: A review of changing impacts and benefits, Technical report, Institute for Sustainable Futures University of Technology, Sydney and Department of Civil Engineering Monash University.

Glaister, B. J. & Mudd, G. M. (2010), 'The environmental costs of platinum – pgm mining and sustainability: Is the glass half-full or half-empty?', *Minerals Engineering* **23**, 438–450.

Gleich, B., Achzet, B., Mayer, H. & Rathgeber, A. (2013), 'An empirical approach to determine specific weights of driving factors for the price of commodities - a contribution to the measurement of the economic scarcity of minerals and metals.', *Resources Policy* **38**, 350–362.

Global Infomine (2013).
URL: *http://www.infomine.com/minesite/*

Goldcorp (2013).
URL: *http://www.goldcorp.com*

Gold Fields (2013).
URL: *http://www.goldfields.co.za/*

Gold mining in Tanzania (2013).
URL: *http://www.tanzaniagold.com/*

Gordon, R., Bertram, M. & Graedel, T. (2007), 'On the sustainability of metal supplies: A response to tilton and lagos', *Resources Policy* **32**, 24–28.

Gordon, R. L. & Tilton, J. E. (2008), 'Mineral economics: Overview of a discipline', *Resources Policy* **33**, 4–11.

Graedel, T., Dubreuil, A., Gerst, M., Hashimoto, S., Moriguchi, Y., Muller, D., Pena, C., Rauch, J., Sinkala, T. & Sonnemann, G. (2010), Metal Stocks in Society-Scientific Synthesis, A Report of the Working Group on the Global Metal Flows, UNEP. Accessed Jan. 2013.
URL: *http://www.unep.org/publications/*

Gupta, C. K. & Mukherjee, T. K. (1990), 'Hydrometallurgy in extraction processes', *CRC Press* **1**, 74–75.

Hagedorn, G. & Hellriegel, E. (1992), Umweltrelevante masseneintrgen bei der herstellung verschiedener solarzellentypen, Endbericht-teil i: Konventionelle verfahren, Forschungsstelle fr Energiewirtschaft, Munchen.

Hansen, D. R., Mowen, M. M. & Guan, L. (2009), *Cost Management: Accounting and Control*, South Western, CENGAGE Learning.

Harmony (2013).
URL: *http://www.harmony.co.za/*

Harmsen, J., Roes, A. & Patel, M. (2013), 'The impact of copper scarcity on the efficiency of 2050 global renewable energy scenarios', *Energy* pp. 1–12.

Harper, E., Kavlak, G. & Graedel, T. (2012), 'Tracking the metal of the goblins: Cobalt's cycle of use', *Environmental Science and Technology* **46**, 1079–1086.

Hein, J., Mizell, K., Koschinsky, A. & Conrad, T. (2013), 'Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: Comparison with land-based resources', *Ore Geology Reviews* **51**, 1–14.

Humphreys, D. (2013), 'New mercantilism: A perspective on how politics is shaping world metal supply', *Resource Policy* **38**, 341 – 349.

IamGold Corporation (2013).
URL: *http://www.iamgold.com/English/Operations/default.aspx*

IPPC (2009*a*), Draft reference document on best available techniques for the non-ferrous metals industries, Technical report, European Comission, Integrated Pollution Prevention and Control.
URL: *http://ftp.jrc.es/pub/eippcb/doc/nfm_2d_07–2009_public.pdf*

IPPC (2009*b*), Draft reference document on best available techniques on the production of iron and steel, Technical report, European Comission, Integrated Pollution Prevention and Control.
URL: *http://ftp.jrc.es/pub/eippcb/doc/isp_d2_0709.pdf*

ITP (2002), Energy and environmental profile of the u.s. mining industry chapter 9 - limestone and crushed rock, Technical report, U.S. Department of Energy. Energy, Efficiency and Renewable Energy.
URL: *http://www1.eere.energy.gov/industry/mining/pdfs/stone.pdf*

Jaber, M. Y. & Guiffrida, A. L. (2008), 'Learning curves for imperfect production processes with reworks and process restoration interruptions', *European Journal of Operational Research* **189**, 93–104.

Jamasb, T. & Kohler, J. (2007), Learning curves for energy technology and policy analysis: A critical assessment, *in* 'Cambridge Working Papers in Economics'.

Jolliet, O., Brent, A., Goedkoop, M., Itsubo, N., Mueller-Wenk, R., Peña, C., Schenk, R., Stewart, M. & Weidema, B. (2003), Final report of the life cycle impact assessment definition study, Technical report, Life Cycle Impact Assessment Programme of the Life Cycle Initiative.

Kahouli-Brahmi, S. (2008), 'Technological learning in energy – environment – economy modelling: A survey', *Energy Policy* **36**, 138–162.

Kameyama, H., Yoshida, K., Yamauchi, S. & Fueki, K. (1982), 'Evaluation of reference exergy for the elements', *Applied Energy* **11**, 69–83.

Kellogg, H. H. (1977), 'Sizing up the energy requeriments for producing primary metals', *Enginnering and Mining Journal* **178**, 61–65.

Kelly, T. & Matos, G. (2011), Historical statistics for mineral and material commodities in the united states., Technical report, USGS, U.S. Geological Survey.
URL: *http://minerals.usgs.gov/ds/2005/140/*

Kennecott Utah Copper Corporation (2004).

Kennecott Utah Copper Corporation (2006).

Kihlstedt, P. G. (1975), 'Energy and mineral exploitation techniques', *Scandinavian Journal of Metallurgy* **4**, 145–149.

Kinross (2013).
URL: *http://www.kinross.com/*

Koltun, P. & Tharumarajah, A. (2008), Life cycle assessment study of rare earth metals for magnesium alloy applications, Technical report, CSIRO.

Kriechbaumer, T., Angus, A., Parsons, D. & Rivas, M. (2014), 'An improved wavelet – arima approach for forecasting metal prices.', *Resources Policy* **39**, 32–41.

Kumah, A. (2006), 'Sustainability and gold mining in the developing world', *Journal of Cleaner Production* **14**, 315–323.

Labys, W., Achouch, A. & Terraza, M. (1999), 'Metal prices and the business cycle.', *Resources Policy* **25**, 229–238.

Lee, C. (1998), 'Formulation of resource depletion index', *Resources, Conservation and Recycling* **24**, 285–298.

Li, G. & Rajagopalan, S. (1997), 'The impact of quality on learning', *Journal of Operations Management* **15**, 181–191.

Lozano, M. & Valero, A. (1993), 'Theory of exergetic cost', *Energy* **18**, 939–960.

Mäkinen, T. & Taskinen, P. (2008), 'State of the art in nickel smelting: direct outokumpu nickel technology.', *Mineral Processing and Extractive Metallurgy* **117**, 86–94.

Margolis, N. (1997), Energy and environmental profile of the u.s. aluminum industry, Technical report, U. S. Department of Energy Office of Industrial Technologies.
URL: *http://www1.eere.energy.gov/manufacturing/resources/aluminum/pdfs/aluminum.pdf*

Martin, W. & Skinner, K. (1998), 'Resource taxation and sustainability: A cge model of the czech republic', *Nonrenewable Resources* **7**.

Martinez, A. (2009), Exergy costs assessment of water bodies: Physical Hydronomics, PhD thesis, Universidad de Zaragoza.

Massari, S. & Ruberti, M. (2013), 'Rare earth elements as critical raw materials: Focus on international markets and future strategies', *Resources Policy* **38**, 36–43.

McDonald, A. & Schrattenholzer, L. (2001), 'Learning rates for energy technologies', *Energy Policy* **29**, 255–261.

McDonough, W. & Braungart, M. (2002), *Cradle to cradle. Remaking the way we make things.*, North Point Press.

McGuire, G. (2003), Managing mine closure risks in developing communities - a case study, kelian equatorial mining, indonesia, *in* 'Mining Risk Management Conference'. Sydney, NSW.

McLellan, B., Corder, G., Giurco, D. & Ishihara, K. (2012), 'Renewable energy in the minerals industry: a review of global potential', *Journal of Cleaner Production* **32**, 32–44.

McMillan, D. & Speight, A. (2001), 'Non-ferrous metals price volatility: a component analysis', *Resource Policy* **27**, 199 – 207.

Meadows, D. H., Meadows, D. L., Randers, J. & Behrens, W. W. (1972), *The Limits to Growth*, Universe Books.

Meadows, D. H., Randers, J. & Meadows, D. L. (2004), *Limits to Growth: The 30-Year Update*, Chelsea Green Publishing Company.

Michaelis, P., Jackson, T. & Clift, R. (1998), 'Exergy analysis of the life cycle of steel', *Energy* **23**, 213–220.

Milton (1998), Porgera mine sustainable report, Technical report, PDAP, Placer Dome Asia Pacific.

Mining Technology (2013).
URL: *http://www.mining-technology.com/projects/*

Minmetals Resources Limited (2013).
URL: *http://www.mmg.com/pages/828.aspx*

Mudd, G. & Diesendorf, M. (2008), 'Sustainability of uranium mining and milling: Toward quantifying resources and eco-efficiency', *Environ. Sci. Technol.* **42**, 2624–2630.

Mudd, G. M. (2007*a*), 'An analysis of historic production trends in australian base metal mining', *Ore Geology Reviews* **32**, 227 – 261.

Mudd, G. M. (2007*b*), 'Global trends in gold mining: Towards quantifying environmental and resource sustainability?', *Resources Policy* **32**, 42–56.

Mudd, G. M. (2007*c*), 'Gold mining in australia: linking historical trends and environmental and resource sustainability', *Environmental science and policy* **10**, 629–644.

Mudd, G. M. (2010), 'Global trends and environmental issues in nickel mining: Sulfides versus laterites', *Ore Geology Reviews* **38**, 9–26.

Mudd, G., Weng, Z., Jowitt, S., Turnbull, I. & Graedel, T. (2013), 'Quantifying the recoverable resources of by-product metals: The case of cobalt', *Ore Geology Reviews* **55**, 87–98.

Murthy, R., Tripathy, S. K. & Kumar, R. (2011), 'Chrome ore beneficiation challenges & opportunities – a review', *Minerals Engineering* **24**, 375–380.

Nappi, C. & Poulin, R. (1998), 'Sustainable development and mine management', *Nonrenewable Resources* **7**, 4.

Naredo, J. (1987), *La economía en evolución. Historia y perspectivas de características básicas del pensamiento económico.*, Ediciones Siglo XXI, Madrid.

Naredo, J. M. & Valero, A. (1998), *Desarrollo económico y deterioro ecológico (Economic development and ecological deterioration)*, Fundación Argentaria.

Newgold (2013).
URL: *http://newgold.com/*

NGU (2008), Mineral resources in norway 2008. production data and annual report, Technical report, Geological Survey of Norway.

Norgate, T. & Haque, N. (2010), 'Energy and greenhouse gas impacts of mining and mineral processing operations', *Cleaner Production* **18**, 266 – 274.

Norgate, T. & Jahanshahi, S. (2010), 'Low grade ores - smelt, leach or concentrate?', *Minerals Enginnering* **23**, 65 – 73.

Norgate, T. & Jahanshahi, S. (2011), 'Assessing the energy and greenhouse gas footprints of nickel laterite processing', *Minerals Engineering* **24**, 698 – 707.

Norgate, T., Jahanshahi, S. & Rankin, W. (2007), 'Assessing the environmental impact of metal production processes', *Journal of Cleaner Production* **15**, 838 – 848.

Ostrovski, O. & Zhang, G. (2005), 'Energy and exergy analyses of direct ironsmelting processes', *Energy* **30**, 2772–2783.

Page, N. J. & Creasey, S. (1975), 'Ore grade, metal production, and energy', *Research of the U.S. Geological Survey* **3**, 9–13.

Piekarczyk, W., Czarnowska, L. & Ptasiski, K.and Stanek, W. (2012), Thermodynamic evaluation of biomass – to – biofuels production systems., *in* '3rd International Conference CPOTE (Contemporary Problems of Thermal Engineering)'.

Primero Mining (2013).
URL: *http://www.primeromining.com/Operations/San-Dimas-Mine/default.aspx*

Prior, T., Giurco, D., Mudd, G., Mason, L. & Behrisch, J. (2012), 'Resource depletion, peak minerals and the implications for sustainable resource management', *Global Environmental Change* **22**, 577 – 587.

PWC (2012), Financial reporting in the mining industry. international financial reporting standards, Technical report, PricewaterhouseCoopers LLP.
URL: *www.pwc.com*

RandGold Resources (2013).
URL: *http://www.randgoldresources.com/randgold/content/en/2009/randgold-home*

Ranz, L. (1999), Análisis de los costes exergéticos de la riqueza mineral terrestre. Su aplicación para la gestión de la sostenibilidad, PhD thesis, Universidad de Zaragoza.

Roberts, M. (2009), 'Duration and characteristics of metal price cycles', *Resource Policy* **34**, 87 – 102.

Rosen, M. (2002), 'Can exergy help us understand and address environmental concerns?', *Exergy* **2**, 214–217.

Rosen, M. A. & Dincer, I. (2001), 'Exergy as the confluence of energy, environment and sustainable development', *Exergy Int. J.* **1**, 3–13.

Rosen, M. A., Dincer, I. & Kanoglu, M. (2008), 'Role of exergy in increasing efficiency and sustainability and reducing environmental impact', *Energy Policy* **36**, 128 – 137.

Rosenqvist, T. (1983), *Principles of Extractive Metallurgy*, McGraw-Hill.

Ruth, M. (1993), *Integrating Economics, Ecology and Thermodynamics*, The Netherlands, Kluwer Academic Publishers.

Ruth, M. (1995*a*), 'Information, order and knowledge in economic and ecological systems: implications for material and energy use', *Ecological Economics* **13**, 99–114.

Ruth, M. (1995*b*), 'Thermodynamic constraints on optimal depletion of copper and aluminum in the united states: a dynamic model of substitution and technical change', *Ecological Economics* **15**, 197–213.

Ruth, M. (1995*c*), 'Thermodynamic constraints on optimal depletion of copper and aluminum in the united states: a dynamic model of substitution and technical change', *Ecological Economics* **15**, 197–213.

Sagar, A. & Frosch, R. (1997), 'A perspective on industrial ecology and its appkation to a metals-industry ecosystem', *Journal of Cleaner Production* **5**, 39–45.

Santos, T. M. & Zaratan, M. L. (1997), 'Mineral resources accounting: a technique for monitoring the philippine mining industry sustainable development', *Journal of Anon Earth Sciences* **15**, 155–160.

Schoots, K., Ferioli, F., Kramer, G. & Van der Zwaan, B. (2008), 'Learning curves for hydrogen production technology: An assessment of observed cost reductions', *International Journal of Hydrogen Energy* **33**, 2630–2645.

SEPA (2012), Inspel till svensk mineralstrategi, N2012/1081/FIN NV-02433-12, The Swedish Environmental Protection Agency, Stockholm.

Shafiee, S. & Topal, E. (2010), 'An overview of global gold market and gold price forecasting shahriar shafiee a,n, erkan topal b', *Resources Policy* **35**, 178–189.

Shields, D. J. (1998), 'Sustainability for nonrenewable resources: Alternative perspectives', *Nonrenewable Resources* **7**, 4.

Skinner, B. J. (1986), *Earth resources*, Prentice-Hall, London.

Söderholm, P. & Sundqvist, T. (2007), 'Empirical challenges in the use of learning curves for assessing the economic prospects of renewable energy technologies', *Renewable Energy* **32**, 2559 – 2578.

Sohn, I. (2006), 'Long-term projections of non-fuel minerals: We were wrong, but why?', *Resources Policy* **30**, 259 – 284.

Stanek, W. (2009), *Evaluation Method of the Ecological Effects in Thermal Processes Using the Exergy Analysis (in Polish)*, Edition of the Silesian University of Technology, Gliwice.

Steen, B. A. (2006), 'Abiotic resource depletion. different perceptions of the problem with mineral deposits', *Int J LCA* **1**, 49–54.

Stewart, M. & Weidema, B. (2005), 'A consistent framework for assessing the impacts from resource use. a focus on resource functionality', *Int J LCA* **10(4)**, 240–247.

Strauss, K., Brent, A. C. & Hietkamp, S. (2006), 'Characterisation and normalisation factors for life cycle impact assessment mined abiotic resources categories in south africa', *Int J LCA* **3**, 162–171.

Suppen, N., Carranza, M., Huerta, M. & Hernandez, M. (2006), 'Environmental management and life cycle approaches in the mexican mining industry', *Journal of Cleaner Production* **14**, 1101–1115.

Svedberg, P. & Tilton, J. E. (2006), 'The real, real price of nonrenewable resources: Copper 1870 – 2000', *World Development* **34**, 501–519.

Szargut, J. (1986), 'Application of exergy for the calculation of ecological cost?', *Bull. Polish Acad. Techn. Sciences* **7-8**.

Szargut, J. (1989), 'Chemical exergies of the elements', *Applied Energy* **32**, 269–286.

Szargut, J. (2005), *Exergy method: technical and ecological applications.*, Southampton, Boston: WIT Press.

Szargut, J. (2008), 'Influence of the pro-ecological tax on the market prices of fuels and electricity', *Energy* **33**, 137 – 143.

Szargut, J., ed. (1993), *Exergy, Ecology and Democracy - Concepts of a Vital Society or A Proposal for An Exergy Tax*, International Conference on Energy Systems and Ecology - ENSEC. Krakow, Poland.

Szargut, J. & Morris, D. (1987), 'Cumulative exergy consumption and cumulative degree of perfection of chemical processes', *Int. J. Energy Res.* **11**, 245–261.

Szargut, J., Morris, D. & Steward, F. (1988*a*), *Exergy analysis of thermal, chemical, and metallurgical processes*, Hemisphere Publishing Corporation.

Szargut, J., Morris, D. & Steward, F. (1988*b*), *Exergy analysis of thermal, chemical, and metallurgical processes*, Hemisphere Publishing Corporation.

Szargut, J. & Stanek, W. (2012), 'Fuel part and mineral part of the thermoecological cost.', *International Journal of Thermodynamics* **15**, 187–19.

Szargut, J., Ziebik, A. & Stanek, W. (2002), 'Depletion of the non-renewable natural exergy resources as a measure of the ecological cost', *Energy Conversion and Management* **43**, 9–12.

Tilton, J. (1996), 'Exhaustible resources and sustainable development', *Resource Policy* **22**, 91–97.

Tilton, J. E. (2001), Depletion and the long-run availability of mineral commodities, Technical Report 14, International Institute for Environment and Development.

Tilton, J. E. (2003), *On borrowed time? Assessing the threat of mineral depletion*, Resources for the Future Press.

Tilton, J. E. (2010), 'Is mineral depletion a threat to sustainable mining?', *The Society of Economic Geologists Newsletter* **82**.

Tilton, J. E. & Lagos, G. (2007), 'Assessing the long-run availability of copper', *Resources Policy* **32**, 19–23.

Torres, C. (1991), Symbolic exergoeconomis : methodology for thermoeconomic analysis of energy sys, PhD thesis, University of Zaragoza.

U. S. Geological Survey (USGS).
URL: *http://www.usgs.gov*

USGS (2011*a*), Mineral commodities summaries, Technical report, U.S. Geological Survey.
URL: *http://minerals.usgs.gov/minerals/pubs/mcs/2011/mcs2011.pdf*

USGS (2011*b*), Minerals yearbook gold, Technical report, U.S. Geological Survey.
URL: *http://minerals.usgs.gov/minerals/pubs/commodity/gold/myb1-2011-gold.pdf*

Valero, A. (1998), Thermoeconomics as a conceptual basis for energy-ecological analysis, *in* S. Ulgiati, ed., 'Advances in Energy Studies. Energy Flows in Ecology and Economy', Musis, Roma, pp. 415–444.

Valero, A., Agudelo, A. & Valero, A. (2010), 'The crepuscular planet. a model for the exhausted atmosphere and hydrosphere', *Energy* pp. 1–9.

Valero, A. & Lozano, M. (1994), *Curso de Termoeconomía*, Universidad de Zaragoza.

Valero, A., Lozano, M. & Munoz, M. (1986), A general theory of exergy saving. i. on the exergetic cost, *in* R. Gaggioli, ed., 'Computer-Aided Engineering and Energy Systems. Second Law Analysis and Modelling', Vol. 3, pp. 1–8.

Valero, A., Martínez, A. & Botero, E. (2003), 'La sostenibilidad ambiental a escala planetaria. el coste físico de reposición del "capital mineral" de la tierra', *Economía Industrial* **352**, 77–93.

Valero, A. & Torres, C. (2004), 'Thermoeconomic analysis', *Exergy, energy system analysis and optimization. UNESCO - EOLSS* .

Valero, A., Uson, S., Torres, C. & Valero, A. (2010), 'Application of thermoeconomics to industrial ecology', *Entropy* **12**, 591–612.

Valero, A. & Valero, A. (2010*a*), 'Exergoecology: A thermodynamic approach for accounting the earth's mineral capital. the case of bauxite – aluminium and limestone – lime chains', *Energy* **35**, 229–238.

Valero, A. & Valero, A. (2010*b*), 'Physical geonomics: Combining the exergy and hubbert peak analysis for predicting mineral resources depletion', *Resources, Conservation and Recycling* .

Valero, A. & Valero, A. (2011), 'A prediction of the exergy loss of the world's mineral reserves in the 21st century', *Energy* **36**, 1848 – 1854.

Valero, A. & Valero, A. (2012), 'From grave to cradle. a thermodynamic approach for accounting for abiotic resource depletion', *Journal of Industrial Ecology* **17**.

Valero, A., Valero, A. & Arauzo, I. (2008), 'Evolution of the decrease in mineral exergy throughout the 20th century. the case of copper in the us', *Energy* **33**(2), 107–115.

Valero, A., Valero, A. & Domínguez, A. (2011), Influence of technical development and declining ore grades on the availability of gold resources, *in* 'SDEWES Proceedings of the 6th Dubrovnik Conference on Sustainable Development of Energy, Water and Environment Systems'.

Valero, A., Valero, A. & Domínguez, A. (2013), 'Exergy replacement cost of mineral resources', *Journal of Environmental Accounting and Management* **1**, 147–158.

Valero, A., Valero, A. & Gomez, J. (2011), 'The crepuscular planet. a model for the exhausted continental crust', *Energy* **36**, 694–707.

Valero, A., Valero, A. & Martínez, A. (2010), 'Inventory of the exergy resources on earth including its mineral capital', *Energy* **35**, 989–995.

Valero, A. & Valero D., A. (2012), 'Exergy of comminution and the thanatia earth's model', *Energy* **44**, 1085–1093.

Valero, A. & Valero D., A. (2014), *Thanatia. The destinity of the Earth's mineral resources. A thermodynamic Cradle-to-Cradle Assessment*, World Scientific.

Valero Delgado, A. (2008), Exergy evolution of the mineral capital on earth, PhD thesis.

Verhoef, E., Reuter, M. & Dijkema, G. (2004), 'Process knowledge, system dynamics and metal ecology', *Journal of Industrial Ecology* **8**, 23 – 43.

WCED (1987), Our common future, Technical report, World Commission on Environment and Development.
URL: *http://www.un-documents.net/our-common-future.pdf*

Weatherstone, N. (2008), International standards for reporting of mineral resources and reserves - status, outlook and important issues, *in* 'World Mining Congress & Expo'.

Weidema, B. P. (2000), Can resource depletion be omitted from environmental impact assessments?, *in* 'Poster presented to the 3rd SETAC World Congress, , Brighton.'.

Weiss, M., Junginger, M., Patel, M. K. & Blok, K. (2010), 'A review of experience curve analyses for energy demand technologies', *Technological Forecasting & Social Change* **77**, 411–428.

Wellmer, F. & Becker-Platen, J. D. (2002), 'Sustainable development and the exploitation of mineral and energy resources: a review', *Int J Earth Sci* **91**, 723–745.

West, J. (2011), 'Decreasing metal ore grades. are they really being drivn by the depletion of high grade deposits?', *Journal of Industraial Ecology* **15**, 165–168.

Willett, K. (2002), Managing australian mineral wealth for sustainble economic development, Technical report, International Institute for Environment and Development.

Wils, B. A. (2006), *Mineral Processing Technology*, Elsevier Ltd.

Worrall, R., Neil, D., Brereton, D. & Mulligan, D. (2009), 'Towards a sustainability criteria and indicators framework for legacy mine land', *Journal of Cleaner Production* **17**, 1426 – 1434.

Xiao, X., Songwen, X., Xueyi, G., Kelong, H. & Ryoichi, Y. (2003), 'Lca case study of zinc hydro and pyro-metallurgical process in china', *International Journal of Life Cycle Assessment* pp. 1–5.

Yaksic, A. andTilton, J. (2009), 'Using the cumulative availability curve to assess the threat of depletion: The case of lithium', *Resources Policy* **34**.

Yelle, L. E. (1979), 'The learning curve: historical review and comprehensive survey', *University of Lowell* **10**, 302–328.

Yellishetty, M., Mudd, G. M. & Ranjith, P. (2011), 'The steel industry, abiotic resource depletion and life cycle assessment: a real or perceived issue?', *Journal of Cleaner Production* **19**, 78 – 90.

Yellishetty, M., Ranjith, P. G., Tharumarajah, A. & Bhosale, S. (2009), 'Life cycle assessment in the minerals and metals sector: a critical review of selected issues and challenges', *Int J LCA* **14**, 257–267.

Yoshiki, K. & Toguri, J. (1993), 'Metals production, energy, and the environment, part i: Energy consumption', *JOM : Journal of the Minerals, Metals and Materials Society* **5**, 15–20.

Zaleta, A., Ranz, L. & Valero, A. (1998), 'Towards a unified measure of renewable resources availability: the exergy method applied to the water of a river', *Energy Conversion and Management* **39**(16-18), 1911–1917.