

EVOLUTION OF THE DECREASE IN MINERAL EXERGY THROUGHOUT THE 20TH CENTURY. 1) THE CASE OF COPPER IN THE US

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ABSTRACT

The aim of this paper is to prove the usefulness of exergy as an indicator for assessing the degradation of mineral resources on earth and measuring scarcity. The exergy analysis includes in one indicator the three features that describe any natural resource: quantity, composition and a particular concentration. Furthermore, through the exergy costs we can additionally take into account the state of technology for obtaining the particular resource. Both indicators have also the advantage that are not subject to monetary policies or current speculation such as the economic assessment. The methodology for measuring the exergy and exergy costs of mineral resources is shown and the exergy decrease of US copper mines due to copper production throughout the 20th century is obtained as an example.

Keywords: Natural resources, Minerals, Chemical Exergy, Concentration Exergy, Exergy costs, Copper production, Exergy degradation.

NOMENCLATURE

b	standard exergy (kJ/kmol)
b_{che}	standard chemical exergy of the elements that compose the substance (kJ/kmol)
ΔG	formation Gibbs energy (kJ/kmol)
e_c	real energy required for mining and concentrating a mineral from the mine
k	unit exergy cost (dimensionless)
n_e	amount of kmol of element e
R	gas constant (8,314 kJ/kmol K)
T_0	standard ambient temperature (298,15 K)
x_c	molar average concentration of a substance in the earth crust
x_i	molar concentration of substance i
x_m	molar average concentration of a substance in the mine
<i>Subscripts</i>	
c	concentration component
ch	chemical component

t total: sum of the chemistry and concentration components

Superscripts

* real, non reversible

INTRODUCTION

The great economic growth experienced throughout the 20th century by many countries is mainly supported by the increasing extraction of natural resources, favored by technological innovation.

As Meadows et al. analyze ([1] and [2]), the current exponential growth cannot longer be supported as natural goods become depleted. Some authors such as Barnett and Morse [3] or Scott and Pearse [4] appealed to the role of technological progress in improving the efficiency of extractive processes and redefining available resources. They stated that there is no evidence for the hypothesis that natural resources will lead to reduction of economic growth. On the contrary, Costanza and Daly [5], Ayres and Nair [6], Cleveland and Ruth [7], etc., believe that

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technology will not overcome resource scarcity and environmental degradation, since human capital ultimately is derived from and sustained by energy, materials and ecological services. Additionally, the argument that resource scarcity will be offset by resource substitution might be valid in the short term, but will fail in the long term when there is equal resource scarcity on all the substitutable materials [8].

One of the keys to stop or at least to slow down the possible collapse that Meadows et al. forecast, is to listen to the signals that the earth is sending out and act immediately according to them. Hence, information is the key factor for transformation to sustainability. The true intertemporal scarcity of environmental goods must be analyzed and appropriate indicators for the scarcity of these goods must be found [9].

Measuring scarcity by means of monetary costs, is not very effective, as discussed next. Even though non renewable resources are becoming more and more scarce, prices have not followed the same trend. According to Hotelling [10], prices should raise with scarcity, since low cost resources normally would be used first and quantities of extraction normally would decrease over time. On the contrary, historical statistics show that costs of extraction and prices have mostly decreased over time [11]. This apparent contradiction is due to technical innovation but also to the lack of information about scarcity. Reynolds [12] states that true scarcity is only revealed through prices towards the end of exhaustion. Until now, natural capital has been treated as a free good, but nowadays it is becoming the limiting factor in development [5].

Another way for measuring scarcity and natural resources depletion is by means of the second law of thermodynamics. Other authors have already studied and showed up the connection between economic scarcity and the entropy law [13], [14].

A rather new discipline called "Exergoecology" [15] is starting to be considered as a future rigorous tool for natural resources accounting. Exergoecology is the application of the exergy analysis in the evaluation of natural fluxes and resources on earth. The consumption of natural resources implies destruction of organized systems and pollution dispersion, which is in fact generation of entropy or exergy destruction. This is why the exergy analysis can describe perfectly the degradation of natural capital.

Besides, exergy quantifies the physical features that make a resource valuable: a particular composition which differentiates it from the surrounding environment, and a distribution which places it in a specific concentration [16], [17]. Unlike standard economic valuations, the exergy analysis gives objective information since it is not subject to monetary policy, or currency speculation. Furthermore, all natural resources can be assessed in terms of exergy and can be summed up. This is not the case if the evaluation is made in terms of mass: we can not add tonnes of oil with tonnes of sillimanite, for instance.

THE EXERGY OF MINERALS

A natural resource can be defined as any form of matter or energy obtained from the environment that meets human needs. Therefore water, air, oil, biomass or minerals are classified as natural resources. This study will deal only with a part of the earth's natural capital: the mineral resources. However a similar analysis could be performed for the exergy evaluation of other resources or even for the sum of them.

The thermodynamic value of a natural resource could be defined as the minimum work necessary to produce it with a specific structure and concentration from common materials in the environment. This minimum amount of work is theoretical by definition and is equal to the material's exergy. The exergy of a system gives an idea of its evolution potential for not being in thermodynamic equilibrium with the environment, or what is the same, for not being in a dead state related to the Reference Environment (R.E.). This R.E. can be assimilated to a thermodynamically dead planet where all materials have reacted, dispersed and mixed.

The physical features that make minerals valuable are mainly their specific composition and the greater concentration in the ores they are found [18]. The minimum theoretical work that nature should invest to provide minerals at a specific composition from a degraded earth is equal to the standard chemical exergy and it can be calculated by means of the exergy balance of a reversible formation reaction:

$$b_{ch} = \Delta G_f + \sum_e n_e b_{che} \quad (1)$$

On the other side, the minimum theoretical work needed to concentrate a substance from an ideal

mixture of two components is given by the following expression:

$$b_c = -RT_0 \left\{ \ln x_i + \frac{(1-x_i)}{x_i} \ln(1-x_i) \right\} \quad (2)$$

The difference between the concentration exergies obtained with the ore grade of the mine (x_m) and with the average concentration in the earth crust (x_c) is the minimum energy that nature had to spend to bring the minerals from the conditions in the reference state to the conditions in the mine. It is right this component of the mineral's exergy what makes exergy a more realistic measure of magnitude than mass, for instance [19]. Furthermore, it invalidates the statement of Brooks and Andrews [20] that running out of minerals is ridiculous because the entire planet is composed of minerals. The energy that nature saves us when concentrating minerals in high grade ores, is too high to reproduce with current technology.

Hence by means of exergy, we can integrate in just one indicator all the characteristics that describe a natural resource: composition, concentration and of course quantity, by multiplying the unitary exergies with the tonnes of the resource considered.

As explained above, exergy accounts for a minimum. However, the real processes designed by man are far from the ideal conditions for reversibility and the energy requirements to obtain a resource are always greater than those dictated by the Second Law. For this reason, we cannot evaluate natural resources solely in terms of reversible processes since this would ignore technological limits, which are much more costly for man from the physical point of view. Therefore, we must include the real physical unit costs in the thermodynamic evaluation of resources. These are defined as the relationship between the energy invested in the real process of obtaining the resource and the minimum energy required if the process were reversible. It has a dimensionless value and measures the number of exergy units needed to obtain one unit of exergy of the product. Generally, the exergy unit cost is tens or even hundreds of times greater than its exergy content. The real thermodynamic value of a resource is determined by its exergy multiplied by the real physical unit cost of the process to obtain it, as in Eq. 3.

$$b^* = b_{ch} * k_{ch} + b_c * k_c \quad (3)$$

Being k_{ch} and k_c , the unit exergy costs for obtaining the mineral from its corresponding dispersed ions in the R.E. and concentrating the mineral from the R.E. to the conditions of the mine, respectively.

Therefore, the exergy costs can account for one more feature than the exergy indicator, namely the state of technology.

THE CASE OF COPPER Copper mining features

Copper is usually found in nature in association with sulfur, as chalcopyrite ($CuFeS_2$), but can be also found as oxides. The primary ore normally has low concentrations of copper but this can be compensated by its abundance. The reserves and reserve base of copper in the US in year 2000 were 45.000 kt and 90.000 kt respectively [21].

The production of pure copper from the ore can be summarized in two processes. The first one deals with the mining and concentrating of low grade ores containing the copper mineral. The second one is fundamentally a chemical process in which the concentrated ore is smelted and refined through an electrolytic process.

The hypothetical processes for obtaining the mineral found in the mine from the reference earth can be outlined as in Fig. 1. As a first approximation, it has been assumed, that the overall copper is found in the mines as chalcopyrite.

At state 0, the earth is composed of only reference substances (R.S.) dispersed in the three subsystems of the R.E.: the lithosphere, atmosphere and hydrosphere. At state 1, the reference substances of the reference environment defined by Szargut et al. [22] composing the mineral (Cu^{+2} and SO_4^{-2} from the hydrosphere and Fe_2O_3 from the lithosphere), react to form $CuFeS_2$. Finally, at state 2, the dispersed chalcopyrite is concentrated from x_c to the ore grade of the mine x_m . The concentration of copper in the reference environment x_c is assumed to be equal to $2,5E-5$ kmol/kmol, which is the current average concentration of copper in the earth crust [23].

The unit concentration cost of copper i.e. the energy required to concentrate copper from x_c to x_m with today's technology was estimated by Valero and Botero [24] as $k_c = 385,61$. This value was obtained considering that the unit concentration cost for the real process of mining and concentrating is

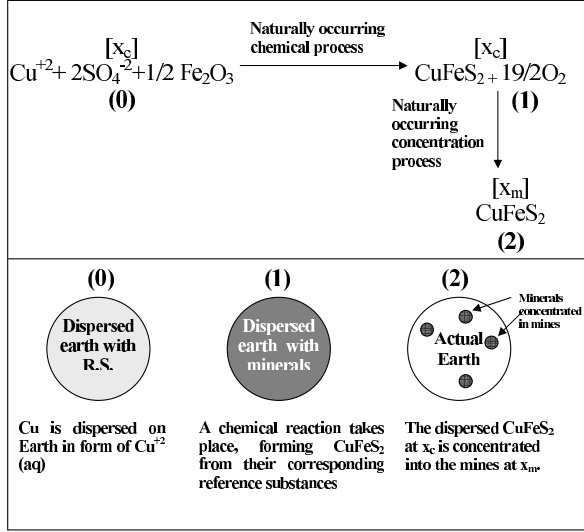


Figure 1: HYPOTHETICAL PROCESSES INVOLVED IN OBTAINING THE MINERAL OF COPPER FROM THE REFERENCE ENVIRONMENT

the same as in the hypothetical process of concentration between the R.E. and the mine conditions. The energy requirement for mining and concentrating considered (e_c) was the one obtained by Chapman and Roberts [8]: 66,7 GJ/ton for an ore grade of 0,5%. The rate between the real energy required and the minimum exergy to concentrate the mineral from the earth crust to the ore grade of the mine gives the unit exergy cost mentioned before. The result obtained means that with current technology, we have to invest 385,61 times more energy for concentrating copper from the R.E. to the mine than in the reversible process. This indicates how far is our technology from reversibility.

The real quantity of energy required for “refining” the mineral between the earth’s crust (as in the Reference Environment) and the conditions in the mine is also usually greater than the standard chemical exergy given by Eq. 1. Valero and Botero estimated the unit chemical exergy costs of sulfides as being at least $k_{ch} = 10$. In this case, the chemical unit cost of refining a mineral from the mine to the commercial state cannot be applied to the process of refining the mineral from the R.E. to the mine, due to the differences of both processes. However, once the refining costs of mineral oxides and sulfides were analyzed, the authors realized that in average, the energy ex-

Table 1: UNIT EXERGY COSTS OF SELECTED MINERALS. After Valero and Botero [24]. * Values in ppm if not specified otherwise

Elem.	Min.	x_c^*	x_m %	e_c GJ/ton	b_c GJ/ton	k_c	$k_{ch} \geq$
Al	Al_2O_3	8%	17	50	0,126	395,7	1
Ag	Ag_2S	0,05	0,01	1582	0,224	7046,5	10
Au	Au	0,0018	0,0015	62245	0,152	408,7	1
Cu	CuFeS	25	0,5	66,7	0,172	385,6	10
Fe	Fe_2O_3	3,5%	50	1	0,022	44,0	1
Hg	HgS	0,08	0,1	157	0,091	1706,9	10
Pb	PbS	20	4	9,5	0,044	212,1	10
Sn	SnO_2	5,5	0,4	187	0,125	1493,0	1
Ti	FeTiO_3	0,3%	10	23	0,066	348,4	1
Zn	ZnS	71,0	3,5	8,1	0,128	62,8	10

penditure for obtaining a ton of the pure element from the oxide was about 80 GJ greater than from the sulfide. This is as if sulfides would have a natural bonus of 80 GJ/ton and a chemical unit exergy cost k_{ch} of 10 in average. On the other side, oxides and monatomic minerals are assumed to have a k_{ch} at least equal to one. Table 1 shows the unit exergy costs of selected minerals.

The exergy decrease of copper mines

Before explaining the exergy decrease of copper mines, it must be pointed out that extraction does not necessarily mean that the inherent exergy of copper is being lost. On the contrary, through the process of mining and concentrating of copper ores, we are increasing copper’s exergy per unit of resource and in fact, that exergy will remain in wires, buildings, industrial machinery and the other products where copper is used. The problem arises when the already refined copper is thrown into landfills when its applications are gone to an end. In that case, the demand of copper must be satisfied by extracting new copper from the mine, exhausting thereby the resource and reducing the exergy of the mine (the mine contains a lower quantity of mineral at a lower grade). Fortunately, thanks to recycling not so many minerals need to be extracted. Therefore, recycling is so important in our society, or in other words, impeding dispersion is vital once a material has been concentrated.

Hence, when we refer to the exergy decrease of copper mines, we are indicating the exergy that the mines are losing through mineral extraction. In practice, this exergy is only lost when copper’s life finishes in landfills or becomes dispersed.

The chemical exergy of copper mines will be calculated assuming that *Cu* is extracted only from chal-

copyrite. This approximation has to be done, since there is a lack of information about the amount of copper extracted from other minerals such as copper oxides and other copper sulfides. Hence, our first goal is to obtain the exergy of state 1 in Fig. 1. The chemical exergy of $CuFeS_2$, calculated with Eq. 1, being $\Delta G_f = -190.9$ kJ/mol and obtaining the chemical exergy of the elements from Szargut et. al [22] is: $b_{chCuFeS_2} = 1534,44$ MJ/kmol. Surprisingly, the chemical exergy of the mineral is higher than that of the pure element: $b_{chCu} = 134,25$ MJ/kmol (11,42 times greater). This is due to the fact that since stability (criterion taken partially by Szargut et al. [22] for choosing the reference substances) does not coincide with abundance in a number of cases, some minerals quite abundant in nature, such as sulfides, have a fairly high chemical exergy that can be considered as an exergy reservoir that earth provides us for free. This helps our technology to avoid huge amounts of commercial energy to be expended in the process of obtaining the corresponding pure element.

The component of the minimum chemical exergy of a substance remains constant over time, since it only depends on its chemical composition. Hence, in absolute terms, the chemical exergy consumption of any substance is proportional to its production rate.

Since the molar relation between Cu and $CuFeS_2$ is 1:1, the chemical exergy decrease of copper mines in the United States in the 20th century can be calculated by multiplying the molar copper primary production with the exergy of chalcopyrite obtained before. The production of copper in the US during the past century (see Fig. 2), was obtained from the *Historical Statistics for Mineral and Material Commodities in the United States* [25], which is a compilation of data from publications primarily of the USGS and USBM, such as the Minerals Yearbook [26].

Figure 3 shows the cumulative chemical exergy decrease of copper mines in the US.

At the end of year 2000, the total chemical exergy decrease of copper mines from the beginning of the century, was 64817,1 Mtoe. This exergy was consumed at an average rate of 641,75 Mtoe per year, although the trend since the seventies reveals an average consumption of around 890 Mtoe/year. The maximum consumption rate was attained in year 1998 (1234,5 Mtoe), while the minimum in

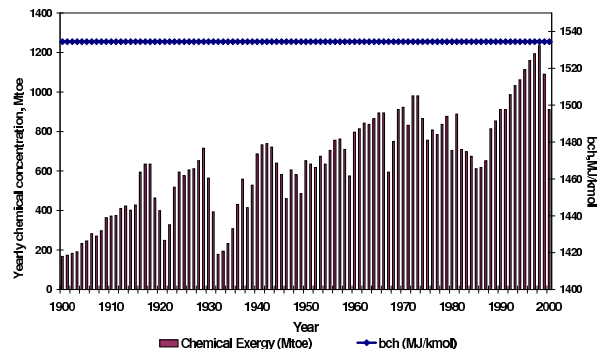


Figure 2: YEARLY CHEMICAL EXERGY CONSUMPTION IN THE U.S. OF CHALCOPYRITE DUE TO COPPER PRODUCTION THROUGHOUT THE 20th CENTURY

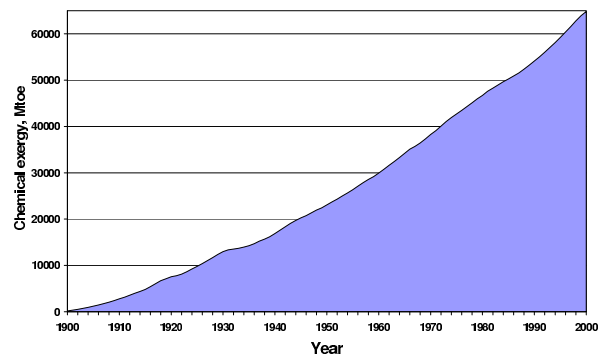


Figure 3: CUMULATIVE CHEMICAL EXERGY DECREASE OF COPPER MINES IN THE U.S. THROUGHOUT THE 20th CENTURY

year 1900 (167,87 Mtoe). Copper production has followed a continuous growth, since it is strongly linked to the electrical and telecommunication industries. The chemical exergy of copper reserves, calculated as chalcopyrite at the end of year 2000, was 25959,14 Mtoe. If we add the cumulative chemical exergy consumption to the exergy reserves at the end of year 2000, we obtain the exergy reserves at year 1900: 90776,24 Mtoe. Similarly, the chemical exergy of copper reserve base at the beginning and end of the century were 116735,38 and 51918,29 Mtoe respectively.

Next, the concentration exergy of the mine (step 3 in Fig. 1) will be calculated with Eq. 2. The concentration exergy of the mine, i.e. the minimum energy that nature had to spend to bring minerals from x_c to x_m , is not constant over time, because it changes with the ore grade of the mine (see Fig. 4). The

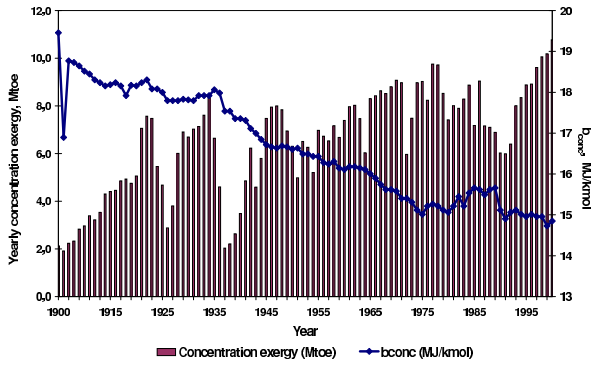


Figure 4: YEARLY CONCENTRATION EXERGY CONSUMPTION IN THE U.S. OF CHALCOPYRITE DUE TO COPPER PRODUCTION THROUGHOUT THE 20th CENTURY

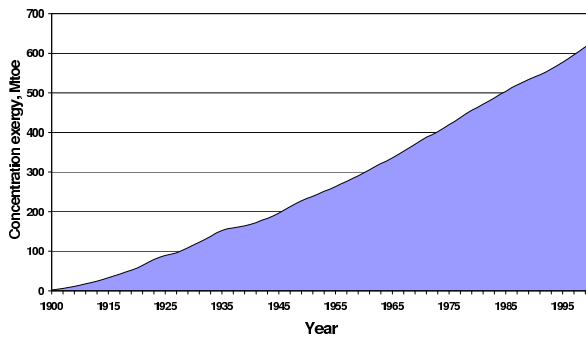


Figure 5: CUMULATIVE CONCENTRATION EXERGY DECREASE OF COPPER MINES IN THE U.S. THROUGHOUT THE 20th CENTURY

molar concentration of chalcopyrite in the mine will be approximated to that of copper (x_m). The mine has the greatest exergy concentration, when the ore grade is the maximum and becomes lower as the ore grade decreases. At the beginning of the century, when the ore grades were at above 0,02 kg of Cu per kg of ore, the concentration exergy was the highest, namely $b_{cCuFeS_2} > 18$ MJ/kmol. In the last years, the ore grades have declined to values less than 0,0045 kg/kg and hence the concentration exergy has decreased accordingly: $b_{cCuFeS_2} < 15$ MJ/kmol. Copper ore grade trends in the US are obtained from the work done by Ruth [27] and completed and updated with information from the Minerals Yearbook [26]. Figure 5 shows the cumulative concentration exergy decrease of copper mines in the US.

At the end of year 2000, the total concentration exergy decrease of copper mines from the begin-

ning of the century was 626,99 Mtoe. This exergy was consumed at an average rate of 6,53 Mtoe per year. The maximum consumption rate was attained in year 2000 (10,77 Mtoe), while the minimum in year 1906 (1,92 Mtoe). The concentration exergy of copper reserves and reserve base in year 1900 were 878,11 and 1129,22 Mtoe respectively, while in year 2000, 251,12 and 502,23 Mtoe. It is clear, that with the present ore grade trends and extraction rates, copper mine reserves will decrease rapidly.

We can now calculate the total minimum exergy decrease of copper mines in the US during the 20th century: $b_t = b_{ch} + b_c = 64817,10 + 626,99 = 65444,09$ Mtoe (41,76% of the proved oil reserves at the end of 2003: 156,7 Gt [28]). This figure gives an idea of the huge amount of energy that we are degrading by extracting minerals. It must be recalled, that this study is only done to copper mines in the US. If we were to replace with “ideal” (reversible) technologies all the mineral resources extracted in the world, there would not be enough energy sources.

As it can be seen, the exergy concentration component is much lower than the chemical one. For more abundant minerals than copper such as aluminium or iron, this fact is even more enhanced. The minimum thermodynamic energy required to separate two substances such as sugar and salt for example, is equal to the energy to mix them, which is in fact very low. In our real and rather ignorant world, this is of course not true and the exergy required to separate substances is much greater than in the reversible case. In order to overcome that problem, we need to resort to the exergy costs of the mine.

Through the unit exergy costs, reversible exergies are converted into real exergies with Eq. 3. That equation assumes that exergy costs are constant over time. In fact this is not completely correct, because there are two factors that must be taken into account. The first one is that technological development improves the efficiency of mining and refining processes and thus costs tend to decrease (theory of learning curves). The second factor is that as extraction continues and technology is being improved, lower quality resources can be extracted. However, the use of lower quality resources requires an increase in energy input, what increases costs. The value of unit exergy costs as a function of time $k(t)$ is currently being studied in more detail by the au-

Table 2: MINIMUM AND NON-REVERSIBLE EXERGY OF US COPPER MINE RESERVES AND RESERVE BASE IN YEARS 1900 AND 2000

Year	RESERVES		RESERVE BASE	
	1900	2000	1900	2000
Minimum exergy, Mtoe				
b_{ch}	90776,2	25959,1	116735,4	51918,3
b_c	878,11	251,12	1138,1	502,23
b_t	91654,31	26210,22	117864,62	52420,63
Non-reversible exergy, Mtoe				
b_{ch}^*	907762,4	259591,4	1167353,8	519182,9
b_c^*	338607,04	96832,59	435439,63	193665,18
b_t^*	1246369,44	356424,02	1602793,46	712848,05

thors of this paper.

If we convert the total minimum exergy consumption into real exergy, making the assumption that the costs are constant, we obtain that: $b_t^* = 64817,10 * 10 + 626,99 * 385,61 = 889944,61$ Mtoe. 73% of the exergy costs are due to the chemical exergy of chalcopryrite and 27% to its concentration exergy. The cost represents the exergy destroyed in US copper mines during the 20th century that will be unable to replace. The unitary exergy cost of copper was in average: 8668 toe/t of Copper extracted.

Table 2 summarizes the minimum and non-reversible exergies of US copper mines at the beginning and end of the century based on reserves and reserve base.

The numbers in table 2 indicate that in just one century, the US copper exergy reserves and reserve base have been reduced to more than one third and to more than one halve respectively.

If the extraction rate remains at near 1100 Mtoe/year, the reserves will become depleted in about 24 years (similarly, the reserve base in 48 years). It could be argued that new discoveries could arise in the future, as it happened in the past. This is certainly true, but the world is now more developed and better explored, and it is difficult to find regions worthy of intensive exploration efforts. This implies that the process of discovery may be slowing down [8]. Furthermore, Roberts and Torren's study of the production cycle of copper [29], concluded that the resource lifetime is far more sensitive to changes in the growth of demand than to extensions of reserve availability due to new discoveries.

As in the case of fossil fuels, the Hubbert peak effect could be applied for mineral resources. Note that

exergy is a much better unit of measure than mass for example for that application, since it contains not only information about quantity, but also about ore grades and composition.

From the results obtained above, it is clear the urgency of becoming aware of the problem and proposing solutions to it. Additionally, at current mineral costs, uncontrolled extraction will probably continue. In order to attain sustainable mining, the value of minerals should be corrected with a factor that accounts for resource degradation, linking thereby the physical and economic approaches. We think this factor should be associated with the exergy degradation rate by means of a discount rate. A good starting point to do so is the work done by Ruth [14], who proposed a methodology to integrate concepts from thermodynamics into economic models of optimal natural resource use and the work of Chapman and Roberts [8], who showed the plausibility that the price of a metal should account on the ore grade and the chemical features of the metal through its Gibbs free energy.

For this purpose, a great amount of information needs to be compiled: world trends of natural resources production and consumption, trends of ore grades and technological developments. Unfortunately, this data is not always available and requires a lot of effort to gather it. Statistics such as the ones from the US Geological Survey, British Petroleum and other entities or works done by other authors studying ore grades [30] and energy resources consumption trends [31], help to accomplish the work. Nevertheless, it is still insufficient. Exergy will not be able to compete against other indicators such as mass until all the required information is available. The current study aims to be the starting point of a larger research effort on the exergy degradation of natural resources, with the purpose to fill the existent knowledge gap about how mankind is destroying natural goods.

CONCLUSIONS

In many cases, the lack of information about the state of natural resources on earth is the key factor for which natural goods are being extracted in an unsustainable way. Appropriate indicators for the scarcity of these goods must be found and the novel discipline called "Exergoecology", could help to find them. The exergy indicator can be a use-

ful tool in order to account natural resources and measure their scarcity. Through exergy, we can assess the three components that describe a natural resource: quantity, chemical composition and its particular concentration. Furthermore, through the exergy costs we can take into account the state of technology for obtaining the particular resource. Hence, instead of needing three or four different inventories for each of the features of a resource, we would need just one, compiling the whole information.

As a case study, we have determined the exergy decrease of US copper mines due to copper extraction throughout the 20th century. The study assumed as a first approximation, that copper is found in the mines only as chalcopyrite. The results indicate that in reversible terms, the exergy decrease was 65444,09 Mtoe. But converting this number into real non-reversible terms with the help of the unit exergy costs, this consumption turned to be 889,9 Gtoe (an average of 8668 toe/t of copper extracted). Additionally the study showed that during the past century, the US extracted the equivalent exergy of 2,5 and 1,2 times of their current national exergy reserves and base reserve of their copper mines, respectively. Even though the analysis was only performed to copper in the US, similar numbers are expected for other substances. These results indicate the high degree of unsustainability of the mining industry.

The current study is the beginning of a broader research on the degradation of natural capital, which expects to improve the current level of knowledge about how mankind is making use of non-renewable resources. Other tasks that remain outside of this paper but that are being currently studied are: 1) application of the methodology to other mineral resources, and 2) obtaining unit exergy costs as a function of time.

REFERENCES

- [1] D. H. Meadows, D. L. Meadows, J. Randers, and W. W. Behrens. *The Limits to Growth*. Universe Books, 1972.
- [2] Donella H Meadows, Dennis L Meadows, and Jorgen Randers. *Beyond the Limits: Confronting Global Collapse, Envisioning a Sustainable Future*. Chelsea Green Publishing Company, 1993.
- [3] H.J. Barnett and C. Morse. *Scarcity and growth*. John Hopkins, Baltimore, 1963.
- [4] Anthony Scott and Peter Pearse. Natural resources in a high-tech economy. *Resources Policy*, pages 154–166, September 1992.
- [5] R Costanza and H E Daly. Natural capital and sustainable development. *Conservation Biology*, 6(1):37–46, 1992.
- [6] R. U. Ayres and I. Kneese. Thermodynamics and economics. *Physics Today*, pages 62–71, 1984.
- [7] C J Cleveland and M Ruth. When, where, and by how much do biophysical limits constrain the economic process? *Ecological Economics*, 22:203–223, 1997.
- [8] P.F. Chapman and F. Roberts. *Metal Resources and Energy*. Butterworths, United Kingdom, 1983.
- [9] M. Faber and J. L.R. Proops. *National Accounting, Time and the Environment*, pages 214–233. Columbia University Press, New York, 1991.
- [10] Harold Hotelling. The economics of exhaustible resources. *J. Polit. Econ.*, 39(2):137–175, 1931.
- [11] Julian Lincoln Simon. *The Ultimate Resource 2*. Princeton University Press, 1998.
- [12] D B Reynolds. The mineral economy. how prices and costs can falsely signal decreasing scarcity. *Ecological Economics*, 31:155–166, 1999.
- [13] N. Georgescu-Roegen. *The Entropy Law and the Economic Process*. Harvard University Press, Cambridge, MA, 1971.
- [14] M Ruth. *Integrating Economics, Ecology and Thermodynamics*, volume 3. Kluwer Academic Publishers, 1993.
- [15] A Valero. Thermoeconomics as a conceptual basis for energy-ecological analysis. In

- S Ulgiati et al., editor, *Advances in Energy Studies. Energy Flows in Ecology and Economy*, pages 415–444, Musis, Roma, 1998.
- [16] A Valero, E Botero, and A Valero D. Exergy accounting of natural resources. *Exergy, Energy System Analysis, and Optimization., from Encyclopedia of Life Support Systems (EOLSS), Developed under the Auspices of the UNESCO Eolss Publishers, Oxford, UK; Online encyclopedia: <http://www.eolss.net>*, [Retrieved May 19, 2005].
- [17] G Wall. Exergetics. *Exergy, Energy System Analysis, and Optimization., from Encyclopedia of Life Support Systems (EOLSS), [<http://www.eolss.net>]*, Retrieved May 19, 2005.
- [18] A Valero, L Ranz, and E Botero. Exergetic evaluation of natural mineral capital (1) reference environment methodology. In G. Tsatsaronis, M. Moran, F. Czesla, and T. Bruckner, editors, *ECOS 2002*, pages 54–61, Berlin, 2002.
- [19] G Wall. Exergy - a useful concept within resource accounting. report 77-42, Institute of Theoretical Physics, Göteborg, 1977.
- [20] D. B. Brooks and P. W. Andrews. Mineral resources, economic growth, and world population. *Science*, 185:13–20, 1974.
- [21] US Geological Survey (USGS). Mineral commodity summaries. report, USGS, 2001.
- [22] J Szargut, A Valero, W Stanek, and A Valero D. Towards an international legal reference environment. In Signe Kjelstrup, Johan E. Hustad, Truls Gundersen, Audun Rosjorde, and George Tsatsaronis, editors, *Proceedings of ECOS 2005*, pages 409–420, Trondheim, Norway, 2005. NTNU, Trondheim.
- [23] SM McLennan. Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochemistry geophysics geosystems*, 2:2000GC000109, 2001.
- [24] A Valero and E Botero. Exergetic evaluation of natural mineral capital (2). application of the methodology to current world reserves. In G. Tsatsaronis, M. Moran, F. Czesla, and T. Bruckner, editors, *ECOS 2002*, pages 62–68, Berlin, 2002.
- [25] US Geological Survey (USGS). Historical statistics for mineral and material commodities in the United States. report, USGS, 2006.
- [26] US Geological Survey (USGS). Minerals yearbook. report, USGS, Various years.
- [27] Matthias Ruth. Thermodynamic constraints on optimal depletion of copper and aluminium in the United States: a dynamic model of substitution and technical change. *Ecological Economics*, 15:197–213, 1995.
- [28] BP. Bp statistical review of world energy. Technical report, www.bp.com/statisticalreview2004, 2004.
- [29] F. Roberts and I. Torrens. Analysis of the life-cycle of non ferrous metals. *Resources Policy*, 1(1):14–28, 1974.
- [30] G M Mudd. Sustainable mining: An evaluation of changing ore grades and waste volumes. In *International Conference on Sustainability Engineering & Science*, Auckland, New Zealand, 2004.
- [31] Robert U. Ayres, Leslie W. Ayres, and Benjamin Warr. Exergy, power and work in the US economy, 1900-1998. *Energy*, pages 219–273, 2003.