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PETERS, Jens; "Reinventing exergy as indicator for resource depletion impacts in LCA". (ISSN: 0032-6895). *Matériaux & Techniques*. 2021, vol 108, num 5-6, p. 504 –

Available at <https://doi.org/10.1051/matech/2021003>

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Reinventing Exergy as Indicator for Resource Depletion Impacts in LCA

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Abstract

While resource aspects are gaining increasing importance for the sustainability assessment of new technologies, the question of how to assess the depletion of abiotic resources is still controversially discussed. Different methodologies exist for their quantification within life cycle assessment (LCA). Among them, thermodynamic approaches have the advantage of considering aspects of absolute quantity (reserves or amount of a substance contained in total in earth's crust) and of quality (concentration of the target element in the mined resource), making them a potentially appealing approach for assessing resource depletion. However, existing approaches are either far from the original thermodynamic idea of exergy or far too complex and not applicable for resource accounting. This work briefly discusses the suitability of exergy-based approaches for resource assessment, and then suggests a simple but comprehensive methodology for quantifying resource depletion related with the concept of chemical concentration exergy (MDP^{ces}). It provides a calculation approach for quantifying the MDP^{ces} and estimates the corresponding values for some representative key metals.

Keywords

Resource depletion, exergy, impact assessment, life cycle assessment, dissipation

Cite this article as:

Jens F. Peters, *Reinventing exergy as indicator for resource depletion impacts in LCA*,
Matériaux & Techniques Volume 108 - Issue 5-6 (2021)

1. Introduction

1.1. The concept of exergy

The ongoing transition towards a renewable energy based, carbon free world economy is raising concerns regarding future raw material demand and the limited availability of global resources [1]. In consequence, efforts are being made to assess the impact of technology developments and transitions in terms of resource depletion. This is often done by accounting the demand of the different materials required for a process or product and compare them to the estimated available world resources or reserves. However, this does not necessarily be representative for the actual reality i.e., reflect actual resource availability, since minerals and ores are available in different concentrations (e.g., lithium or gold are contained in seawater in considerable amounts, but their extraction is not feasible under economic or technical aspects due to the extremely low concentrations)[2]. In order to overcome these limitations, several methodologies for quantifying resource depletion impacts have been developed within the LCA community[3], [4]. These include (i) classic distance to target approaches that contrast available resources / reserves with the specific demand caused by the assessed process or product [5], [6]; (ii) concentration focused approaches that try to estimate the additional effort (in terms of energy or money) required by future generations for extracting a material due to reduced concentration (the best accessible and most highly concentrated minerals are always exploited first) [7], [8]; (iii) top-down approaches that quantify the (non-) contribution of the resource extraction to a political target [9], and, finally, (iv) thermodynamic approaches [10]–[12]. However, all of them suffer some drawbacks. Above all, the different value of ores of different concentrations is not considered by the most common methodologies i.e., the depletion impact assigned to a given amount of metal is independent of the quality of the resource (the concentration of the desired metal within the specific ore). This holds true also for the mentioned 'additional effort' methods, which also use only global average values and no specific ore concentrations. Exergy based methods are an exception in this regard, offering a possibility to assess resource values and thus the impact of their depletion based on scientific concepts (thermodynamics)[13].

Exergy is a concept that stems from thermodynamics. It is closely related with the second law of thermodynamics and refers to the quality of energy [14], [15]. The second law manifests the irreversibility of natural processes, stating that a system progresses towards a state of maximum entropy (maximum disorder) at equilibrium i.e., that differences in pressure, temperature and other physical and chemical potential tend to even out in an isolated system. In other words, it is a manifest of the universal principle of decay observable in nature and the so-called 'arrow of time' according to which a closed system advancing through time irrevocably becomes statistically more disordered [15]. While on the first glimpse this seems to have little to do with resources, on the second it actually does: Being exergy based on the second law of thermodynamics it considers the entropy of the assessed system, which is also related to differences in concentration.

In general, the exergy of a substance is composed of four components (kinetic, potential, physical and chemical) [16], [17]. Physical exergy is related with temperature and pressure, the chemical exergy is composed of both the exergy of composition (or enthalpy; which is close to the heating value for fuels), and the exergy of concentration. In classic thermodynamic exergy, the concentration exergy is a function of average concentration of a substance in the reference environment and the concentration within the deposit. Therefore, it can be appealing for quantifying the quality of a resource under thermodynamic aspects and thus for measuring the impacts of its depletion.

1.2. Limitations

However, the practical implementation of exergy for evaluating resources faces several challenges: First, any exergy accounting requires the definition of a reference environment, which should be in thermodynamic equilibrium. This turns out to be quite challenging [18], [19]: Can the earth in its current state (not in equilibrium) be considered as a reference environment or should rather a hypothetical earth in thermodynamic equilibrium / of maximum entropy be assumed? Secondly, exergy commingles the two aspects of energy content (formation enthalpy / heating value) and availability (concentration), since chemical exergy contains both aspects of enthalpy and resource concentration. This is coherent and due to the very nature of exergy, but can be misleading when applied for resource evaluation[20]: energy resources (even very abundant ones like coal) show high exergy, while even very scarce, but highly inert (= low enthalpy) substances like e.g. gold, show comparably low exergy, determined solely by their concentration exergy[21].

Still, exergy is receiving continuing interest for resource depletion accounting, being it an objective, science based thermodynamic approach that requires few assumptions [3]. For a more detailed review of the existing exergy based resource depletion assessment methods we refer the reader to previous works [19], [20], [22]

2. Charting the way forward

Ultimately, we are interested in a methodology based on thermodynamic principles (exergy or entropy, respectively) that allows for quantifying the scarcity of resources and thus their value in terms of availability, but also in terms of quality of a specific ore. For this purpose, it is worth having a quick look at the different stages a mineral or metal passes during its residence time within in the technosphere (or industrial metabolism). Huge efforts are spent on extracting minerals from their deposits, concentrating them and bringing them to another oxidation state, thus increasing their exergy on the expense of destroying exergy in the corresponding industrial processes. The obtained materials are then stored within the technosphere, forming building blocks of the industrial metabolism, where they are present at high exergy state in often pure form (e.g., construction materials). Finally, after the end-of-life of the building block they were forming part of, they are either recycled or disposed. In other words, they are reincorporated in the industrial metabolism in a different configuration or rejected to the environment where they form a new deposit (probably as some type of waste pile) with its corresponding concentration. Additionally, all along this process chain, small fractions of the resource are “lost”, i.e., dissipated to the environment. From a resource availability perspective, this is the major problem, since these fractions are then re-introduced into the environment at concentrations close to the background (the equilibrium) concentration, from where a recovery is extraordinarily difficult. This is exactly reflected by the concept of concentration exergy.

From such a holistic point of view, resource depletion is rather an issue of resource dissipation than resource availability, being the mineral resources contained within the earth's crust never lost, but rather distributed / diluted up to their background concentration. Applied consequently and coherently for LCA and sustainability analysis, this requires a dissipation-oriented resource accounting approach, thoroughly modelling and assessing the whole life cycle of the assessed product or process. The production stage causes the depletion of resources which are then locked in within the industrial metabolism forming part of an industrial product (but not accessible because in use). After the end-of-life, these are then available again in high quality (often in rather pure form) as new resources, stockpiled as waste (with an average concentration within the waste, forming a so-called ‘urban mine’, or dissipated again into the environment in a concentration close to their background concentration. This can also be considered as a distance-to-target approach towards the final dead state, the total thermodynamic equilibrium, in turn perfectly reflecting

the very nature of natural processes, with life making use of ('external' solar) exergy for concentrating resources, thus acting against this thermodynamic tendency towards ever-increasing entropy. Ultimately, the earth is not a closed system as long as we dispose of a continuous influx of external exergy from the sun. While the extraction of the mineral from the ore requires exergy depending on the formation enthalpy of the ore and the target mineral, we do not consider this as a matter of resource availability or depletion, but rather of the required inputs, which in turn are covered already by other impact categories like GHG emissions (for fossil chemical exergy) or cumulative energy demands.

3. Towards an applicable methodology

3.1. Approach

In the following, a first draft of a resource depletion assessment methodology based on exergy principles is outlined. Note that in this resource-oriented proposal, only the concentration exergy is considered, while the formation enthalpy is disregarded. Recalling that the focus is on resource availability and resource value in terms of availability for human purpose, it is consistent to exclude all formation exergy from our considerations. In sum, exergy is always destroyed in any step of the resource production process, but as long as there is a constant exergy influx from the sun, this does not need to be a problem. We can therefore consider energy to be unlimited and therefore changes in the chemical composition of a material (i.e., changes in its chemical exergy of formation or enthalpy) to be irrelevant in terms of their availability.

As already mentioned, two aspects need to be covered: The absolute concentration of the mineral (its absolute scarcity), and the relative concentration (its concentration in the specific ore relative to the background concentration), defining the value of the ore. For this purpose, the thermodynamic equilibrium would be defined exclusively in terms of concentration exergy (disregarding formation enthalpy). In other words, the required thermodynamic equilibrium is a maximum entropy state in terms of resources distribution. Consequently, this would take the current average composition of earth's crust as reference environment, assuming a homogeneous mixture (the reference environment in terms of resources). We essentially need to separate this from the formation enthalpy of the substance, which, though relevant in terms of resource quality (a low enthalpy rock formation will require more energy for extracting the target material e.g., metal), it is not so in terms of availability.

In a first attempt, we suggest here to use the exergy model as suggested by Morris & Szargut [23], but with some important modifications. The chemical exergy of formation (enthalpy) is disregarded, since it is not directly related with availability of resources, but with the exergy input required for processing / purifying it. This, in turn, will be covered by other impact categories, given that exergy by itself is not a limiting factor (solar influx). Also, mass-based background concentrations are used for the different elements i.e., their mass share within earth's crust [24] (unlike Morris & Szargut, who base their calculations on molar concentration).

The concentration exergy scarcity value (*ces*) ces_i of element *i* in a specific ore can thus be calculated according to Equation 1:

$$ces_{i,ore} = -C * \ln\left(\frac{x_{i,bg}^2}{x_{i,ore}}\right) \quad (\text{Equation 1})$$

with

- $C = 2.479$ (calculated as the product of R (gas constant) and T (normal temperature) divided by 1000). This is an arbitrary number and can well be

omitted, but is maintained for allowing easier comparison with other exergy based calculations.

- $x_{i,bg}$ = the background concentration of the element (its average concentration in earth's crust) [24]
- $x_{i,ore}$ = the specific concentration of element i in the ore

The ces is loosely related to the model suggested by Morris & Szargut, but with some major modifications. The important aspect is the logarithmic approach for accounting for the background concentration. However, as previously mentioned the calculation is changed to a mass-ratio basis. Therefore, also the use of the gas constant R (as suggested by Morris & Szargut) is not useful anymore (it was neither meaningful for assessing solid resources in the original formula, but did at least fit the units). This is substituted by a constant here. The main difference is the inclusion of both the background concentration ($x_{i,bg}$) and the actual concentration of the target mineral within the ore ($x_{i,ore}$). In this way, both the absolute scarcity and the ore quality are accounted for.

However, due to the logarithmic approach, the scarcity values are quite compressed, and show a substantially lower spread than other resource depletion assessment methodologies [2], [3], [25]. In order to make them comparable with existing LCIA methods (which usually normalize the characterization values to a common reference substance like iron or antimony), the ces is also normalized to the value for the background concentration of iron and then expanded exponentially again in order to increase the spread according to Equation 2.

$$MDP_{i,ore}^{ces} = \exp((ces_i / ces_{Fe,bg}) - 1) \quad (\text{Equation 2})$$

With

- $ces_{i,ore}$ = ces value for the element i within the specific ore
- $ces_{Fe,bg}$ = ces value for iron at background concentration

The advantage of this approach is its simplicity on the one hand, and its capacity of taking into account both the absolute concentration of a given element in earths crust and its specific concentration. Table 1 provides values for some relevant elements. The background concentration is taken from literature, while for the ore grades, some values are picked arbitrarily from the ecoinvent database. The influence of the ore grade can be observed clearly, with lithium from a lithium rock deposit (i.e., spodumene) obtaining a higher MDP^{ces} than cobalt or lithium brines. Lithium and cobalt show comparable abundance within earths crust, but the spodumene contains lithium at higher concentrations, giving it a higher MDP^{ces} value. This is also reflected by the higher process efforts required for cobalt extraction and purification, and correspondingly higher impacts in other impact categories. Pure metallic gold shows an extraordinarily high value, caused by its low general abundance and its very high concentration when obtained in metallic form (note that this would correspond to a deposit of pure metallic gold. When the metallic gold is contained in e.g. sand, its average concentration within this 'ore' or carrier material would need to be used). Within an ore at correspondingly low concentrations (4ppm in Table 1), its concentration exergy and thus its MDP^{ces} is substantially lower, being the ore grade much closer to the average background concentration.

Table 1. MDP^{ces} values for some selected elements

Element	background concentration[24]	concentration in ore	ces _{i,ore}	MDP ^{ces} _{i,ore}
Al	8.23%	24%	8.84	1.27
Au	4.00E-09	100%	95.87	253,259.81
Au	4.00E-09	4.3E-4%	65.24	3453.69
Cu	6.00E-05	0.22%	33.03	37.74
Cu	6.00E-05	0.76%	36.10	58.07
Cu	6.00E-05	1.83%	38.28	78.81
Fe	5.63%	70%	13.38	2.40
Fe	5.63%	5.63%	7.13	1
Li (Spod.)	2.00E-05	2%	43.94	174.46
Li (Brine)	2.00E-05	0.15%	37.52	70.91
Mg	2.33%	25%	15.20	3.10
Mn	0.10%	60%	33.23	38.86
Co	2.50E-05	0.20%	37.13	67.10

3.2. Applicability

In order to obtain a first impression of the viability of the methodology, the MDP^{ces} is calculated for 1kg of copper (market mix according to ecoinvent 3.4.[26]) and compared with the other two readily available exergy-based impact assessment methodologies, CEENE and CExD (Figure 1). Copper is a common metal whose mining processes are modelled in detail within the database and for which ores of different grades and concentrations are considered. It is covered by all considered impact assessment methods and thus allows for a meaningful comparison between the methods (CEENE and CExD do not cover some other key metals like e.g., lithium or gold). A more detailed description of the CExD and CEENE including their coverage, strengths and weaknesses can be found in previous publications [2], [22] and is not be repeated here. The abiotic resource depletion potential according to CML (reserve base) is also quantified as additional reference.

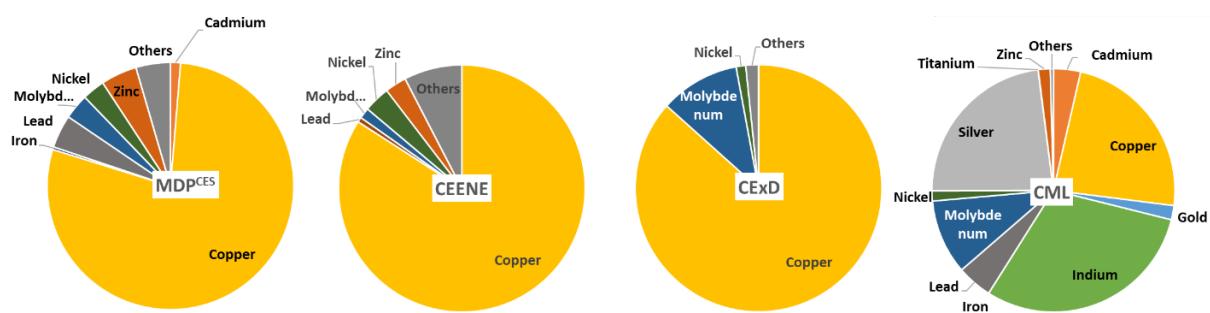


Figure 1. Contribution of major resource flows to the total metal depletion impact of 1 kg of copper metal according to the four different impact assessment methods. MDP^{ces} = concentration exergy scarcity, CEENE = Cumulative exergy extraction from the natural environment, CExD = Cumulative exergy demand and CML = abiotic resource depletion potential (reserve base) according to the CML methodology

The results obtained with the MDP^{ces} are found to be well in line with those obtained by the other two exergy-based methods, while differing substantially from the CML method. Copper depletion is the main impact with all three methods, unlike CML, where it contributes less than one quarter to the total. The latter can be attributed to the high weight given to silver and indium by the CML method, metals that are

obtained as co-products in zinc and copper mines. However, this is also partially related to the ecoinvent modelling approach, where the depletion of mining by-products is partially allocated also to the target metal.

The primary novelty of the MDP^{ces} approach is its rigorous consideration of ore concentrations (unless CEENE and CML, who apply one single characterization factor to a given metal, independent of the quality of the ore it is obtained from). Therefore, Figure 2 breaks down the impacts obtained per kg of copper (market mix) to the different mining processes, in turn associated with different mining sites and different ore grades. The copper ores mined in Europe ('Cu, prim, ReR' in Figure 2) have (according to the ecoinvent modelling approach) a high copper concentration of 1.82%, while those from North America ('Cu, prim, RNA') contain only 0.22% copper. In consequence, they show a higher relative contribution to the total resource depletion under MDP^{ces} than with CEENE or CML, who do not distinguish between ore qualities (see Table 1 for the corresponding MDP^{ces} values).

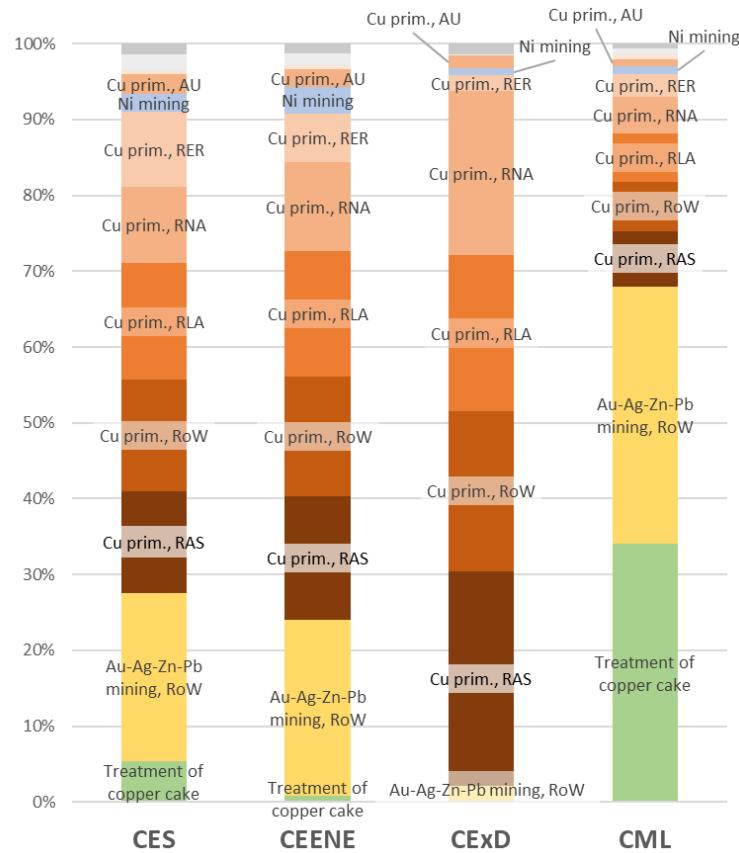


Figure 2. Major process contributions to the total resource depletion impact of 1 kg of copper metal obtained with the different impact methodologies. MDP^{ces} = concentration exergy scarcity, CEENE = Cumulative exergy extraction from the natural environment, CExD = Cumulative exergy demand and CML = abiotic resource depletion potential (reserve base) according to the CML methodology

4. Conclusions

The present work outlines an approach for estimating resource depletion impacts, closely following the concept of exergy. It is appealing due to its simplicity and its capacity to account both for the absolute scarcity of a given element, but also for the quality of the mined resource in terms of its concentration in the target ore. While a first application to a common metal, copper, gives promising results, it still needs to prove its broader applicability for all types of industrial processes by means of representative case studies and its linking with an established inventory database (i.e., ecoinvent). Possible difficulties might arise when assessing mixed ores that

contain more than one metal, when the target element is not distributed homogeneously within the carrier bulk material, or for assessing bulk materials like sand or gravel that are not mined for obtaining a particular element, but used as mineral for e.g., construction purposes. Future works targeting these aspects would be required for validating the final applicability of the methodology in different contexts.

Apart from that, also a different accounting approach is suggested, shifting from a pure extraction-oriented perspective towards a dissipation approach. After all, the dissipation of resources to concentrations close to their background concentration is often the real problem of resource depletion, much less their extraction, being the latter rather a process of making them available than a depletion. This is not directly related to the suggested resource depletion assessment methodology, but rather a shift of perspective. It would require substantially higher efforts for modelling the individual processes, thoroughly determining all dissipative losses and always taking a full life cycle perspective. This is essentially a community task and would require future works to include a more thorough end-of-life modelling, tracing the fate of substances along the whole life cycle. While still far from common practice, the increasing availability of data in all fields of industrial ecology gives hope that this will become more relevant in future, allowing a more meaningful resource assessment in line with the idea of an industrial metabolism and the corresponding circular economy.

Acknowledgements

This work has been funded by the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement No. 754382.

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Cite this article as:

Jens F. Peters, *Reinventing exergy as indicator for resource depletion impacts in LCA, Matériaux & Techniques Volume 108 - Issue 5-6 (2021)*