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Resource Assessment methods in Industrial Ecology and Process Engineering: a critical review towards improved consideration in LCA

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Title: Resource Assessment methods in Industrial Ecology and Process Engineering: a critical review towards improved consideration in LCA

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Abstract: Resource use and its impacts remain central concerns in industrial ecology. This review examines major Resource Assessment Methods (RAM) to enhance the measurement of impacts on the natural resource Area of Protection in Life Cycle Assessment (LCA).

Within this objective, Thermodynamic Rarity, Exergy Cost Analysis, and Statistical Entropy Analysis have been analysed following a PRISMA literature selection process. Two of their components are critically investigated: their metrics (parallel to characterisation factors) and frameworks (parallel to system models).

The reviewed metrics—chemical exergy, concentration energy, and statistical entropy (SE)—are all rooted in the Gibbs free energy of mixing. Chemical exergy is the most robust, capturing both geological scarcity and the linkage effects of chemical association within resource matrices. Concentration energy addresses scarcity with additional assumptions, while SE offers broader applicability when concentration data are incomplete. Among the frameworks, Exergy Cost Analysis offers two principles of high relevance for resource-oriented LCA: its "resource rule" defines system boundaries based on flows lacking upstream supply chains, and its "co-product rule" partitions burdens according to the physical value embodied in each co-product.

1 Introduction

Life Cycle Assessment (LCA) quantifies how product systems impact safeguard subjects, known as Areas of Protection (AoP) (Guinée et al., 2011). The impacts on the natural resource AoP (Dewulf, Benini, et al., 2015) reflect how much a product system is damaging the initial potential value held by its input resources for future needs in the technosphere (Berger et al., 2020). As with every Life Cycle Impact Assessment (LCIA) method, resource-oriented methods assign Characterisation Factors (CFs) to flows inventoried in a Life Cycle Inventory (LCI) based on system models established during the Goal and Scope (G&S) phase (Schulze et al., 2020).

The UNEP GLAM2 Task Force classified the resource-oriented LCIA methods into four categories based on an analysis of their CFs' theoretical foundations (Sonderegger et al., 2020). They notably recommended that resource-oriented LCIA methods update their CFs regularly, expand their abiotic resource coverage, incorporate secondary resources, and integrate quality-based characterisation of dissipative flows (Berger et al., 2020)—requiring developments at both LCI and LCIA phases (Beylot et al., 2024). The research shift from resource-use to resource-dissipation accounting opened the door to various LCIA methods that are addressing these recommendations differently, with no consensus to date (Beylot et al., 2024).

Some approaches focus on output emission elementary flows (van Oers et al., 2020; Owsianiak et al., 2022; Greffe et al., 2026) or input natural resource flows (Charpentier Poncelet et al., 2021; Charpentier Poncelet, Loubet, et al., 2022). Others argue that a more complete inventory of dissipative resource flows requires a system model that explicitly tracks the dissipated resource flows among all the LCA flows (Beylot et al., 2024; Lai & Beylot, 2023).

At the LCIA level, several CF proposals have emerged to translate dissipative flows into value loss for the resource AoP. Some studies rely on economic valuation, such as economic importance (Santillán-Saldivar et al., 2023) or market prices (Ardente et al., 2023; Dewulf et al., 2024). Other approaches employ snapshot proxies like service time (Charpentier Poncelet et al., 2021; Charpentier Poncelet, Loubet, et al., 2022) or additional energy requirement (Greffe et al., 2026). Because these snapshot CFs are derived from external assessment tools, their dependence on regular updates echoes the Task Force's recommendation (Berger et al., 2020), as analysed for the service-time proxy by Beylot et al. (2024).

In parallel, circularity strategies have gained policy traction (European Commission, 2020; US EPA, 2024; Yunpeng et al., 2022). Therefore, some studies investigate the integration of circularity indicators directly within LCA (Cilleruelo Palomero et al., 2024) to inform the impacts on the resource AoP (Hackenhaar et al., 2024). In theory, the initial potential value of resources is partially lost through dissipation, and this lost value is precisely what linearity means; therefore, measuring dissipation equals measuring (lack of) circularity (Charpentier Poncelet, Helbig, et al., 2022). Yet circularity indicators remain inventory-based (Hackenhaar et al., 2024): their system models track material and energy flows but lack an impact assessment step translating dissipation into value loss. For instance, ISO59020:2024 still relies on material/energy-based indicators , equivalent to input-based inventory indicators like cumulative energy demand (Rohrlich et al., 2000) and cumulated raw material demand (Wiesen & Wirges, 2017), which apply CFs directly to inventory flows without modelling impact pathways. The missing element is a physically grounded, intrinsic flow property (or, intrinsic quality; (Vulsteke et al., 2026)) that can carry value and thus bridge inventory tracking to LCIA. Thermodynamic potentials can offer precisely such an intrinsic property. Because resource flows carry exergy and dissipation implies exergy destruction, a thermodynamic metric can link the physical tracking of flows to the loss of their potential value for future use—without relying on external economic or time-based proxies. These methods are historically classified as thermodynamic accounting methods (Berger et al., 2020; Sonderegger et al., 2020). The link between thermodynamic accounting and dissipation reasoning can be traced back to Amini et

al. (2007), who quantified exergy losses during metal recycling as a direct measure of dissipation outside the LCA framework. Even earlier, (Dewulf & Van Langenhove, 2004) implicitly considered dissipation by confronting the Cumulative Exergy Demand (CExD, later applied to ecoinvent by (Bösch et al., 2007)) with the exergy content of the functional unit's reference flow: the difference represents exergy dissipated during the life cycle. Assessing dissipation in LCA has been recognised as interconnected with the challenge of not only accounting for elementary flows, but also intermediate flows, in the step of impact characterisation (Beylot et al., 2024; Heijungs, 2024). Indeed, among the actions that compromise resource accessibility, several—such as downcycling, hoarding, and abandoning—occur within the technosphere itself (Dewulf et al., 2021). This remains an active frontier in LCA development (Heijungs, 2024; Sacchi et al., 2025).

Addressing the disconnect between physical flow tracking and value loss assessment requires looking beyond LCA's traditional focus on elementary flows, toward Resource Assessment Methods (RAM) from other Industrial Ecology (IE) methodologies that combine rigorous system models. This article aims to resolve a dual gap from a theoretical point of view: circularity indicators do not translate physical flows into value loss for the resource AoP, and resource-oriented LCIA methods lack both dissipation-compliant system models and consensus on CFs.

A systematic review based on PRISMA methods was therefore conducted to screen such RAM. The technical goal is to scrutinise these methods' parameters for their completeness in measuring both the LCIA on the resource AoP and product systems' circularity performance. The review therefore asks two questions. First, which intrinsic physical property is the most suited to reflect the value of resource flows? Second, which existing system-model rules are compatible with dissipation-oriented LCA? Answering both lays the basis for an LCIA method that measures resource impact and circularity within a single framework.

The remainder is structured as follows: Section 2 details the critical review methodology; Section 3 classifies RA approaches, analysing their strengths, limitations, and LCA compatibilities; Section 4 synthesises key findings and outlines future directions.

2 Methods

2.1 Screening the relevant Resource Assessment Methods

The first phase of the review identified metrics and frameworks for measuring system resource viability with the systematic PRISMA methodology (Moher et al., 2009; Page et al., 2021) to ensure transparency and reproducibility in the selection process.

2.1.1 Obtain a List of Documents

A Scopus search was conducted from 1995 to the beginning of 2025. The keywords used to scope documents on metallic and mineral resources—covering repurposing, loss of resource value, and physical grounding—along with the final list of 79 Articles, Reviews, Conference Papers, Book Chapters, and Editorials, are available in Online Resource 1.

2.1.2 Obtain a List of Relevant Resource Assessment Methods

Secondly, screening criteria were applied to identify documents that optimise systems using RAMs. The selected documents must employ or develop a method that targets system resources for optimisation and relies on a formalised accounting framework. Additionally, the method should require a physical balance of flows and provide sufficient detail on system resources. At the end, the selected documents design or use an RA method applied outside the scope of LCA, thought for different IE frameworks. Indeed, this study aims to investigate the potential of integrating RAMs into LCA. Further details on each criterion, along with example analyses, are provided in Online Resource 1.

9 documents remained at the end of the screening process, from which the RA methodologies were extracted and classified. The detailed PRISMA flow diagram (Haddaway et al., 2022) is shown in Online Resource 1.

2.1.3 Classification of Resource Assessment Methods

The screened documents do not describe the fundamental details of their RAM.

In this work, we therefore further investigate the literature behind the screened RAM, identifying their foundational sources, the documents where the methods are best described or applied.

However, the critical review must sub-classify each method in order to identify aspects relevant to be integrated within the different LCA phases to lay the basis for operationalising a dissipation-oriented LCA.

The RAMs are subclassified according to two components:

- The method’s framework is the IE counterpart of the system model concept in LCA (Schulze et al., 2020). It structures and processes its variables via rules or standards that govern arithmetic operations. These variables are RAM’s metrics.

- The method's metric serves as a proxy for resources (parallel to the CFs of an LCIA method). A metric can either be attributed to a resource flow because it represents a flow-intrinsic property (applicable at the LCI level) based on a measurable physical attribute, or it results from the cumulative use of an intrinsic property obtained with an

IE external assessment model (parallel to a final LCIA score or a product-oriented LCA study (Schrijvers et al., 2020)).

Fig. 1 illustrates this using the example of the Cumulative Exergy Extracted from the Natural Environment (CEENE), rooted in the work of Dewulf et al. (2007).

The CEENE LCIA score is assigned to the functional unit's reference flows, becoming a candidate metric (blue rounded boxes) for these product flows. The formalised framework is that of LCA (green boxes). The CEENE's CFs are metrics that are based on the intrinsic exergy content of resource elementary flows (a sub-metric), or on other sub-metrics derived throughout an impact pathway (thus represented as green boxes), such as the exergy deprived from the ecosphere because of land occupation in CEENE's CFs. The chain only stops with measurable metrics (yellow rounded boxes) such as, e.g., the Helium (He) partial pressure in the atmosphere used for chemical exergy calculations.

This example demonstrates that a derived metric is always computed within some mathematical framework, and conversely, a framework exists to produce a derived metric.

At the end of the classification process, RA metric and framework candidates are selected.

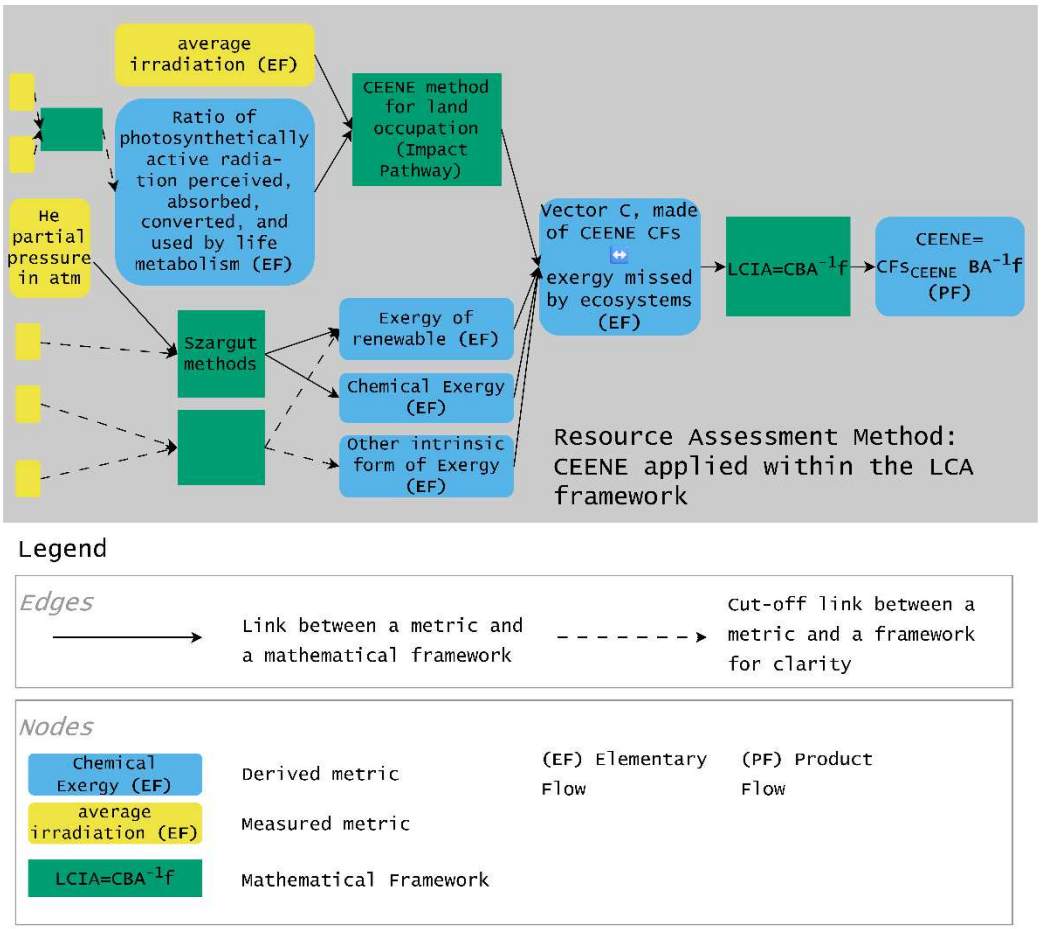


Fig. 1: Example of how an LCIA resource-oriented method will be classified according to the framework developed. Elementary Flows (EF) and Product Flows (PF) indicate what is the flow type the metric addresses, e.g., chemical exergy addresses mineral resource EFs

2.2 Critical Analysis

The critical analysis of the RAM's metrics and frameworks requires formalising key variables, whose definitions and notations are detailed in Online Resource 2, Section 1, Nomenclature and Abbreviations.

2.2.1 Analysis of Metric Components

To resolve the gap between circularity tracking and the operationalisation of dissipation-oriented LCIA, this research focuses on flow-intrinsic, physically based RA metrics that proxy the resource potential value. This focus on physical-property-based resource value analysis rests on the premise that a universal, reproducible metric offers the most objective foundation for assessing circularity across human economies. In addition, the measurable

variables at the root of each metric chain are the easiest to identify (see the example with the CEENE LCIA of Fig. 1).

Flow-intrinsic RA metric candidates underwent a critical analysis focusing on three main criteria:

- Complexity was assessed based on the number and variety of required input measurable variables and the steps needed to process them in order to implement the CF metric candidate within LCA datasets, e.g., the undefined datasets of ecoinvent (De Wachter et al., 2026), which are the initial LCI data that are collected before being handled so that LCI results can be obtained,

- The robustness evaluation process starts with an in-depth analysis of the physical bases of the RA metrics screened, until measurable metric variables (yellow rounded boxes in Fig. 1). Then, the RA metrics coverage of a product system's resources (Dewulf, Mancini, et al., 2015) and their ecoinvent operability with the assets represented in (Dewulf, Benini, et al., 2015) are analysed. A critical analysis of their resource value proxies has been pursued through analysis of their input data and calculation methods to determine the metrics corresponding to the LCA safeguard subject (AoP).

- Transparency is crucial for assessing the viability of a method in IE (Hertwich et al., 2018) and was evaluated based on the ease of obtaining required input variables from stakeholders and the ease of sharing model data when the metric is used.

2.2.2 Analysis of Framework Components

The RA framework component was evaluated against:

- System boundary setting (parallel to G&S phase).

- Multi-functionality problem identification (parallel to G&S phase) and mathematical translation when constructing the model to obtain inventory results (parallel to LCI phase).

- Hotspot identification, contribution analysis and system optimisation to support decision-making (parallel to Life Cycle Interpretation phase).

3 Results

Section 3.1 presents the RAM identified from the screened documents; Section 3.2 scrutinises the selected RA method along with its candidate's RA metrics and frameworks; and Sections 3.3 (metric-level) and 3.4 (framework-level) deliver the critical evaluation.

3.1 Screening Results

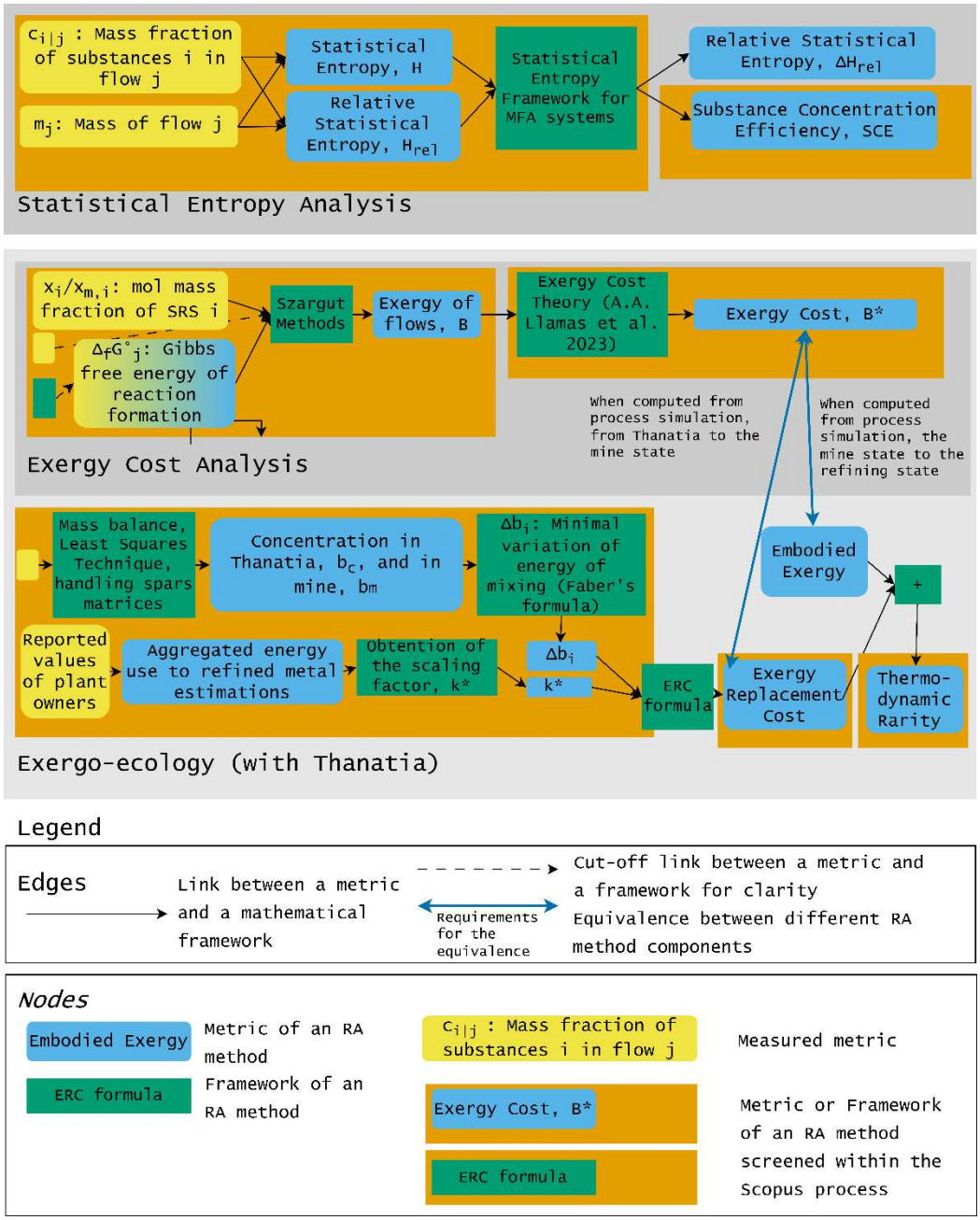


Fig. 2: Classification of screened RAM components. Sky blue rounded rectangles represent metrics which could be considered for use to derive LCIA Characterisation Factors. Bluish green rectangles represent mathematical frameworks relevant to goal and scope definition, and LCI applied to resource-oriented LCA studies.

Traditional exergy analysis (Amini et al., 2007; Llamas et al., 2023; Reuter et al., 2015; Yao et al., 2011), Exergy Replacement Cost (ERC) (Domínguez & Geyer, 2017; Kolagar et al., 2019), thermodynamic rarity (TheRy) (Valero & Valero, 2019), and Substance concentration

efficiency (Tanzer & Rechberger, 2020) are the different RAM—frameworks and metrics—screened and analysed in this article. Fig. 2 illustrates how these methods are scrutinized.

3.2 Classification of Resource Assessment Methods

3.2.1 Exergy Cost Analysis

As shown in Fig. 2, a distinction is made between the exergy assigned to a flow j, and the cumulative exergy required to produce the flow (i.e., the exergy cost (Stanek, 2017; Szargut, 2005)). The exergy cost is obtained by conducting an Exergy Cost Analysis (ECA) based on the formalised exergy cost theory, a framework analysed in Section 3.4.2.

The exergy metric quantifies a potential physical value (Cornelissen & Hirs, 2002; Gaudreau et al., 2012; Wall, 1977). Exergy comprises external and internal components (Simpson & Edwards, 2011). The external exergy components (radiative, kinetic, and potential) have not been of main interest in resource-oriented LCA, given the nature of flows entering product systems (non-exhaustible resources (Dewulf, Benini, et al., 2015), and similar conclusions are formulated for other industrial systems analysis (Nguyen et al., 2014). The internal exergy components (thermal, mechanical, chemical and nuclear) have been used much more extensively to build CFs. To understand internal exergy, we must conceptualise two subsystems: a resource j made of Standard Reference Species (SRS) i, which is out of equilibrium with the environment that is composed of Environment Reference Species (ERS) k. The environment acts as a thermal, mechanical, and chemical reservoir where intensive state properties (T^{env}, p^{env}, g_k^{env}) remain constant during the interaction with resource j, to preserve reversibility (Palazzo, 2021; Simpson & Edwards, 2011). By analogy, nuclear exergy requires a reference 'dead state' defined by the most stable nuclide, with the exergy of unstable isotopes quantified by their deviation from this nuclear equilibrium (Audi et al., 2003). Nuclear exergy is restricted to fissionable elements (e.g., uranium isotopes) and thus appears within few LCI flows (Dewulf et al., 2007). Thermal and mechanical exergy are often grouped under the term physical exergy (Szargut, 2005), though some authors prefer the term physico-chemical exergy to explicitly account for phase changes between the resource state and the environmental reference state (Hack & Reuter, 2025). While foreground systems with extreme temperatures or pressures may exhibit significant physical exergy, background LCI flows are typically modelled at standard conditions, rendering this contribution negligible. Consequently, the critical analysis focuses exclusively on chemical exergy, the component already central to CExD and CEENE (see Fig. 1), while the two methods yield different CFs for equivalent mineral resources (Sonderegger et al., 2020). This is because CExD uses 0.63 MJ-eq, the median chemical exergy value reported for ores by (Finnveden & Östlund, 1997), and derives

CFs solely from the metal mass fraction and allocation factor of the ore elementary flows. CEENE, by contrast, accounts only for the exergy of the mineral fraction of the ore containing the metal, while excluding the gangue fraction assumed to remain chemically unaltered in the beneficiation tailings (Dewulf et al., 2007; Sonderegger et al., 2020).

Despite its widespread use, the physical foundations of chemical exergy remain underexplored in the LCA literature, and its systematic application as a metric for thermodynamic dissipation has not yet been assessed. We address this gap in Section 3.3.1.

3.2.2 Exergo-ecology

The Exergo-ecology methods (developed by researchers at the University of Zaragoza (Valero et al., 2023)) produce a final score named Thermodynamic Rarity (TheRy) (Valero Capilla & Valero Delgado, 2014), which characterises pure chemical elements regardless of their concentration or chemical form within resource flows.

The metric is based on two terms: the ERC and the "concentration exergy", i.e., the exergy cost required to concentrate the bearing mineral and refine its pure chemical elements: $Thery = ERC + E^*$ (see Fig. 2 for a schematic representation). The ERC can be calculated in two ways: through the ECA mathematical framework (analysed as candidate RA framework in Section 3.4.2), or as $ERC = k^* \cdot \Delta b_{c,i}$, where k^* represents the linear increase in effort required to concentrate a resource using best available human knowledge (Magdalena, 2024). Therefore, both the ERC and the underlying TheRy comprise human economies' input data, hence fall outside the critical analysis scope for RA metrics, which must be physically based only.

For more potential of integration insights, we refer to the UNEP GLAM2 mineral resource task force that describes the ERC as the closest thermodynamic accounting approach to addressing mineral resource availability for human purposes, while the model still lacks "clear cause-and-effect relationships" (Sonderegger et al., 2020). Others acknowledge the variability of these metrics with technology improvement and time (Stanek, 2017), similar to the critics formulated by Beylot et al. (2024) on the snapshot dimension of some mineral resource CFs. Ultimately, TheRy inherits the robustness concerns from the ERC, while they both inherit the uncertainties from the modelled exergy cost calculations for metal concentration.

While TheRy can be used to estimate the theoretical additional humans' efforts to reconcentrate a dissipated resource that was refined (ERC stops at its mine state), the concentration exergy, $\Delta b_{c,i}$, represents the minimal natural energy investment to concentrate a resource from a finite theoretical dead state (Thanatia (Valero, Agudelo, et al., 2011; Valero, Valero, et al., 2011),

mol fraction x_c) to its mine state (mol fraction x_m). $\Delta b_{c,i}$ and the underlying concentration energy, $b_{c,i}$, are candidate RA metrics analysed in Section 3.3.2.

3.2.3 Statistical Entropy

The substance-based RAMs are rooted in Statistical Entropy Analysis (SEA) applied to the Material Flow Analysis (MFA) framework (Rechberger & Brunner, 2002; Rechberger & Graedel, 2002). Recent efforts to unify SE metric computation and optimisation are found in (Cencic & Rechberger, 2024), with alternative perspectives in (Schach et al., 2024). The SE formula is analogous to Shannon's information entropy (Shannon, 1948), where the probability p_i of a symbol is replaced by the mass fraction $c_{i|j}$ of target substance i in flow j (other parallels summarised in Table 2.1 of Online Resource 2).

To account for flow significance, SE is weighted by the flow's mass fraction, where n_S is the number of predefined substances i, and δ equals 0 or 1 depending on whether a 'rest' fraction is considered:

$$H^{+}_{I|j} = -\frac{M_j}{M_{stage}} \sum_{i=1}^{n_s+\delta} c_{i|j} \log_2 c_{i|j} \qquad Eq.1$$

$H^{+}_{I|j}$ is expressed in binary units and represents the average number of binary choices needed to describe flows based on their resource composition. To maintain comparability among flows with varying levels of known composition and resource diversity, Eq. 1 is further normalised by the maximum system SE, $H^{max}_{I|J}$ (Cencic & Rechberger, 2024), yielding the Relative SE (RSE) (Rechberger & Graedel, 2002). RSE is thus expressed in normalised units, and denoted H^{rel} following the notation of (Cencic & Rechberger, 2024). Because the amount of encoding operation to separate a resource flow into its valuable elements could reflect the efforts to recover those elements, both SE and RSE can serve as candidate CFs. These metrics will be analysed further in Section 3.3.3.

SE is computed for element mass-balanced systems (Laner et al., 2017), discretised into sequential stages and analysed in Section 3.4.1. The variation of RSE across a stage, ΔH^{rel}, is given in Eq. 2.

$$\Delta H^{\mathrm{rel}} = \frac{\sum_{\mathrm{j} \in \text{ stage x+1}}^{n_F} H^{+}_{I|\mathrm{j} \in \text{ stage x+1}}}{H^{max}_{I|J}} - \frac{\sum_{\mathrm{j} \in \text{ stage x}}^{n_F} H^{+}_{I|\mathrm{j} \in \text{ stage x}}}{H^{max}_{I|J}}$$

$$= H^{\mathrm{rel},+}_{I|J_{\text{stage x+1}}} - H^{\mathrm{rel},+}_{I|J_{\text{stage x}}} \qquad Eq.2$$

3.3 Critical Analysis: Metrics

Having introduced the key RAM—Exergo-ecology, Statistical Entropy Analysis, and Exergy Cost Analysis—we now critically examine their underlying assumptions, limitations, and suitability as LCIA CFs. An extended version of the fundamental criticisms detailed in this section has been shared in Online Resource 3. Fig. 3 maps how the three metrics originate from the Gibbs free energy of mixing and reveals their assumption dependencies

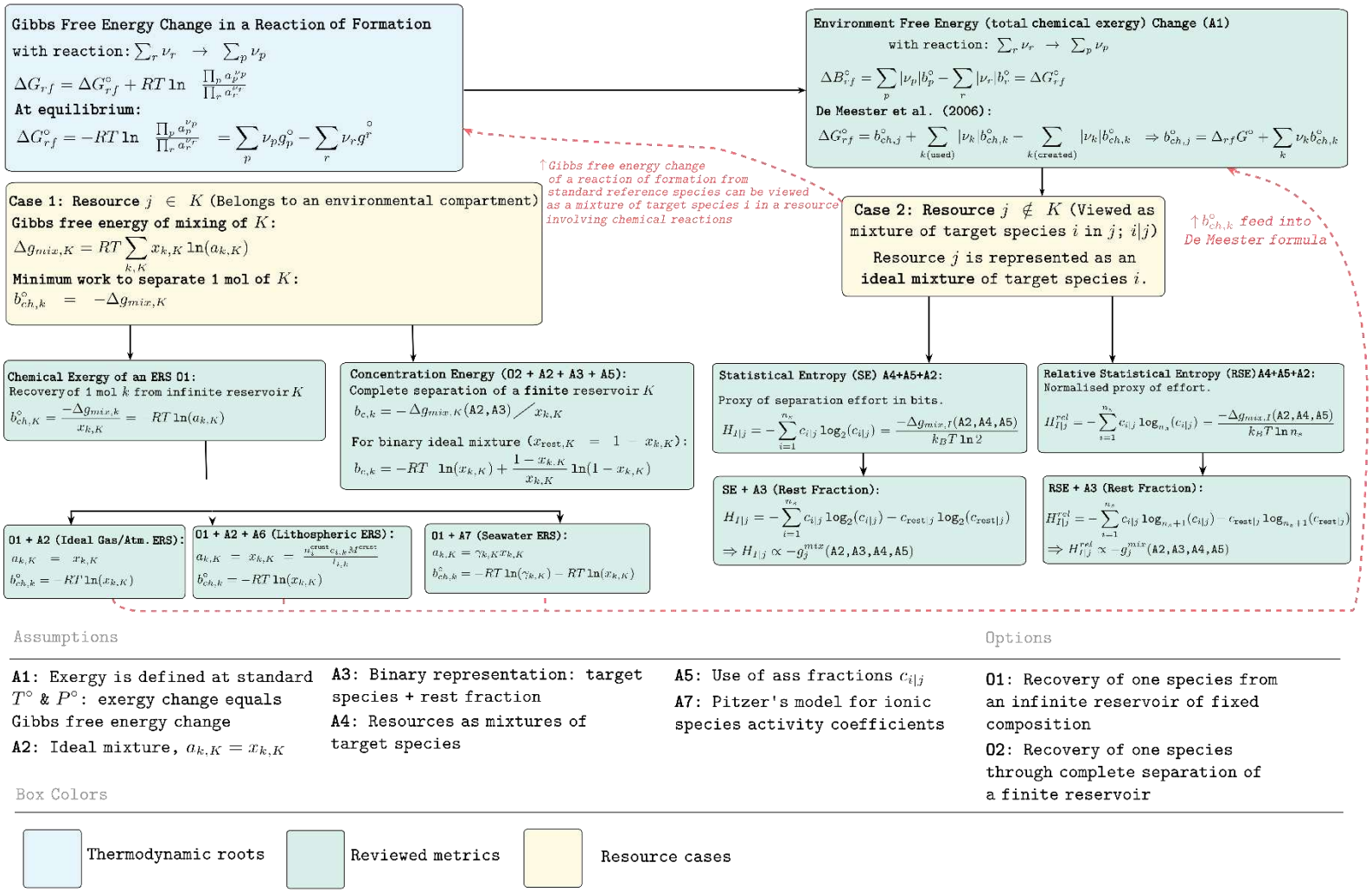


Fig. 3: Diagram maps of the hierarchical relationships between Gibbs free energy change of formation (thermodynamic root) and reviewed RA metrics. Thermodynamics foundations are represented within blue boxes. Different resource treatment cases are represented with grey boxes: Case 1 for resources within environmental compartments, and Case 2 for resources viewed as mixtures of target species. Green boxes are representing reviewed metrics. Assumptions (A1–A7) and operational options (O1–O2) are annotated throughout. The legend clarifies symbols, assumptions, and methodological options.

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3.3.1 Chemical Exergy Metric

As described above, the chemical exergy of a resource flow, $B^{\circ}_{ch,j}$, is a process function which represents the difference between two exergy state functions, noted with the letter X in Eq. 3. At constant pressure and temperature of the environment (reversibility conditions), and, such as assumed by Szargut (2005), at standard conditions, X simplifies to the Gibbs free energy. Hence, chemical exergy, expressed in Eq. 3, corresponds the difference between the Gibbs free Energy of a resource j at standard condition, G°_{j}, and the Gibbs free energy of its fully decomposed products (i.e., formed and created Environment Reference Species (ERS), of symbol k and amount $N_{k,j}$) at environmental conditions (Simpson & Edwards, 2011), $G^{env}_{k,j}$.

$$B^{\circ}_{ch,j} = X^{\circ}_{j} - X^{env}_{k,j} = G^{\circ}_{j} - \sum_{k,j} N_{k,j} \cdot G^{env}_{k,j} \quad Eq.3$$

However, $G^{env}_{k,j}$ is difficult to derive directly. The specific exergy of an ERS, $b^{\circ}_{ch,k}$, can be expressed as a function of the activity of that species in the environment, a_k, using Eq. 4.

$$b^{\circ}_{ch,k} = g^{\circ}_{k} - g^{env}_{k} = -RT^{\circ} \ln a^{env}_{k} \qquad Eq.4$$

Researchers have developed different paths to obtain the exergy of a resource j. Either directly in function of the ERS expressed in Eq. 5 (De Meester et al., 2006), or in function of the Standard Reference Species (SRS), of symbol i, expressed in Eq. 6 (Szargut, 1989).

$$B^{\circ}_{ch,j} = \sum_{k,j} N_{k,j} \cdot b^{\circ}_{ch,k,j} + \Delta G^{\circ}_{rf,k,j\rightarrow j} \quad Eq.5$$

$$B^{\circ}_{ch,j} = \sum_{i,j} N_{i,j} \cdot b^{\circ}_{ch,i,j} + \Delta G^{\circ}_{rf,i,j\rightarrow j} \quad Eq.6$$

To attribute chemical exergy to a resource, the standard chemical exergy of ERS $b^{\circ}_{ch,k}$ must first be determined (Step 1), followed by its Gibbs free energy of formation from reference species (Eq. 5 or 6), which acts as two potential mixing exergy contributions. Two routes exist for this mixing term. The direct route, via Eq. 6 is complex and data-scarce. The indirect route, via Eq. 5 , benefits from widely available thermodynamic data, but it first requires computing the SRS exergies (Step 2)..

3.3.1.1 Step 1: Environment Reference Species Exergy

To get the ERS exergy values, the analyst chooses between partial (site-specific) or comprehensive (global) reference environments (Szargut et al., 2005). LCA practitioners have favoured Szargut's

comprehensive approach (Bösch et al., 2007; Dewulf et al., 2007), where each ERS is assigned to a specific environmental compartment: atmosphere, hydrosphere, or lithosphere. As Fig. 3 shows, $b^{\circ}_{ch,k}$ corresponds to the partial molar Gibbs free energy of mixing of k (Eq. 4), following Option O1—recovery of one species from an infinite reservoir. Its robustness is compartment-dependent, with three distinct assumption branches.

For atmospheric ERS, ideal mixing (A2, $a_k = x_k$) is assumed, which is reasonable given near-zero non-ideality. For seawater ERS, Pitzer's model (A7) accounts for ionic activity coefficients ($a_k = \gamma_k \cdot x_k$), improving physical fidelity. For crustal ERS, ideal mixing (A2) is imposed alongside a homogeneous non-equilibrium environment (A6), requiring the mole fraction to be expressed as $x_k = \frac{1}{l_{i,k}} \cdot n_i^{crust} \cdot c_{i,k} \cdot M^{crust}$. These compartment-specific values propagate directly into resource chemical exergy via Eq. 5, as indicated by the dashed red arrow in Fig. 3.

A first robustness criticism arises here: spatial variations in elemental composition affect the intrinsic work potential, yet no region-specific dead states exist (e.g., for Siberian soils or the French Jura). This limitation suggests that partial reference environments may be more appropriate to LCA, particularly given recent advances in regionalised LCA (Mutel & Hellweg, 2023).

A second, more fundamental criticism concerns Szargut's selection of ERS. Within each compartment, the chosen ERS must balance abundance and chemical stability—a subjective criterion that leads to inconsistencies. For example, the stable species Sb_2O_5 is used for antimony despite greater abundance of Sb_2S_3, while for nitrates, scarce but stable species like $Ca(NO_3)_2$ are discarded in favour of more abundant species to compute b°_{Ca}, b°_{Na}, b°_{K} (Szargut et al., 2005). This reveals the core contradiction noted by (Gaudreau et al., 2012): Szargut's environment is simultaneously treated as an equilibrium 'dead state' (to justify the exergy reference) and as a non-equilibrium empirical reality (to justify the choice of abundant species over stable ones).

Furthermore, each ERS must correspond to one SRS (Szargut, 1989), this constitutes an additional calculation stage. The least reliable computational path noted in the literature is the crustal one (Rivero & Garfias, 2006), (A2+A6 in Fig. 3), given by Eq. 7:

$$b^{\circ}_{ch,k} = -\mathrm{RT}\ln\left(\frac{1}{l_{i,k}} \cdot n_i^{crust} \cdot c_{i,k} \cdot M^{crust}\right) \qquad Eq.7$$

This approach suffers from several well-documented limitations. First, n_i^{crust} is reported as a single value without uncertainty, despite the upper continental crust being mineralogically

heterogeneous and complex (Hystad et al., 2017). Second, the method assumes ideal solution behaviour ($\gamma_k = 1$, A2), a major assumption (Rivero & Garfias, 2006). Third, the product $n_i^{crust} \cdot c_{i,k}$ implicitly assumes that a single reference species represents each element, ignoring the possibility of that element existing stably in multiple mineral forms. This "one ERS per element" rule, combined with Szargut's subjective stability threshold, introduces further arbitrariness (Gaudreau et al., 2012). The combined effect of these limitations significantly undermines the robustness of the resulting $b_{ch,k}^{\circ}$ values.

3.3.1.2 Step 2: Standard Reference Species Exergy

Chemical exergy of SRS is computed by sequential back-calculations. Some SRS are also ERS, so their exergies are known from Step 1; for SRS formed solely from ERS (e.g., Si with O2 and SiO2), Eq. 6 can be directly applied. These values are then cascaded through Eq. 5. However, the values obtained inherit robustness criticisms from the choice of ERS reference environment. For example, with a seawater reference environment, nickel's ERS is Ni^{2+} and yields a chemical exergy of 232.7 kJ/mol (Stanek, 2017; Szargut et al., 2005) while with NiO as ERS in the continental crust, the exergy value goes to 242.6 kJ/mol (Rivero & Garfias, 2006)—a 4.3% discrepancy.

Despite these documented variations, no study provides estimated uncertainties for $b_{ch,i}^{\circ}$. We address this gap using alumina as a case study, comparing two reference species for aluminium: sillimanite (Szargut, 1989) and kaolinite ($Al_2Si_2O_5(OH)_4$) (De Meester et al., 2006). The detailed calculations are available in Online Resource 4. Reference exergies $b_{ch,k}^{\circ}$ are taken from (De Meester et al., 2006; Szargut et al., 2005) or HSC Chemistry 10.8 (Metso, 2026a) . Gibbs free energies of formation are sourced from the original studies, HSC, or FactSage (FactPS database). The sequential back-calculation proceeds as follows:

For Sillimanite:

$$(1)\ b_{O_2}^{\circ} = b_{O_2}^{\circ}$$

$$(2)\ b_{Si}^{\circ} = b_{SiO_2}^{\circ} - \Delta g_{rf,\ Si+O_2 \rightarrow SiO_2} - b_{O_2}^{\circ}$$

$$(3)\ b_{Al}^{\circ} = \left(b_{Al_2SiO_5}^{\circ} - \Delta g_{rf,\ 2\cdot Al+2.5\cdot O_2+Si \rightarrow Al_2SiO_5} - 2.5 \cdot b_{O_2}^{\circ} - b_{Si}^{\circ}\right)/2$$

For Kaolinite:

$$(1)\ b_{O_2}^{\circ} = b_{O_2}^{\circ}$$

$$(2.1)\ b_{Si}^{\circ} = b_{SiO_2}^{\circ} - \Delta g_{rf,\ Si+O_2 \rightarrow SiO_2} - b_{O_2}^{\circ}$$

$$(2.2)\ b^{\circ}_{H_2} = b^{\circ}_{H_2O} - \Delta g_{rf,\ H_2+0.5\cdot O_2 \rightarrow H_2O} - 0.5 \cdot b^{\circ}_{O_2}$$

$$(3)\ b^{\circ}_{Al} = \left(b^{\circ}_{Al_2Si_2O_5(OH)_4} - \Delta g_{rf,\ 2\cdot Al+4.5\cdot O_2+2\cdot Si \rightarrow Al_2Si_2O_5(OH)_4} - 4.5 \cdot b^{\circ}_{O_2} - 2 \cdot b^{\circ}_{Si} - 2 \cdot b^{\circ}_{H_2}\right)/2$$

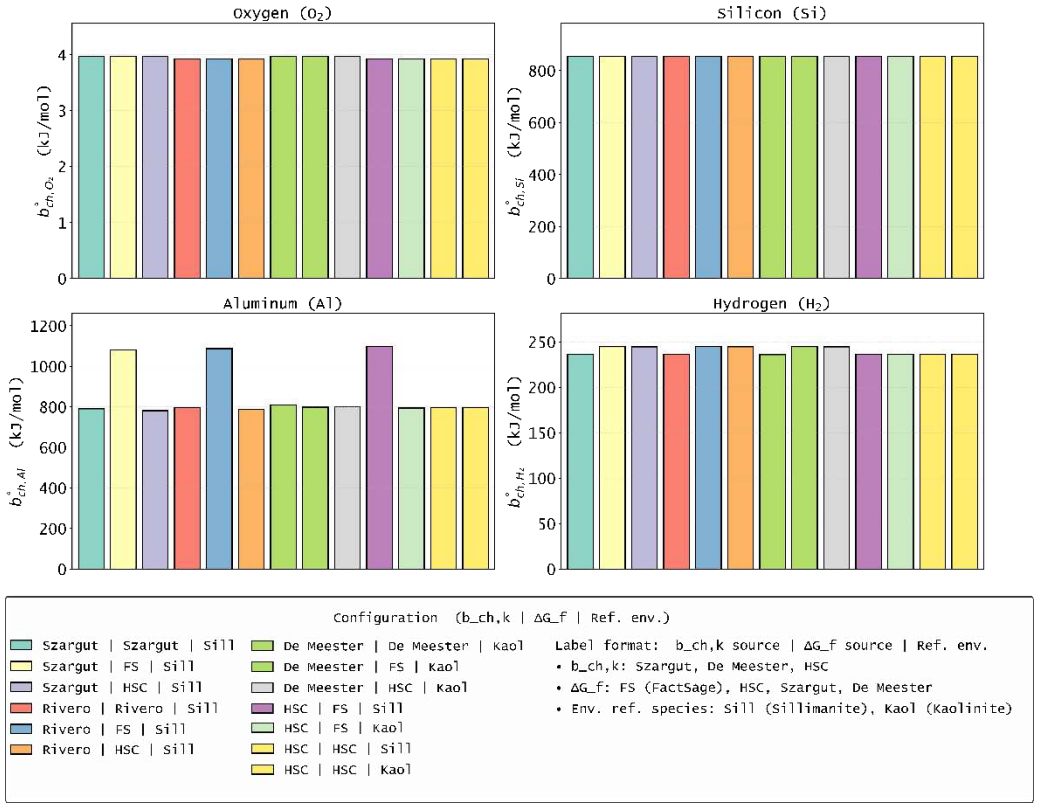


Fig. 4: Standard reference species chemical exergy ($b^{\circ}_{ch,i}$) of O_2, Si, Al, and H_2 across ten configurations.

The Fig. 4 results reveal substantial differences in calculated SRS chemical exergies depending on the modelling assumptions. To isolate the contribution of each assumption, Fig. 5 displays the paired-effects sensitivity analysis. The factors varied were: (i) the source of standard chemical exergy values $b^{\circ}_{ch,k}$, (ii) the source of the Gibbs free energies of formation (Δg°_{rf}), and (iii) the selected ERS.

The sensitivity analysis shows that $b^{\circ}_{ch,i}$ sensitivity is element-specific. O_2 is essentially insensitive (maximum effect: 0.05 kJ/mol). Si is relatively stable, exhibiting mean paired effects of 1.28 kJ/mol for the $b^{\circ}_{ch,k}$ source and 0.15 kJ/mol for the Δg°_{rf} source; the ERS choice has no effect (SiO2 in all cases). H_2 shows intermediate sensitivity (mean paired effects of 8.5 kJ/mol and 4.3 kJ/mol respectively).

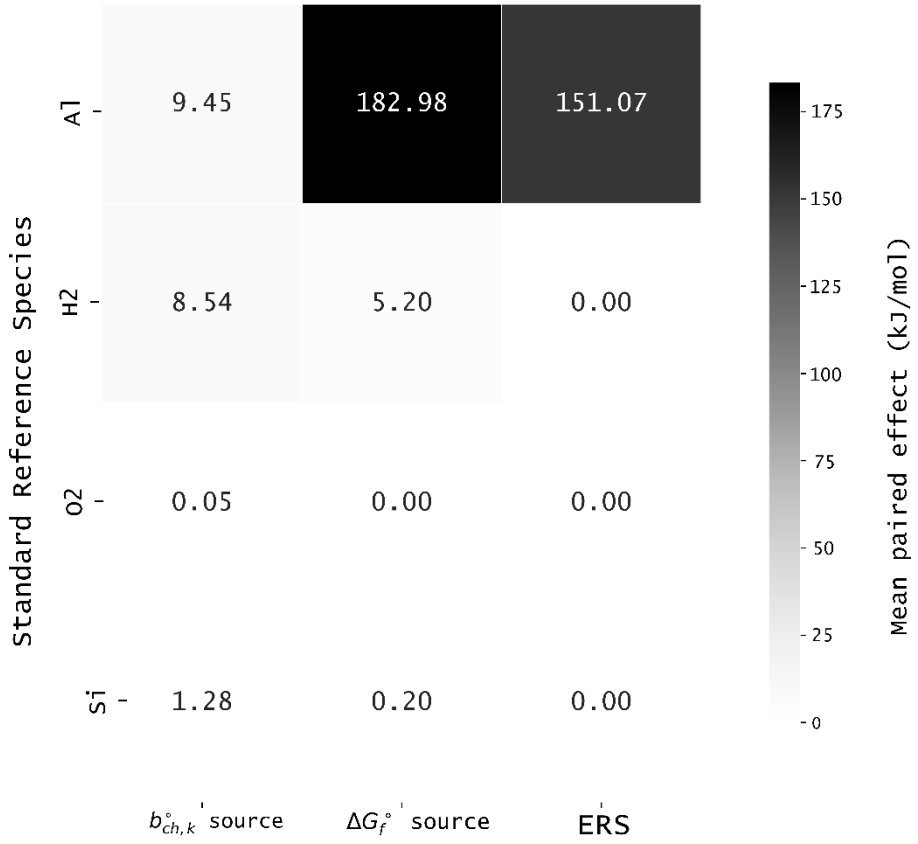


Fig. 5: Paired-effects sensitivity analysis of standard reference species chemical exergy ($b^{\circ}_{ch,k}$) for O_2, Si, Al and H_2. Mean paired effects quantify the average change induced by varying one modelling choice ($b^{\circ}_{ch,k}$ source, ΔG°_f source, or ERS) while holding the remaining factors constant. Standard deviations indicate interaction effects between modelling choices.

In contrast, Al is highly sensitive to all three factors. The dominant contribution is the Δg°_{rf} source (mean effect: 183 kJ/mol; maximum: 301 kJ/mol shown in Fig. 4; computed over 5 paired combination at fixed $b^{\circ}_{ch,k}$ and ERS), followed by the choice of ERS (151 and 302 kJ/mol, respectively). The $b^{\circ}_{ch,k}$ source has a smaller influence (9.4 and 14.8 kJ/mol, respectively),

indicating consistent calculation across sources despite relying on the discredited Eq. 7, and that the exergy of reference species (scarcity dimension) is low compared to the chemical effects (ΔG_{fr}°). This instability reflects the cumulative propagation of uncertainties through the assumption hierarchy visualised in Fig. 3: computing b_{Al}° requires the exergies and thermodynamic properties of multiple aluminosilicate reference species, so uncertainties propagate through several calculation steps. In general, computing $b_{ch,i}^{\circ}$ involves 86 different ERS: 10 gaseous, 23 aqueous, and 53 mineral (Stanek, 2017). In total, 584*1* independent variables must be manipulated, each carrying its own uncertainty, which collectively reduces the robustness of the metric.

3.3.1.3 Step 3: Mixing Exergy Contributions

As Fig. 3 shows, chemical exergy of a resource combines two thermodynamic components: the scarcity value of the reference species (ERS from Step 1) and the reaction term linking them (ΔG_{rf}°) in Eq. 5 and 6). This second term captures the chemical bonds and interactions that must be overcome to recover pure metals. The dashed red arrow from Case 2 to the Gibbs free energy box shows that this reaction can itself be viewed as a mixture of target species involving chemical reactions, a connection the other metrics do not make.

The mixing term calculus adds another layer of complexity. For a product system with n_F flows, the total number of input variables becomes $n_v = n_F + 584$. The nature of this term depends on the flow type.

For pure compounds, ΔG_{rf}° can be obtained from experimental (calorimetry, equilibrium measurements, electrochemical techniques) or theoretical approaches (ab initio quantum chemistry, statistical mechanics, group additivity methods), as illustrated in Fig. 2. Ideally, a study of the resource reaction formation from the ERS would be preferred, but this remains data scarce. Alternatively, ΔG_{rf}° values can be found for the reaction formation from SRS (involving intermediate Step 2). For complex minerals (e.g., platinum group minerals; (Olivotos & Economou-Eliopoulos, 2016)), thermodynamic data are frequently scarce or unavailable,

1 $\sum_{i=env\ compartment}^{3}(\mathrm{n}_{\mathrm{variables}} * \mathrm{n}_{ref\ species}) = 2 \cdot 10 + 5 \cdot 53 + 13 \cdot 23 = 584$ variables for getting the 86 chemical reference substance exergy. Imagine there is n_F flows to characterise, with the Szargut methodology, it corresponds to n_F Gibbs free energy of formation ΔG_f°.

necessitating estimation methods or commercial databases (Li et al., 2017). This dependency on curated or proprietary data compromises transparency.

For ores and mineral mixtures, ideal mixing is applied: $b_{mix-id} = \Delta g_{mix} = -T^{env}\Delta s_{mix} = -\sum_{i,j} RT^{env}\, x_{i,j} \ln x_{i,j}$ (Dewulf et al., 2007; Valero Capilla & Valero Delgado, 2014), ignoring chemical interactions: $b_{mix-ex} = \Delta g_{ex} = \Delta h_{mix_{|p_{cst}=p^{env}}} - T^{env}\Delta s_{ex} = -\sum_{i,j} RT^{env}\, x_{i,j} \ln \gamma_{i,j}$ as criticised by (Hack & Reuter, 2025).

This ideal mixing assumption (A2 in Fig. 3) neglects precisely the linkage effects that the reaction formation pathway captures for pure compounds. For particulate flows in liberation processes, emerging methods quantify excess entropy from automated mineralogy relative to a fully liberated reference (Fernandes et al., 2021). Determining this excess mixing term remains essential to enhance robustness.

Despite these complexities, the chemical exergy, and more extensively the exergy metric offers extensive resource coverage (see Online Resource 3). Coverage can be further expanded to land and marine surfaces by accounting for the exergy deprived from the ecosphere (Dewulf et al., 2007; Taelman et al., 2014), or via emergy (Wang et al., 2020).

3.3.2 Exergo-ecology Metrics

The primary component of the ERC and the TheRy is the natural replacement exergy, $\Delta b_{c,i}$ (See Fig. 2). The concept originates from Faber's work on the separation of ideal mixtures (De Vilbiss & Brown, 2015; Faber, 1984; Rosa & Rosa, 2008). The specific formulation of concentration exergy, b_c, is given in Eq. 8:

$$b_c = -RT^{\circ}\left[\ln(x_i) + \frac{1-x_i}{x_i}\ln(1-x_i)\right] \quad Eq.8$$

Where R is the ideal gas constant, T° is the standard temperature, and x_i is the molar fraction of the resource element i in the mineral mixture, considered as a solution j. The natural replacement exergy, $\Delta b_{c,i}$, is then the variation of concentration energy between two molar fractions x_c (Thanatia dead state) and x_m (mine state), expressed as:

$$\Delta b_{c,i} = RT^{\circ}\left[\ln\frac{x_c}{x_m} + \ln\left(\frac{(1-x_c)^{\frac{(1-x_c)}{x_c}}}{(1-x_m)^{\frac{(1-x_m)}{x_m}}}\right)\right] \quad Eq.9$$

As shown in Fig. 3, the concentration energy concept follows Option O2 with assumptions A2 (ideal mixture) and A3 (binary representation, where the reservoir is treated as the target species

ii and a collective "rest" fraction). Physically, it represents the total Gibbs free energy of mixing the binary system, scaled per mole of the target resource i—i.e., the theoretical work required to fully separate i from a finite reservoir, normalised by the amount of i recovered. In contrast, $b^{\circ}_{ch,k}$ (Option O1 alone), concentration energy incorporates additional assumptions, placing it lower in the robustness hierarchy.

The complexity of the metrics hinges on determining an element's molar fraction, x_c, ased on average concentrations of the Thanatia's model (Valero, Agudelo, et al., 2011; Valero, Valero, et al., 2011). Required input data include the average concentration of each element in its host mineral within a regional ore deposit, and crustal chemical composition estimates from (Rudnick & Gao, 2003) and mineralogical compositions from (Grigor'ev, 2007).

These values are subject to uncertainty, not reported as far as the authors know. Otherwise, a list of the major assumptions behind the computation of 67 elements is provided in section 5 of (Valero, Valero, et al., 2011). A further robustness criticism arises from the assumption behind the Faber formula displayed in Eq. 8 (Faber, 1984), which assumes that volumetric fractions equal molar fractions in the Earth's crust (De Vilbiss & Brown, 2015). Unlike chemical exergy of a resource, which accounts for both scarcity and chemical linkage effects between species (as shown by the dual pathways in Fig. 3), concentration exergy captures only the scarcity dimension.

On resource coverage, $\Delta b_{c,i}$ can characterise every resource that originates from the ground, even fossil-based resources (extension of the ERC methodology developed by (Whiting et al., 2017)). However, land or heat resource flows cannot be quantified (more detailed in Online Resource 3).

3.3.3 Statistical Entropy

As shown in Fig. 3, SE and RSE originate from Case 2, where the resource is treated as a mixture of target species—which inherently implies A4— and where mass fractions replace mole fractions (A5). SE is proportional to the Gibbs free energy of mixing: $H_{I|j} = -\Delta g_{mix,I}/(k_B T \ln 2)$. In terms of complexity, SE metrics require few input variables, i.e. for LCA, the mass fraction of the n_S substances inside the n_F LCA flows of a product system.

Nonetheless, SE robustness can be criticised because of its reliance on concentration alone. Recent work in mineral liberation analysis (Schach et al., 2024) demonstrates that particle-scale properties—including size distribution, density gradients, magnetic susceptibility, and surface wettability—fundamentally govern practical separation efforts requirements. Since these properties alter the actual encoding complexity (i.e., the minimum information required to isolate

resource-elements), concentration-based statistical effort representations may systematically misestimate real separation costs in cases where liberation state varies significantly from composition. Rechberger's formalism therefore rests on one assumption: for reversible separation, particle-level properties can in principle be managed by ideal technology, so that recoverability is ultimately governed by element concentration alone.

A second limitation arises from SE's elemental uniformity: e.g. diluting iron identically to gold yields identical entropy values, despite their different physical value—as captured by other RA metrics like $b_{ch,i},\ \Delta b_{c,i}$. It means that if the gold resource element is by magic replaced by iron, and inversely, in all the smartphone's components of (Roithner et al., 2022), the SE value will remain the same. Therefore, the environmental difficulties of getting the elements—influenced by their chemical stability within the ore, their scarcity (e.g. gold is 10^6 more scarce than iron (Palacios et al., 2019)), or their instrumental value are disregarded. We will need an additional statistical factor that weights the element SE in function of all the others.

The use of H_{max} may convert the binary unit to a "normalized unit", H^{rel}. Practically, it means that the measure of the statistical efforts can be compared across distributions, as tested by the statistical community as reported in (Wilcox, 1973). Computationally, the RSE (H^{rel}) is obtained by changing the logarithm base 2 to n_s in Eq. 1, without requiring additional computational steps. This normalised SE metric permits the analysis of multi-resource-made systems, hence a continuity in systems' comparison.

When a rest fraction is included (A3 in Fig. 3), the logarithmic base adjusts to $n_s + 1$ for RSE. This approach is debatable, as neglecting the rest fraction's composition may undermine objectivity, despite enabling a focus on selected resource elements (Cencic & Rechberger, 2024).

On resource coverage, SE is applied only to incorporated flows—mass or volume-based resources (Amatuni et al., 2024)—including water, metallic ores, minerals, fossil fuels, nuclear ores (by isotopes), air, and biomass (Dewulf, Mancini, et al., 2015). Consequently, energy and land cannot be characterised (more details are provided in Online Resource 3).

For all the metrics where detailed concentrations are required, there is a data accessibility issue. In LCA practice, it is common that concentrations in products are not reported together with input/output flows at the process level, and in resulting LCI datasets. A key associated challenge is access to complete data, in some cases in the context of potential confidentiality. The rest fraction of the SEA method enhances transparency by enabling the sharing of sensitive industrial

data. However, it also limits reproducibility and prevents impact-specific inventories requiring detailed flow compositions to environmental compartments.

ΔH^{rel} of Eq. 4 is described as "the tendency of a [set] substance to be accumulated or diluted by a process" (Cencic & Rechberger, 2024). For our grid of analysis, it corresponds to the supplementary average amount of encoding operation required to harvest the resource a product system is transforming—therefore, SE or RSE are proxies of the difficulties in obtaining the chemical elements within the flow. Their variation should directly inform the resource AoP, as resource unavailability reduces the potential value held for future needs. The assumption hierarchy in Fig. 3 confirms this: SE/RSE carry the largest assumptions (A2, A3, A4, A5), trading thermodynamic fidelity and the ability to capture chemical linkage effects for computational simplicity. They yield an informational proxy rather than a thermodynamic measure of resource quality.

3.4 Critical Analysis: Frameworks

Two frameworks that optimise systems based on how to limit dissipation have been reviewed: the information dissipation with SEA, and the ECA with the exergy cost theory that formalises the design of exergy efficient systems.

3.4.1 Exergy Cost Analysis Framework

The exergy cost theory—and the underlying thermoeconomics—links monetary cost with thermodynamic irreversibilities (Sciubba & Wall, 2007). To quantify the cumulative exergy consumption, which traces "the total chain of processes from natural resources to the considered product" (Szargut, 2005), a productive structure is required which translates the physical structure's input/output flows into Fuels and Products per UPr (Tsatsaronis & Winhold, 1985), analogous to an LCA system model (term used according to ecoinvent nomenclature (Wernet et al., 2016)). This productive structure is grounded in four rules (Valero et al., 1986), complemented by the waste rule to address both external and internal irreversibilities (Torres & Valero, 2021). The exergy cost theory productive structure is fully operationalised in TAES lab software (Torres et al., 2023), and partially in HSC Chemistry (internal only) (Llamas et al., 2024; Metso, 2026b).

3.4.1.1 System boundary (G&S)

The resource rule states that flows described as "in absence of external assessment", i.e., without any supply chain at input or output, must be characterised by a cost equal to their exergy value (intrinsic physical potential). These flows are the system's resources (Torres & Valero, 2021). In

LCA terms, this concerns both elementary flows and the reference flows of empty (cut-off) Unit Processes (UPrs) and of the functional unit. The system boundary is thus explicitly defined by identifying all flows that are not connected to a modelled transformation UPr.

3.4.1.2 Multi-functionality (G&S)

The co-product rule distributes the cost of co-products based on their intrinsic exergy content (Torres & Valero, 2021). Mathematically, this translates into a linear system where the cost of each co-product flow is proportional to its exergy share. This offers a physically grounded solution for multifunctionality resolution in attributional LCA, avoiding subjective partitioning factors.

3.4.1.3 Waste considering (G&S)

Thermoeconomics also attribute to productive units the cost of waste formation and treatment in dissipative units (Torres & Valero, 2021). Five methods exist (Torres et al., 2023); the 'exergy' method aligns with LCA: both attribute waste treatment cost/impact back to the process that generated the waste, based on external resources consumed.

3.4.1.4 Irreversibility tracking (LCI modelling phase)

Direct irreversibilities per UPr are internal $I_{u,int} = F_u - P_u$; and external $I_{u,ext} = R_u$ (cumulative exergy inputs crossing the system boundary attributed to waste-producing processes). Dissipation, as with internal exergy irreversibilities, is considered at the UPr level and may not be modelled by a specific flow but discovered by the comparison of the other exergy values.

3.4.1.5 Exergy cost (LCI-LCIA results obtentions)

The exergy cost (indicated by an asterisk) is obtained by applying the mathematical framework of exergy cost theory. Links between flows and processes are treated following the exergy cost theory rules, leading to a cost, parallel to an LCIA score in LCA (highlighted in Fig. 1). The product costs of a UPr, P_u^*, equals the cost of its fuels F_u^* plus residues R_u^*; the cost is conservative, analogous to path contribution analysis in LCA (van der Meide et al., 2025).

3.4.1.6 Hotspot identification (Interpretation)

Since no background data exist, the direct exergy irreversibilities $I_{u,int} + I_{u,ext}$ serve hotspots analysis. The unit exergy consumption, k_u, identifies direct losses (see Eq. 10) (Torres & Valero, 2021).

$$k_u = \frac{F_u + R_u}{P_u} = \frac{F_u}{P_u} + \frac{R_u}{P_u} = \left(1 + \frac{I_{u,int}}{P_u}\right) + \frac{I_{u,ext}}{P_u} \quad Eq.10$$

Ideal process has a $k_u = 1$. Higher values pinpoint hotspots.

Indirect exergy irreversibilities, involving exergy cost (F^*, P^* and R^*), can serve the hotspots analysis in ECA. However, this unit cost is of non-interest in LCA in which the impact of the output reference flows is equal to the sum of the input UPr product flows impact (impact conservation principle).

3.4.1.7 Thermoeconomic diagnosis (Interpretation)

Thermoeconomic diagnosis compares a reference state with an operating state (e.g., different temperatures or pressures) via multiple state definitions and resource cost tables (Torres et al., 2023). It computes malfunction costs and irreversibility variations, quantifying the fuel impact increase due to degraded performance, analogous to a combined scenario and contribution analysis in LCA.

3.4.1.8 Integration with LCA

Exergy cost formalism adds five features missing in resource-oriented LCA: (1) a resource rule for boundary definition (G&S), (2) a co-product rule with mathematical translation for multi-functionality (G&S), (3) direct irreversibility tracking per UPr (LCI-LCIA modelling), (4) hotspot identification via the principle of unit direct and indirect cost (Interpretation), and (5) thermoeconomic diagnosis for scenario analysis (Interpretation).

3.4.2 Statistical Entropy Framework Irreversibilities

SEA requires a stage diagram as a system model. Construction starts from a physical MFA diagram: flows are predefined per UPr and directly correspond to the function of the MFA (e.g., study the copper stocks with the European Union (Spatari et al., 2002)): the system boundary is limited to the foreground (opposite to LCA's inclusion of background).

In LCA, the defined technology matrix **A** (see Fig. 1) is not the model itself. Whereas MFA diagrams already contain quantified physical flows, the amount of each technosphere flow in LCA is unknown until A is scaled to satisfy the demand vector materialising the functional unit (Heijungs & Suh, 2002). Consequently, UPrs may appear multiple times in the resulting physical supply-chain representation. Hence, stage-diagram construction is not directly applicable to LCA. However, the variation in RSE between UPR, ΔH_{UPr}^{rel} of Eq. 2, may still provide valuable insights, even if a stage-level analysis cannot be performed.

4 Discussion

This section returns to the two questions posed in the Introduction and consolidates their answers. It then examines the practical conditions for implementing them within current Life Cycle Inventories, and closes on the limitations of the review approach.

4.1 Question 1: The Requirements for Resources Physical Potential Values

The outcomes of Section 3.1 demonstrated that RA metrics can be classified according to whether they correspond to a direct measurable property of the resource flow (yellow rounded boxes in Fig. 1 and 2), or to derived properties that result from a chain of applied frameworks to measurable and intermediate derived metrics (blue rounded boxes in Fig. 1 and 2). The RA metrics critically analysed were all derived metrics, whereas they are in principle measurable quantities. Indeed, calorimetric experiments reproducing a series of reversible chemical reactions and diffusion processes that bring the resource into equilibrium with ERS can, in principle, yield the enthalpy changes underlying chemical exergy, although such measurements have been argued impracticable because the dead state exists only as a non-equilibrium mutual stationary state (Simpson & Edwards, 2011). Similarly, SE can, in principle, be derived from experimentally measured substance and particle distributions obtained through compositional analyses, laser diffraction, SEM-based mineral liberation analysis, or computed tomography (Schach et al., 2024).

Section 3.2 reviewed chemical exergy $b^{\circ}_{ch,j}$, concentration energy $b_{c,i}$ and SE/RSE. They are all derived from intrinsic thermodynamic or statistical properties of resource flows and can therefore provide a physically grounded link between inventory tracking and resource value loss, consistent with our initial objective.

Fig. 3 summarises their physical basis. $b^{\circ}_{ch,j}$ through $b^{\circ}_{ch,k}$, and $b_{c,i}$ account for the scarcity of resources (greater scarcity corresponds to greater resource value). Among these, $b^{\circ}_{ch,k}$ is rooted to the Gibbs free energy of mixing with fewer assumptions than $b_{c,i}$. The linkage effect associated with the recoverability of target substances embodied in resources is captured by $b^{\circ}_{ch,j}$ through both ΔG°_{fr}, as well as by the SE/RSE metrics. ΔG°_{fr} captures the thermodynamic contribution arising from the chemical association of the embodied SRSs (if Step 2, if not the ERSs) within the resource, and thus reflects the energetic requirement for dissociation or reforming (reversibility) of the compound. In contrast, SE approximates this effect solely from the mass distribution of selected substances within the resource (A5). Moreover, SE/RSE can be related to the Gibbs free

energy of mixing, albeit under at least three simplifying assumptions and a scaling factor (A2, A4, and A5).

On this basis, $b^{\circ}_{ch,j}$ have been analysed as the most scientifically robust candidate metric that proxies the larger variety of potential resource value dimensions (geological scarcity and effects of stability and instrumental value).

Flow exergy can also be assigned to product flows. Their intrinsic exergy values, however, differ substantially from the cumulative exergy required to produce them. These observations result from the application of both LCIA methods like CExD (Lourioux, 2025) or CEENE, or ECA methods (Valero & Valero, 2013). For illustration, one may consider a copper cathode product: its specific chemical exergy is approximately $b_{Cu} = 2.11\ MJ.kg^{-1}$, whereas its CExD (for non-renewable material and energy resources) associated with the ecoinvent 3.12 cradle-to-gate production datasets ranges between $61\ MJ.kg^{-1}$ in Sweden from gold mine operation and refining and $344\ MJ.kg^{-1}$ from the cobalt production process of geography "global" (calculus detailed in Online Resource 4). These results remain logical and strengthen the robustness of exergy. The exergy of copper — its maximum perceivable work — equals the work invested to produce it only if every production step is reversible. Since real transformations are irreversible, the two quantities differ. However, this potential work—exergy—can be captured by human economies, reflecting a physical potential instrumental resource value (Verones et al., 2017).

$b^{\circ}_{ch,j}$ remains the target of robustness criticism; the choice of reference environment, ERS, and the thermodynamic properties used for its computing lead to differences (see Fig. 4 for Al). Secondly, the exergy theory is extremely complex, and critics may be raised on the transparency dimensions caused by lack of public thermodynamic data. Furthermore, in terms of practicability, the linkage term of complex compounds (e.g., the ΔG°_{fr} of complex waste products) is sometimes not provided by any database. In addition, there is no recommended technique yet to quantify the difference in exergy between a uniform system and a system composed of comminuted particles (comminution exergy). SE can be proposed to compute this comminution exergy mixing term, e.g., through the statistical distribution of a separation property with trump curves (Schach et al., 2024).

Furthermore, in relation to LCA, the exergy assigned to input mineral resources remains contestable. CExD assigns a single median value (0.63 MJ-eq) to all metal-bearing ores, based on the metal mass fraction and an economic allocation. CEENE characterises only the mineral

fraction and assumes that the gangue remains chemically unaltered in the tailings. This ignores the physical value that gangue retains today, for instance as construction material or in mining backfill applications (Keskin et al., 2026).

Despite being less physically reliable, SE retains valuable features for LCA, notably the rest fraction and local H_{max}. The rest fraction—although avoidable (Cencic & Rechberger, 2024)—can address gaps in current LCI database flow compositions, while local H_{max} can enable comparison of product systems for which different amounts of chemical element concentrations are recorded. This opens the question of whether SE can be reframed as a proxy for losses of economically or critically valuable elements induced by system configuration. Since $H_{I|j}^{+}$ (see Eq. 1) lacks a weighting factor for pure elements, a proxy term accounting for economic value may be introduced to correct the mass distribution of substances relative to a reference. Eq. 11 compensates for this lack by mimicking the $\gamma_{i,j}$ used to compute the Gibbs free energy of non-ideal mixtures; an economic activity coefficient $\omega_{i|j}$ that translates the relative economic importance of targeted substance can be added to the RSE formula:

$$H_{I|j}^{\mathrm{rel}+,economic} = -\frac{M_j}{M_{stage}} \sum_{i=1}^{n_s+\delta} c_{i|j} \log_{n_s+\delta}\left(\omega_{i|j} \cdot c_{i|j}\right) \quad eq.11$$

In conclusion, possible considerations of the reviewed RA metrics in resource-oriented LCA studies should strike the right balance between applicability (larger potential for SE/RSE) and robustness of the fundamental concepts it relies on (larger for exergy).

4.2 Question 2: Compliant Goal and Scope for Resource-Oriented LCA

The exergy cost framework reviewed in Section 3.4.2 provides a physically grounded basis for resource-oriented LCA. Its application requires that the G&S phase explicitly aligns with thermodynamic accounting principles.

Unlike established LCIA methods such as CExD or CEENE, which apply CFs to elementary flows using the conventional LCA mathematical framework (see Fig. 1), future flow physical value approaches can implement two key rules from exergy cost theory: the resource rule and the co-product rule.

The resource rule (César Torres and Valero 2021) defines the system boundary by identifying flows without an upstream supply chain—these inputs and outputs carry an intrinsic cost equal to their exergy value; these flows can be elementary or products. In conventional LCA, cut-off criteria

(Heijungs & Suh, 2002) may treat certain input waste or output product flows as burden-free, even though they retain physical content and thus value for the product system or for future systems. Within a resource-oriented LCA perspective, this implies that such product flows require characterisation—a topic of active debate both conceptually (Heijungs, 2024) and operationally (Heijungs, 2026; Sacchi et al., 2025, 2026). This boundary definition supports circularity assessment by enabling the tracking of all resource value circulation.

The co-product rule offers some potential for improving state-of-the-art practice with regard to multi-functionality issues. ISO 14044 requires that partitioning reflects "quantitative change in the products or function delivered by the system" (ISO14044:2006). When the function is understood as thermodynamic potential, exergy reflects the measure of that quantitative change. ECA partitions cumulative exergy consumption among co-products in proportion to their exergy content. This logic extends to any resource-oriented LCIA method: resource use represents a loss of potential value; the burden attributed to each co-product should reflect how much of that value it preserves and carries forward. Accordingly, the Allocation Factor (AF) for co-product j shall equal its share of the re-available potential value generated by the multifunctional activity, as advocated by (Mas-Fons et al., 2026; Reuter et al., 2023), and expressed in Eq. 12:

$$AF_j = \frac{q_j \cdot |CF_j|}{\sum_j q_j \cdot |CF_j|} \quad Eq.\ 12$$

Where q_j is the amount of the co-product in the UPr expressed in the LCI's physical unit and $|CF_j|$ is the absolute characterisation factor representing the physical potential value.

4.3 Needed Improvement of the Life Cycle Inventories

The G&S rules proposed in Section 4.2 impose new data demands on LCIs. Three requirements follow directly:

- Elementary and product flow characterisation: SE- or exergy-based CFs require physical properties of resource flows (elemental composition, ΔG°_{rf}) that are not systematically reported in current LCI databases. For dissipation-based LCIA, this extends to at least emission flows.

- Co-product characterisation for partitioning: the co-product rule (Eq. 12) requires exergy or SE values for each co-product of multifunctional UPrs; without these, the AFs cannot be computed.

- Uniform application across foreground and background: ISO 14044 requires that allocation procedures be applied uniformly throughout the product system. The co-product rule must therefore be implementable not only in the foreground model but also in background datasets.

The foreground task depends on the LCA practitioner's expertise and can be challenging for exergy-based AFs when co-products involve complex phase chemistry—for instance, metallurgical slags and off-gases in metallurgical-grade silicon production (Bartie et al., 2021)—which demands adequate determination of solution chemistry (Hack & Reuter, 2025), often hosted in commercial thermodynamic databases.

Background databases present a more structural barrier. For ecoinvent, elemental composition is sporadically recorded, with only a mandatory minimum property list uniformly required (Wernet et al., 2016); ΔG_{rf}° values are absent. Other databases do not even permit the recording of flow properties. The need for concentration data has been raised repeatedly (Beylot et al., 2021; Heijungs, 2024), and compositionally balanced LCIs have been demonstrated via resource flow analysis in isolated case studies (Beylot et al., 2021; Dewulf et al., 2024; Lai & Beylot, 2023). Yet these remain exceptions, not standard practice.

If both LCIA characterisation and multifunctionality partitioning rely on the same physical value proxy, the attribution of resource impacts across the product system is internally consistent. Achieving this consistency, however, requires a parallel evolution of LCI databases to supply the necessary flow properties. Without this, neither resource dissipation nor circularity performance can be robustly measured from a life cycle perspective.

4.4 Limitation of the current study

The principal limitation stems from the PRISMA screening process (Section 2.1). The keyword strategy targeted metallic products, resource value loss, and physically grounded methods. While this ensured alignment with the research goal, it may have excluded relevant RAM using different terminologies. Notably, emergy-based methods (Odum, 2000) did not appear in the screened IE literature and were thus not critically analysed. Future work could broaden the search to assess whether emergy or other physically grounded proxies offer complementary features for resource-oriented LCA.

A second limitation concerns the classification scheme (Section 2.1.3). Distinguishing metrics from frameworks is analytically useful but involves subjectivity, as a derived metric always depends on the framework that computes it, and vice versa. The boundary blurs where metric and computational structure are tightly coupled, as in ECA. This warrants caution when extending the classification to RAM not reviewed here.

A further limitation concerns the evaluation criteria (Section 2.2). Metrics were assessed conceptually for robustness and transparency, but without formal uncertainty analysis, despite a preliminary sensitivity study for chemical exergy in Section 3.3.1. Finally, framework features—system boundary setting, multifunctionality resolution, and hotspot identification—were examined in principle but not tested against a common case study. Both additions would strengthen the comparative basis of the conclusions drawn.

5 Conclusions and Perspectives

We have conducted a non-exhaustive literature review on how to improve the quantification of the impacts on the resource AoP based on RA metrics and frameworks reviewed within the IE discipline with the screening PRISMA process.

This study highlighted the common roots of the reviewed RA metrics in the Gibbs free energy of mixing. Exergy emerged as the most robust metric for proxying the physical value of a resource. It is grounded in the laws of thermodynamics with fewer assumptions, and it reflects both the scarcity and the linkage effects of chemical elements, two dimensions that determine the accessibility of a resource's value. Furthermore, as it is defined for reversible decomposition, it also reflects a resource's potential instrumental value. We must note that SE is less robust but offers higher applicability in cases of incomplete concentration data.

The exergy cost theory provides the rules for setting exergy analysis, and these rules are analogous to the Goal and Scope of LCA. The system boundary of LCA should extend to unmodelled activities according to the “resource rule”, and the allocation strategy is inherent to the cost—exergy, in ECA— following the “co-product rule”. If this logic is operationalised, it will signify that the resource value made inaccessible to other product systems (LCIA score attributed to a reference flow of a multifunctional unit process) will be shared in relation to the resource value delivered to other product systems. Since all wastes and co-products of a multifunctional unit process embody a share of the total value used to create their own value, this approach ensures that

the impact is attributed in proportion to each share of embodiment, thereby bringing ontology in resource-oriented attributional LCA studies.

However, these upgrades of current exergy-based LCIA methods, in view of assessing intrinsic circularity with a decision-relevant metric, require deep improvement of LCI datasets. For exergy, this would include exergy of natural resources, cut-off product flows, and co-products of multifunctional UPrs. More structurally, elemental composition and ΔG_f° values must become standard properties in LCI databases. This parallel evolution is necessary for the proposed characterisation and co-product partitioning to be applied uniformly across foreground and background systems. It would require a deep, structural, change to current resource-oriented LCA practice on data, at the Goal and Scope definition, and therefore the underlying LCI and LCIA phases; a change that is necessary for resource indicators to be truly supportive of sounder decision-making.

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Online Resources

Online Resource 1: This online resource provides PRISMA literature screening details, including Scopus search keywords, screening criteria applied, annotated document list (79 items), and the PRISMA flow diagram (XLSX file).

Online Resource 2: This online resource provides the literal and mathematical abbreviations used in this article, along with some additional information on how statistical entropy used in material flow analysis is correlated to information theory (DOCX file).

Online Resource 3: This online resource provides the critical review matrix that contain the classified criticisms and comparative analysis of the reviewed RAM metrics and frameworks (XLSX file).

Online Resource 4: This online resource provides the Jupyter notebooks used to produce Figures 4 and 5 and the code to obtain the CExD scores used for comparison in the Discussion section (IPYNB files), along with the underlying calculations, offering

additional details for readers interested in the theoretical background (https://doi.org/10.5281/zenodo.23399016).

Fig. Legends

Fig 1. Legends [: Example of how an LCIA resource-oriented method will be classified according to the framework developed. Elementary Flows (EF) and Product Flows (PF) indicate what is the flow type the metric addresses, e.g., chemical exergy addresses mineral resource EFs within the CEENE method, and a CEENE score address any kind of PFs.]

Fig 2. Legends [Classification of screened RAM components. Sky blue rounded rectangles represent metrics which could be considered for use to derive LCIA Characterisation Factors. Bluish green rectangles represent mathematical frameworks relevant to goal and scope definition, and LCI applied to resource-oriented LCA studies.]

Fig 3. Legends [Diagram maps of the hierarchical relationships between Gibbs free energy change of formation (thermodynamic root) and reviewed RA metrics. Thermodynamics foundations are represented within blue boxes. Different resource treatment cases are represented with grey boxes: Case 1 for resources within environmental compartments, and Case 2 for resources viewed as mixtures of target species. Green boxes are representing reviewed metrics. Assumptions (A1–A7) and operational options (O1–O2) are annotated throughout. The legend clarifies symbols, assumptions, and methodological options.]

Fig 4. Legends [Standard reference species chemical exergy ($b^{\circ}_{ch,i}$) of O_2, Si, Al, and H_2 across ten configurations.]

Fig 5. Legends [Paired-effects sensitivity analysis of standard reference species chemical exergy ($b^{\circ}_{ch,k}$) for O_2, Si, Al and H_2. Mean paired effects quantify the average change induced by varying one modelling choice ($b^{\circ}_{ch,k}$ source, ΔG°_{f} source, or ERS) while holding the remaining factors constant. Standard deviations indicate interaction effects between modelling choices.]

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