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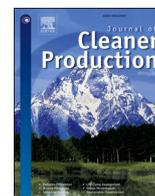
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A grave-to-cradle analysis of lithium-ion battery cathode materials using material and energy circularity indicators

Minerva Vierunketo^a, Anna Klemettinen^a, Markus A. Reuter^b, Annukka Santasalo-Aarnio^c, Rodrigo Serna-Guerrero^{a,*}

^a Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, P.O. Box 16200, 00076, Aalto, Finland

^b SMS-Group GmbH, Eduard-Schloemann-Straße 4, 40237 Düsseldorf, Germany

^c Department of Mechanical Engineering, School of Engineering, Aalto University, PO Box 14400, FI-00076 AALTO, Finland

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ABSTRACT

The future demands for lithium-ion batteries required for powering the electrification transition in transportation and energy storage will lead to vast amounts of waste, demanding proper end-of-life strategies. As various recycling routes are continuously developed to address this issue, a significant challenge is the fair comparison of processes entailing different unit operations and transformation stages. Indeed, the choice of metallurgical or direct recycling routes results in diverse materials flows and energy demands. To allow a suitable comparison between technologies, this work presents a grave-to-cradle analysis of cathode materials (i.e., lithium cobalt oxide) considering three recycling processes representative of the most popular routes (i.e., pyrometallurgical, hydrometallurgical, and direct recycling). Unlike previously published works, a system-level analysis of both material recovery and energy preservation was carried out using statistical entropy and exergy analysis, respectively. Furthermore, comparison of processes using exentropy, a recently proposed circularity parameter combining both material recovery and energy preservation, was performed for the first time. The results highlight the need of a robust multidimensional analysis of processes to properly determine their suitability according to the needs of the circular economy. When materials and energy preservation were analyzed independently, two different routes were identified as optimal. The need of a robust multidimensional analysis of processes to properly account for the goals of the circular economy is thus highlighted. Exentropy analysis suggested that direct recycling provides the optimum alternative in terms of energy utilization for the recovery of materials.

1. Introduction

In the search to reduce the environmental impact caused by greenhouse gas emissions, alternative technologies are needed to replace the use of fossil fuels for energy production and transportation (Thompson et al., 2020). One of the preferred technologies is lithium-ion batteries (LIBs), which enable the transition to cleaner energy production due to their high energy density, flexible design, long lifespan, safe handling, and low self-discharge (Wu et al., 2022; Zhang et al., 2019). LIBs were commercialized in 1991, and their worldwide demand and production rate have steadily increased ever since (Erakca et al., 2021). A sharp increase in LIB waste is thus expected in the near future (Zhang et al., 2019), especially due to the increase in electromobility (dos Santos et al., 2021). The fastest growing waste stream has reported to be waste electrical and electronic equipment (Lv et al., 2018), and spent batteries

are already the fastest growing type of waste electrical and electronic equipment (Rey et al., 2021). Therefore, proper end-of-life (EOL) treatment strategies for LIBs are urgently needed. Recycling is an important EOL strategy, as it is required when other suitable strategies, such as reuse and remanufacturing, cannot be applied anymore (dos Santos et al., 2021).

Adopting the terminology common in life-cycling assessment, the recycling of materials and their subsequent treatment to reach conditions suitable for their use in remanufacturing constitute a “grave-to-cradle” process. In the particular case study hereby presented, EOL batteries (grave) are treated and transformed to produce cathode active materials for new batteries (cradle). LIB recycling routes are typically classified as either pyrometallurgical, hydrometallurgical, or direct recycling methods (Goyal et al., 2023). Pyrometallurgical processes are considered simple, easy to scale-up, demand relatively low production

* Corresponding author.

E-mail address: rodrigo.serna@aalto.fi (R. Serna-Guerrero).

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costs and do not require strict pre-sorting of battery feed, while hydrometallurgical processes have a good technology readiness, a low energy consumption, and can potentially recover a wide variety of materials (Harper et al., 2019). However, both methods present some disadvantages: pyrometallurgical operations require large capital investments, may demand high amounts of energy, and produce hazardous gases (Lim et al., 2022), whereas hydrometallurgical operations consume vast amounts of water and chemicals, and have slow processing rates (Asadi Dalini et al., 2020). In both cases, a fraction of metals is lost due to recycling inefficiencies or thermodynamic limitations, while non-metallic materials, e.g., plastics, graphite, and electrolyte, are not recycled due to the lack of economic motivation or infrastructure (Rey et al., 2021; Richa et al., 2017). Alternatively, direct recycling represents a promising solution to treat EOL battery materials as it can be utilized to recover active battery components in their useful chemical form, including graphite which is lost with the state-of-the-art (SoA) technologies (Sinn et al., 2023). Previous research suggest that direct recycling routes are also less energy demanding than pyrometallurgical methods while consuming smaller amounts of chemical reagents than hydrometallurgical processes (Harper et al., 2019; Lim et al., 2022). Direct recycling is however still under development, as only a little is known about it (Wu et al., 2022). It is also considered of low flexibility and high complexity (Harper et al., 2019), as it is being affected by the type of LIBs fed into the process (Premathilake et al., 2023).

As the different recycling strategies present advantages and limitations, a systematic comparison is needed. Previously, process evaluation and comparison has been made by for example Tao et al. (2023a), who conducted life cycle assessment (LCA) on five different recycling technologies including pyrometallurgical, hydrometallurgical, and their combination to determine their environmental impacts. Later, Tao et al. (2023b) used a similar approach to compare hydrometallurgical and physical separation methods for lithium iron phosphate (LFP) battery recycling. Gu et al. (2021) compared two different hydrometallurgical recovery routes with three different scenarios using the recoveries of Li and Co as benchmark. Zhang et al. (2023) compared the effect of three different pre-treatment methods to the leaching efficiency of Li, Mn, Co, and Ni. Fahimi et al. (2022) analyzed the sustainability of 33 different laboratory-scale LIB recycling technologies using a tool based on embodied energy and carbon footprint. Energy was also used in the study by Wang et al. (2022), who compared the specific energy consumption of different electrochemical processes recovering Li.

Nevertheless, the above-mentioned comparisons are based on parameters that do not account for a systemic perspective of materials and energy preservation, as required by the goals of the circular economy (CE) mentioned by e.g., Bocken et al. (2016), Geissdoerfer et al. (2017), and Serna-Guerrero et al. (2022). In addition, the previously published comparisons of recycling routes do not consider that each technology results in different material streams and that the products obtained may be found in different chemical form. To overcome the above-mentioned limitations and provide a robust analysis, the present work compares three carefully selected LIB recycling processes (including direct recycling, hydrometallurgical, and pyrometallurgical routes) under the following conditions: i) a grave-to-cradle analysis from EOL batteries to LiCoO_2 (LCO) to have a fair benchmark of product species; ii) using objective circularity indicators based on physical and chemical properties; and iii) a system-level evaluation of energy and material preservation.

Recently, our research group proposed a method combining statistical entropy and exergy analysis into a novel circularity indicator called “exentropy” (Vierunketo et al., 2023). Exentropy (χ) presents a system-level analysis of material and energy preservation simultaneously, as it tells whether the irreversible loss of exergy can be justified by the effective concentration of materials. In its first proof-of-concept work, χ was applied for the optimization of process conditions in a hydrometallurgical recycling process. Considering its ability to simultaneously evaluate two circularity dimensions (i.e., materials and energy

flows), it is hypothesized that χ can also be used as a comparison parameter. To that aim, however, a necessary expansion on the exentropy methodology is hereby introduced to compare processes with different number of stages. With this first effort to compare different recycling methods, it is expected to show that a multidimensional indicator can provide a more robust assessment of the circularity of the processes.

2. Methodology

2.1. Process simulation of battery recycling processes

Three commercial battery recycling processes were chosen for a comparison: a pyrometallurgical recycling process, a hydrometallurgical recycling process, and a direct recycling process based on LIB recycling processes by Umicore Valéas™ (Cheret and Santen, 2007) and Retrie (McLaughlin and Adams, 1999; Smith and Swoffer, 2013a, 2013b). These processes were carefully selected since they are representative of the most commonly researched LIB recycling routes. Furthermore, these are patented technologies already at the stage of commercial implementation, thus proven to treat large streams of EOL batteries, as presented in studies by e.g., Dunn et al. (2014); Sonoc et al. (2015), and Vezzini (2014). Finally, the selected processes represent State-of-the-Art technologies currently in use (Bocken et al., 2016), whose patents provide sufficient information for their simulation.

All three processes were simulated with HSC Chemistry 10® software (Metso Outotec) to obtain the mass and energy balances, and to calculate the exergy content of each stream. All the data required for the simulation was compiled from recently published scientific literature, but, due to space limitations, all process descriptions with figures and references can be found in the Supplementary Information. The technological routes of the processes are based on published literature, and the representative process technologies were compiled considering data similarities between the various research articles and original patents. For simplicity, the input energy required was assumed to be electricity from an unknown source. The flows of chemical reagents were based on reaction stoichiometry. For a fair comparison, we evaluated these processes using the same feed characteristics (LIBs) and the same target product, namely LCO ready for remanufacturing. The mass fractions of each component used in this study are presented in Supplementary Information in Fig. S1, which are representative of typical commercial batteries (Velázquez-Martínez et al., 2019a).

2.1.1. Pyrometallurgical process

The feed for all simulated processes was kept equal to 4500 t/a, based on the reported capacity of the industrial hydrometallurgical process, although the Umicore process reportedly has a capacity of up to 7000 t/a. The process uses a smelter to separate metals of high economic value in the form of an alloy, followed by hydrometallurgical extraction as described by different research from e.g., Pinegar and Smith (2019), Velázquez-Martínez et al. (2019a), and Vezzini (2014). The detailed description of the processing steps can be found in Supplementary Information.

The process flow diagram of the pyrometallurgical process is also presented in Fig. S2 in Supplementary Information. The energy consumption of smelting, solvent extraction and firing were based on data found in different literature (Dunn et al., 2014; Wu et al., 2022), while the energy consumption of leaching, Fe separation and oxidation were calculated by the simulation software. The energy consumption values in all stages are summarized in Supplementary Information, Table S1.

2.1.2. Hydrometallurgical process

The hydrometallurgical process by Retrie to recover Li from EOL LIBs was chosen as a case study (McLaughlin and Adams, 1999; Smith and Swoffer, 2013a, 2013b). The detailed process description and the corresponding flowsheet can be found in Supplementary Information

(Fig. S2). Energy consumption of different units other than evaporation was obtained from different existing literature (Dunn et al., 2014; Pinegar and Smith, 2019; Wu et al., 2022). The energy consumption of evaporation was calculated by the process simulation software. All the values are presented in Supplementary Information (Table S2).

2.1.3. Direct recycling process

As the idea of the recovery of active battery materials in their unaltered chemical form gains traction, patents in the use of mechanical and physical separation have been published (Smith and Swoffer, 2013a, 2013b). Such processes were used in the present work to simulate direct recycling.

This process is presented in Fig. S3 in Supplementary Information along with the detailed description of the process. Energy consumption of different units other than flotation was obtained from the different existing literature (Dunn et al., 2014; Wu et al., 2022). All the values are presented in Supplementary Information (Table S3).

2.2. Circularity indicators of mass and energy flows

2.2.1. Statistical entropy analysis (SEA)

The study of material flows is fundamental to evaluate recycling systems. SEA is a concept originally envisioned by information theory (Shannon, 1948), which is combined with material flow analysis (MFA) to trace the concentration or dilution of components in a system (Rechberger and Brunner, 2002). SEA-MFA has proven as a useful tool to trace the preservation of materials at a systemic level, i.e., accounting for all main-, side-, and waste streams in studies by e.g. Nimmegeers and Billen (2021), Nimmegeers et al. (2021), and Velázquez-Martínez et al. (2019b). According to MFA, a process can be described to consist of transformative processes (u) in between stages (q), which are described by streams (s) including different components (i). The concept of MFA is visualized in Fig. 1.

As the aim in recycling is to concentrate substances, the statistical entropy (h) should decrease throughout the process. Statistical entropy is calculated using a mass flow and concentration of a component in that stream, as described in Eq. (1).

$$h_{i,s} = -\dot{m}_{i,s} c_{i,s} \log_2(c_{i,s}) \geq 0 \quad (1)$$

Where $h_{i,s}$ [information bits], $\dot{m}_{i,s}$ [dimensionless] and $c_{i,s}$ [fractional] are the statistical entropy, standardized mass fraction and concentration of a component i in the stream s, respectively. For the calculation of standardized mass fraction, Eq. (2) and Eq. (3) are needed:

$$\dot{m}_{i,s} = \dot{m}_s \left/ \sum_s \dot{X}_i \right. \quad (2)$$

$$\dot{X}_i = \dot{m}_s c_{i,s} \quad (3)$$

where \dot{m}_s is the mass flow in the stream s, \dot{X}_i is the total substance flow of component i in the units of mass flow, and $c_{i,s}$ [fractional] is the concentration of the component i in stream s.

Statistical entropy of a stage ($H_{i,q}$) is a sum of statistical entropies in all streams at that stage, as described in Eq. (4). The maximum statistical entropy ($H_{i,q}^{max}$) is typically the same as the value of the statistical entropy in the first stage. Relative statistical entropy (RSE) can be used to compare different elements inside the system, and its value in each stage q is the ratio of $H_{i,q}$ to the value of $H_{i,q}^{max}$, as described in Eq. (5).

$$H_{i,q} = \sum_q h_{i,s} \quad (4)$$

$$RSE_{i,q} = H_{i,q} / H_{i,q}^{max} \quad (5)$$

2.2.2. Exergy analysis (ExA)

In addition to material flows, the study of energy preservation is also relevant in the definition of CE. To that aim, exergy analysis can be used to estimate the irreversible energy losses in a system (Carneiro and Gomes, 2019). The total exergy of a system ($Ex_{tot,s}$) consists of physical, chemical, kinetic, and potential exergy. However, kinetic and potential exergy are a magnitude lower than physical and chemical exergy, so they are often neglected in the calculations. Thus, the total exergy of a system can be said to consist predominantly of physical ($Ex_{ph,i}$) and chemical exergy ($Ex_{ch,i}$) and is calculated using Eq. (6).

$$Ex_{tot,s} \approx Ex_{ch,i} + Ex_{ph,i} \quad (6)$$

In this work, the process simulation software calculates the total exergy of species according to Eq. (7) (Metso Outotec):

$$Ex_{tot} = \sum_k n_k b_k^{ref} + \Delta G_{f(25^\circ C, 1 \text{ bar})}^0 + \left(N_i - N_{i(25^\circ C, 1 \text{ bar})} - T_{25^\circ C} (S_i - S_{i(25^\circ C, 1 \text{ bar})}) \right) \quad (7)$$

Where n_k is a mass flow or stoichiometric amount of an element or a compound in a stream. The standard Gibbs free energy of formation ($\Delta G_{f(25^\circ C, 1 \text{ bar})}^0$) and elemental exergies of elements (b_k^{ref}) are obtained from the software database. The software also requires a temperature for each stream to obtain enthalpies (N) and thermodynamical entropies (S)

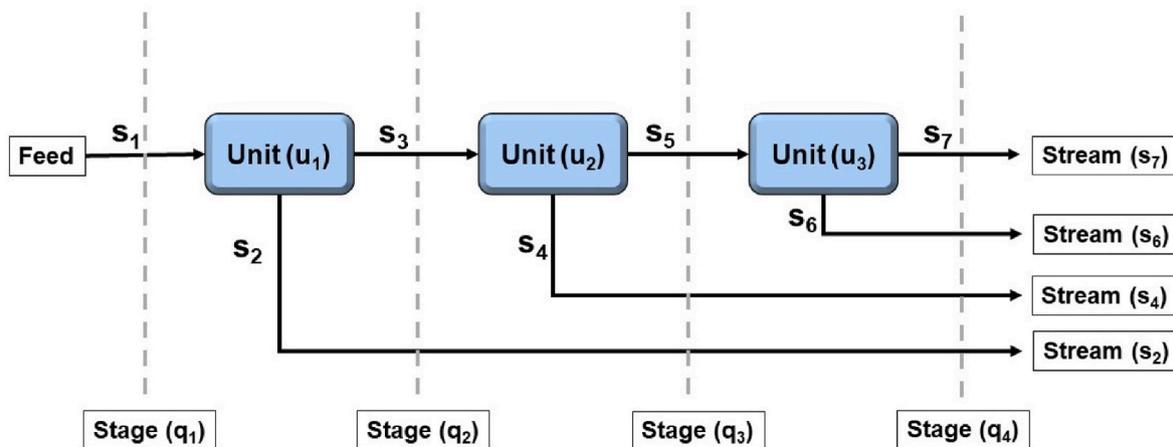


Fig. 1. Schematic representation of process elements according to material flow analysis (MFA) methodology.

of species in the given temperature (T) and in standard state (25 °C, 1 bar).

In addition to streams, HSC also calculates the exergy of heat according to Eq. (8).

$$Ex_{heat} = q * (1 - T_0 / T_{heat}) \quad (8)$$

Where q is heat flow, T_0 is the temperature of the standard state (25 °C), and T_{heat} is the temperature of the heat source.

The transformation of resources through a process result in work, heat, products, by-products, and waste that embody a part of intake exergy. Unlike energy, exergy does not follow the laws of conservation and thus, the output exergy may not be equal to its input value (Reuter et al., 2019). To write the exergy balance in a conservative form, a term called exergy destruction (Ex_D) is introduced. While not a physical flux, Ex_D quantifies energy degradation during a process. The conservative form of exergy balance is presented in Eq. (9).

$$Ex_{Feed} + Ex_{Energy} = Ex_{products} + Ex_{waste} + Ex_Q + Ex_D \quad (9)$$

Accordingly, the input exergy comprises of exergy of materials in the feed (Ex_{Feed}) and energy sources (Ex_{Energy}), while the output exergy contains the exergy of materials in product streams ($Ex_{products}$), exergy of materials in waste streams (Ex_{waste}), exergy due to heat transfer (Ex_Q), and Ex_D .

Ex_D can only be zero in the theoretical case of fully reversible processes. In reality, all transformative stages destroy exergy as a result of thermodynamic entropy generation (Reuter et al., 2019). Ex_D can be studied further by using an indicator called fractional exergy destruction (FEx_D), which can be used to trace the relative contribution to Ex_D after each stage in a process, according to Eq. (10):

$$FEx_D = Ex_{D,i} / Ex_{D,tot} \quad (10)$$

Where $Ex_{D,i}$ is the exergy destruction in one unit and $Ex_{D,tot}$ is the exergy destruction in the whole process.

From a different perspective, relative exergy content (REX) reflects the preservation of exergy relative to the total input exergy. REX is defined by dividing the exergy content of a stage by the exergy content at the first stage (Ex_{max}), as in Eq. (11):

$$REX = \frac{\sum Ex_{s,q}}{Ex_{max}} \quad (11)$$

Where $\sum Ex_{s,q}$ is the sum of the exergies of all streams in stage q , and Ex_{max} is the total input exergy to the system.

2.2.3. Exentropy (χ)

RSE and REX respectively analyze the efficiency of materials and energy conservation in a system, in an independent manner. Their one-dimensional evaluation may be problematic since the evaluation of energy or mass flows alone may result in contradicting results on process optimization, as demonstrated in a recent publication from our team (Vierunketo et al., 2023). For that reason, χ was proposed to provide a more robust analysis under the premise that exergy destruction is justified only by the effective concentration of materials. In other words, the right way to close material loops is to use energy in the most efficient manner possible towards the preservation of all materials in a system. To establish the balance of such resource requirements, χ accounts for a normalized difference between exergy and statistical entropy, as described in Eq. (12).

$$\chi_q = REX_q - RSE_q \quad (12)$$

In ideal situations, REX should be as high as possible (minimum exergy destruction) and RSE should tend to zero (maximum material concentration). Whenever exergy losses outweigh the benefits of material concentration, negative values of χ are obtained reflecting an inefficient process. On the contrary, positive values of χ result from

scenarios where exergy destruction is justified by a significant concentrating action. Because the maximum possible value of χ is the same as the total number of stages in a system ($q_{tot} * 1$), exentropic efficiency (χ_{eff}) can be calculated to provide a normalized parameter to compare processes with different number of stages, as in Eq. (13).

$$\chi_{eff} = \frac{\sum \chi_q}{q_{tot} * 1} * 100 \% \quad (13)$$

Where $\sum \chi_q$ is the sum of exentropies in all stages in a process.

3. Results and discussion

3.1. Comparison of the processes using statistical entropy analysis (SEA)

SEA was carried out on the three investigated LIB recycling routes following the most representative elements, and the results are presented in Fig. 2. As seen, the value of RSE decreased throughout all three processes indicating that all of them accomplish the aim of concentrating materials, even when losses in side streams are considered. For each process, the streams outlines were organized according to MFA methodology. For the interested reader, a schematic representation of streams and stages are found in Supplementary Information (Fig. S5—Fig. S7).

The elements traced in the pyrometallurgical process (Fig. 2a) were the main metallic components in the battery feed, namely Fe, Cu, and Co. In this particular case, the “Others” stream contains materials such as Li, Al, or graphite that are not recovered for battery manufacturing with this process, rather reporting to the slag or to the off-gases stream. Admittedly, the slag could be treated hydrometallurgically to extract Li, but in SoA pyrometallurgical processes, it is downcycled into lower value products such as additives in the cement manufacturing (Latini, 2022). The results show that, after smelting, the metallic elements only have a modest decrease of RSE. To properly interpret this, it is necessary to keep in mind that the MFA methodology requires that all material inputs to the system are accounted for from the beginning. Consequently, the large water streams used for leaching are accounted in the feed and thus influence the values of RSE already in Stage 1. In other words, from a system-level perspective, this process represents a scenario in which battery materials remain diluted until the process water is recovered. Indeed, after their respective leaching stages, Cu and Fe are efficiently separated as seen from the decreasing values of RSE in Stages 4 and 5, respectively. As water remains in the process until solvent extraction and oxidation, a notable decrease in the RSE for Co occurs after the oxidation stage, where most of the water is removed. Finally, Co slightly concentrates after the firing step, as it becomes part of a highly pure LCO stream.

In the hydrometallurgical process (Fig. 2b), the elements traced were the main metallic components, namely Fe, Cu, and Co, and in addition Al and Li, since these are also recovered using hydrometallurgical processing. Fe from the casing and peripherals was separated efficiently by a screen attached to the hammer mill, as seen in the decrease of RSE for Fe. Both Cu and Al foils are separated in the following screening step, which supports a well-documented behavior of black mass in the literature (Ruismäki et al., 2020; Zhang et al., 2020). Although Cu and Al foils are efficiently separated and in a pure metallic form, their RSE does not reach a value of zero since they remain mixed together. Li and Co on the other hand remain highly diluted in the feed to the hydrometallurgical extraction stages. This is again the result of considering water process streams from the start of the process, similarly to the case of pyrometallurgical process described above. Therefore, a decrease in the RSE of Li and Co is only perceived by Stage 9, where most of the water and other impurities are filtered out from the process. Firing also decreases the RSE of both Li and Co, as the extracted Li and the precursor Co_3O_4 finally react to produce a stream of LCO.

The direct recycling process (Fig. 2c) traces the same elements as

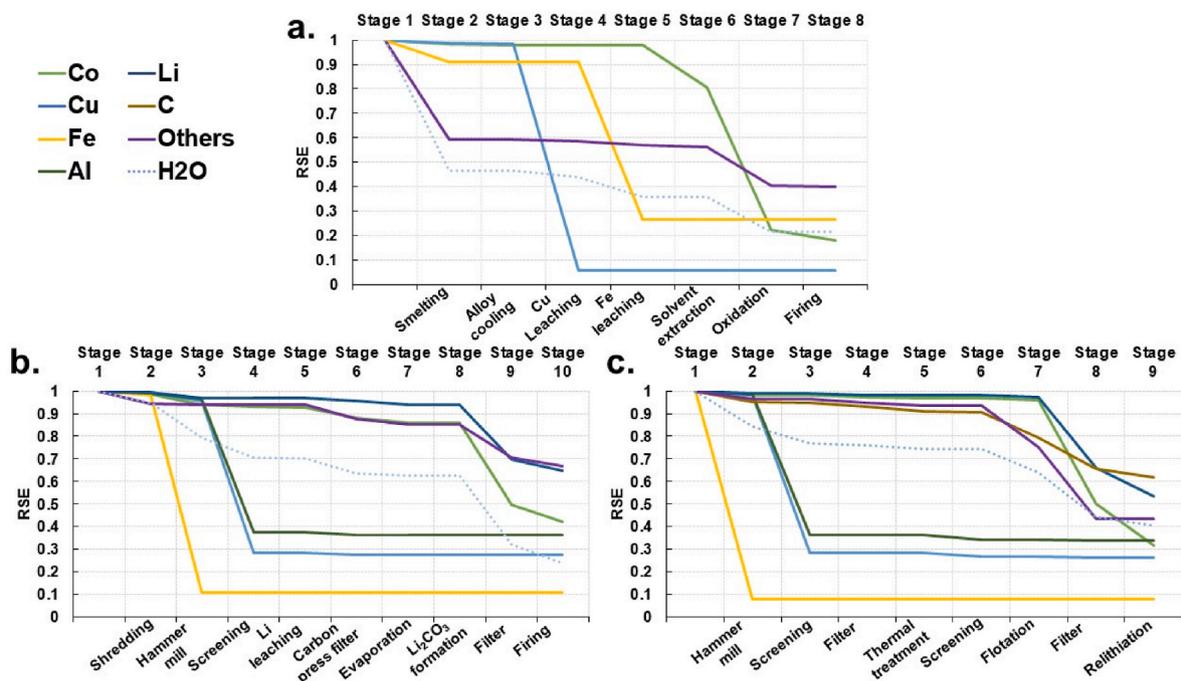


Fig. 2. Relative statistical entropy (RSE) of elements for (a.) pyrometallurgical, (b.) hydrometallurgical, and (c.) direct recycling process.

hydrometallurgical process, i.e., Fe, Cu, Co, Al, and Li, and in addition also graphite (C), as it is recovered during froth flotation. The process starts with milling and screening, similarly to the hydrometallurgical route. This combination has proven efficient in removing Fe and metallic foils (Al and Cu), as reflected in the decreasing RSE values for Fe, Cu, and Al. Again, there is no notable decrease in RSE during the stages between the first filtering and flotation, as the elements and components remain diluted at a system-level. The second screening step further aids the concentration of Cu and Al foils. By Stage 7, the flotation of graphite from LCO appears to be accomplished, as seen in its decreasing value of RSE. The RSE values for C and LCO are further reduced after the second filtration step (Stage 8), as most of the process

water is removed. During relithiation, the remaining C is converted into carbon dioxide while producing a high purity LCO stream.

As seen in Fig. 2, all the materials studied reach a comparatively low value of RSE at the end of the pyrometallurgical process. It can be argued that, according to the RSE analysis, this is the most efficient route in terms of materials concentration and preservation. This is further corroborated when comparing the total RSE levels of the processes (which are described in Supplementary Information and visualized in Fig. S8), since the pyrometallurgical process produces the lowest final value of RSE.

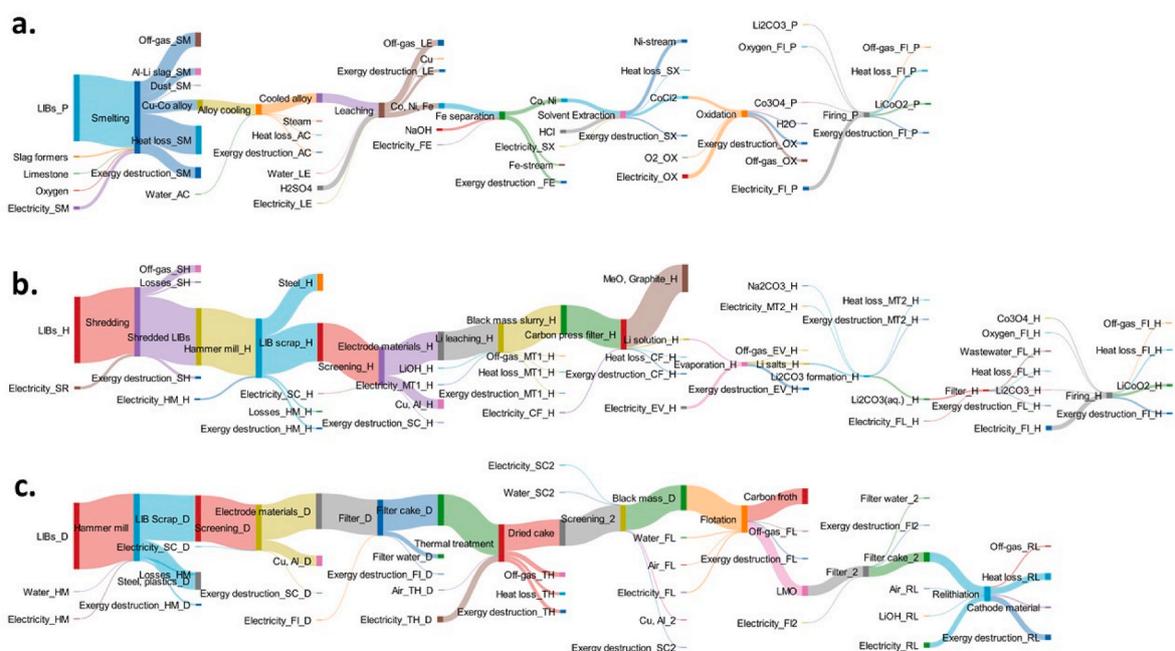


Fig. 3. Sankey diagrams representing the exergy content of streams for (a.) pyrometallurgical, (b.) hydrometallurgical, and (c.) direct recycling process.

3.2. Comparison of the processes using exergy analysis

While RSE is a useful tool to analyze material flows, another parameter is necessary to trace the efficient use of energy in transformative processes. For this reason, exergy analysis was performed on the three processes under study. Fig. 3 shows a visualization of exergy flows to help identifying the main sources of exergy destruction. The exergy values of all processes are presented in Supplementary Information (Table S7 – Table S9). It is worth clarifying that for the purposes of this study, exergy losses in the form of heat or materials side streams are not considered to negatively affect exergy efficiency. This is admittedly uncommon but, following the principles of a CE, it is understood that these exergy sinks still have the potential of use or recovery through heat integration or by using further purification stages in the case of chemical exergy. Indeed, materials should not be considered as a waste under the CE framework. For this reason, it is only the irreversible loss of exergy (i.e., exergy destruction) that is considered to represent irreparable losses of energy in the system.

According to the exergy analysis of the pyrometallurgical process (Fig. 3a), only a minor fraction of the exergy flows produced after the smelter is conserved in the form of a metal alloy. The exergy destruction associated with smelting is high, resulting from the inherent inefficiencies of electrical heat generation. Similarly, the exergy destruction is also significant during oxidation and firing. According to the work by Ignatenko et al. (2007), there are two types of losses of exergy identified in recycling systems, namely external and internal losses, which can be used to measure the efficiency of resource use in the system. One type of internal loss, called the conversion loss, results from the thermodynamic inefficiencies associated with the use of energy, for instance to operate equipment. High-temperature processes usually demand vast energy flows, currently obtained from energy production methods with inevitable losses. Regarding the external exergy losses, these are associated with the inefficiencies in the utilization of chemical reagents added into the process. As seen in Fig. 3a, there are various chemical species fed to the smelting unit, as reagents are needed to reduce oxides and promote the formation of slag to achieve the required alloy grade. External losses also occur during leaching, Fe separation, and solvent extraction, where a notable amount of exergy is added to the system in the form of chemical reagents (i.e., H₂SO₄, NaOH, and HCl solutions).

In the hydrometallurgical process (Fig. 3b), exergy is largely conserved until the carbon press filter, since the obtained filtered cake contains large molar fractions of species with the highest chemical exergy. On the other hand, the resulting Li-containing filtrate is a low exergy stream, which is not surprising since Li represents a minor mass fraction in the LIB materials mixture. Evidently, the exergy contained in the filtered materials cannot be qualified as exergy losses since graphite and metal oxides may be utilized after further treatment. Exergy analysis points out that it is not unreasonable to recover only Li but, since this is considered the main recovered product by the Retrieval process, the fate of the other materials is out of the scope of this work. This also exemplifies why a circularity analysis should focus on exergy destruction, rather than the arbitrary definition of a single material species as product. The interested reader can however find efforts by various research groups regarding the recovery of transition metals via hydrometallurgical processes (Li et al., 2019; Milevskii et al., 2022; Tran et al., 2021), or the recovery of graphite before or after leaching of battery materials (Jegan Roy et al., 2023; Perumal et al., 2022; Zhu et al., 2023). After filtration, the energy demand and associated exergy destruction during evaporation and firing are comparatively higher, as they are high-temperature processes. Evidently, the recovery of wide variety of materials is needed to promote exergy preservation, as the output LCO stream contains only a small fraction of the exergy content fed into the system.

In the direct recycling route (Fig. 3c), the exergy content of the feed is distributed into the two resulting material streams after the hammer

mill, namely “LIB Scrap” representing the battery active materials mixture (black mass) and casing materials, labeled as “Steel, plastics”. The exergy content of the “LIB Scrap” stream was reduced after the separation of Cu and Al during the screening steps prior to thermal treatment. Further exergy destruction occurs as water is separated in the first filtering step, and after binder is removed during thermal treatment. Thermal treatment also involves heat losses with a relatively high exergy destruction, resulting from the inefficient use of energy for heating. All these side streams however carry a lower amount of exergy compared with the active material mixture. Indeed, the b_k^{ref} of graphite and LCO are relatively high, and its preservation is the distinctive feature of direct recycling. After froth flotation, a split of the exergy flows finally occurs as the active materials are separated. Again, while this work focuses on closing the loop of cathode active material, the exergy embedded in the graphite anode is not considered a loss, as it maintains the potential of being used for battery remanufacturing. The “LMO” stream mainly contains the LCO which is further filtered and relithiated to create cathode material for new batteries. After filtration, most of the exergy is preserved by the filter cake since the b_k^{ref} of water is comparatively lower than that of LCO. During relithiation, thermodynamic inefficiencies in the use of reagents and consumption of energy inevitably lead to some exergy destruction.

The values of exergy destruction for each recycling route are presented in Fig. 4. The use of parameters such as cumulative Ex_D and FEx_D help identifying optimization points by illustrating, which units contribute the most to exergy destruction.

Among the three processes hereby studied, the pyrometallurgical process (Fig. 4a) had the highest total Ex_D by far. As seen, the smelting unit alone generates an Ex_D of 382 kW, a higher value than the entire hydrometallurgical process. Indeed, smelting is one of the most exergy destructive stages, as it consumes a great number of different resources. This can be observed in Fig. 3 as multiple inputs (both materials and energy) are fed into the unit. The direct recycling process (Fig. 4c) had a slightly higher exergy destruction than the hydrometallurgical process (Fig. 4b), largely due to the Ex_D associated with relithiation. The only other significant exergy destructive stage in direct recycling is the thermal treatment required for black mass pre-treatment. In the hydrometallurgical process, the most exergy destructive units were comminution (shredding and hammer mill), precipitation, and firing. The value of Ex_D during shredding (87 kW) was slightly higher than that of evaporation (82 kW). As may have been expected from thermodynamic principles, a clear correlation between the consumption of resources (energy and reagents) and exergy destruction is obtained for all processes. Invariably, the stages operating at high temperatures and/or consuming chemical reagents, resulted in higher contributions to Ex_D .

Hence, according to exergy analysis, the best option would be the hydrometallurgical process, as it destroys the least amount of exergy. This contradicts the findings obtained with RSE, where the pyrometallurgical process was considered optimal. The results for the REX for the whole process are described in Supplementary Information and visualized in Fig. S6.

3.3. Comparison of the processes using exentropy analysis

As discussed in the Introduction section, evaluation of processes based on a single dimension can result in a skewed vision that may not correspond to the multi-dimensional needs of the CE. Indeed, the results in Sections 3.1 and 3.2 identified two different processes as optimal when evaluated with either RSE or REX. A multidimensional indicator, such as exentropy (χ) is thus necessary for a more robust evaluation. The results for analysis of χ are presented in Fig. 5.

It is seen that both pyrometallurgical and hydrometallurgical process had a negative value of χ at the beginning of the process, indicating that these early-stage units were not concentrating enough material to afford the cost of exergy destroyed. Particularly during the pyrometallurgical process, smelting destroys plenty of exergy while not resulting in the

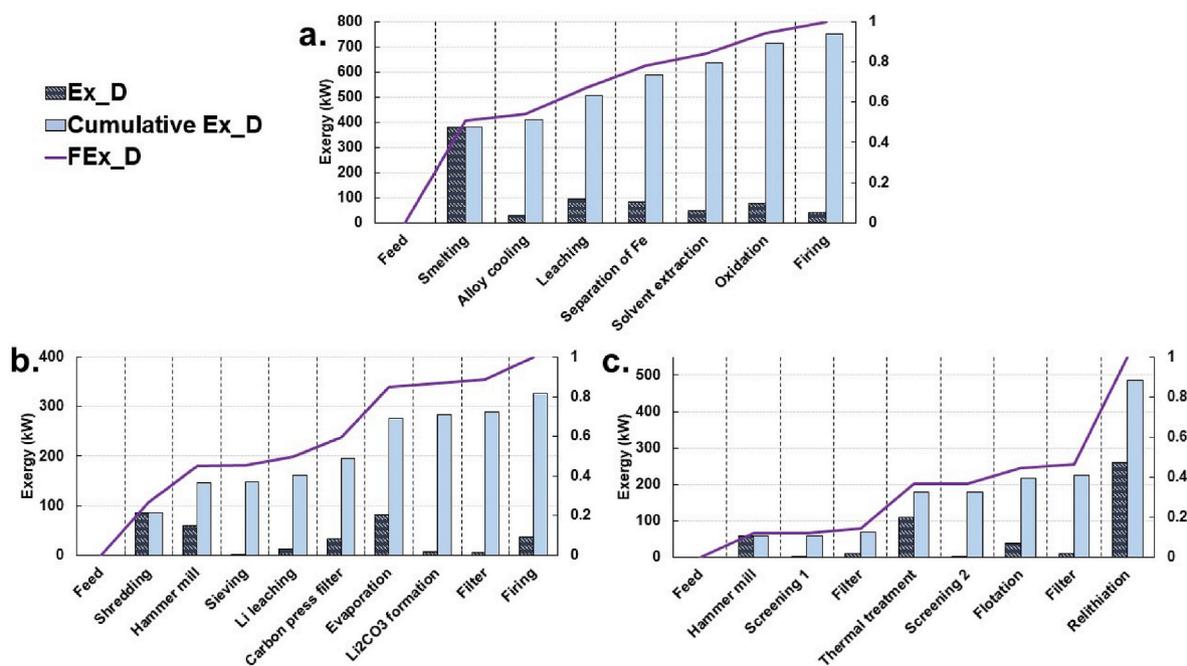


Fig. 4. Exergy destruction in each unit and fractional exergy destruction (FEx_D) for pyrometallurgical (a.) pyrometallurgical, (b.) hydrometallurgical, and (c.) direct recycling process.

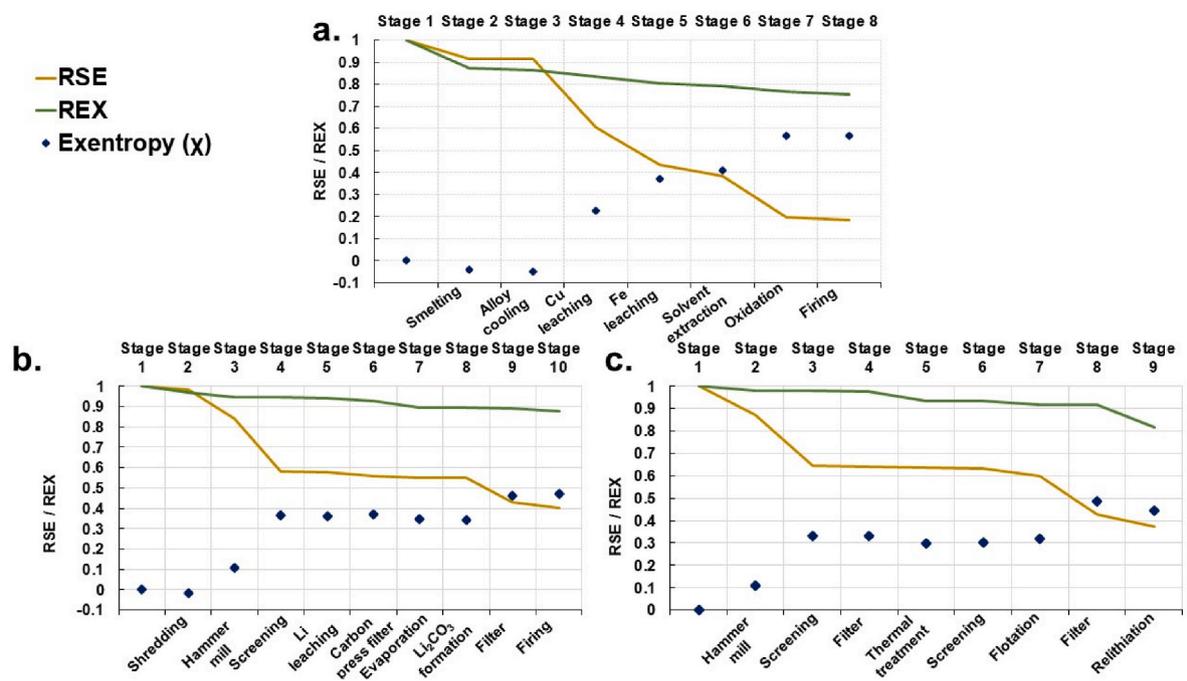


Fig. 5. Analysis of χ for (a.) pyrometallurgical, (b.) hydrometallurgical, and (c.) direct recycling process.

immediate concentration of materials, as components are either mixed in an alloy or lost in the form of slag or off-gases. This is later compensated during the subsequent extraction of metallic components, resulting in a positive χ value for the entire process. The hydrometallurgical process was affected by the negative χ values at the beginning of the process during the shredding step while the pyrometallurgical process was the least efficient due to its highly exergy destructive smelting stage. The total exentropies for the pyrometallurgical, hydrometallurgical, and direct recycling process were 2.05, 2.81, and 2.62, respectively. However, the processes hereby studied do not contain the same

number of stages, so the values of χ cannot be directly compared. This is because a process with a high number of stages could achieve a higher value of χ compared to a process with a smaller number of stages, even though that latter process would visibly be much more efficient. Therefore, a relative parameter such as χ_{eff} is required. The resulting values of χ_{eff} were 25.6%, 28.1%, and 29.2% for the pyrometallurgical, hydrometallurgical, and direct recycling process, respectively. This shows that the direct recycling process was the most efficient in terms of both material concentration and exergy preservation. Certainly, processes with high materials concentrating action and low exergy

destruction are desired, so it is necessary to develop quantitative indicators accounting for these conditions simultaneously. In other words, using the multi-dimensional exentropy analysis in process comparison can be used to identify the option more akin to the CE goals, in contrast to the limited analysis provided by SoA indicators.

Even though both pyrometallurgical and hydrometallurgical methods are currently dominating in the industry, a study by Xu et al. (2023) stated that the recycling cost for the direct recycling process is the lowest compared to hydrometallurgical and pyrometallurgical recycling, making direct recycling an attractive method. The present study also shows in quantitative terms that it is the preferred option for the CE of LIBs. Improved recycling technologies are required to increase the LIB recycling efficiency both in terms of cost, energy consumption, and material preservation (Xu et al., 2023). Reconditioning of cathodes may also represent a better option environmentally, since cathode materials are considered the second largest contributor after cell manufacturing to material costs and greenhouse gas emissions of battery manufacturing (Ciez and Whitacre, 2019). Also, Chen et al. (2023) stated that greater environmental benefits from battery remanufacturing are obtained when direct recycling routes are applied in battery recycling. Furthermore, to reach higher recycling efficiencies, a wider variety of materials should be recycled from EOL LIBs. For example, graphite represents 15–20 % of LIBs total mass which would be lost in pyrometallurgical processes (Vanderbruggen et al., 2022) making necessary the use of physical separation methods.

The evolution of exentropy values throughout the processes also aid in finding optimization points. For instance, exentropy analysis consistently identified high-temperature operations as problematic due to its taxing impact on exergy destruction, although thermochemical processing of black mass has been consistently reported as a suitable pre-treatment method for the removal of the binders (Vanderbruggen et al., 2022). The use of exentropy analysis for the further optimization of recycling processes, including the integration of heat flows are thus interesting avenues of research worth studying in the future. Furthermore, since environmental impact parameters have proven useful in the assessment of recycling technologies (Chen et al., 2023), exentropy analysis could further be expanded in that direction. For instance, Tas et al. (2024) recently demonstrated the benefits of combining SEA and LCA in their work, while Bartie et al. (2021) presented a combination of exergy analysis and LCA for the assessment of solar panels life cycle and multi-metal processing plants, respectively. Expanding the dimensions in the circularity analysis of processes could further support the decision-making on the engineering of circular solutions.

As it might be possible to develop direct recycling methodologies using environmental assessment (Chen et al., 2023), exentropy analysis could further be combined with LCA to include the environmental impacts. Tas et al. (2024) already combined SEA and LCA in their work, so this kind of hyper-spherical method combining materials, energy, and environmental impacts could further enhance the results from different CE analyses.

4. Conclusions

The objective comparison of recycling technologies remains a challenging task, particularly since a proper evaluation needs to address complex streams of materials and energy flows. The present work thus provided a comparison of battery recycling routes based on a robust analysis of materials and energy flows. The use of parameters such as RSE and REX provided a more objective comparison of processes, since the works available in the published literature typically claim one route as more beneficial, often based on vague or subjective assessments. According to the results hereby presented, RSE supports the use of a pyrometallurgical route, while hydrometallurgical process was the most efficient according to REX. Based on these exemplary case studies, it was shown that when only one dimension of circularity (i.e., mass or energy flows) is independently considered, contrasting results may be obtained.

Thus, exentropic efficiency was also tested, as a parameter for the comparison of recycling processes. According to exentropy analysis, direct recycling is the optimal choice when mass and energy preservation are considered simultaneously. Although the results obtained provide a robust analysis on the efficiency in the recovery of materials, it is also useful to acknowledge the limitations of the present study. Certainly, a general challenge on the use of process simulation software is the reliability of the data and models used to perform simulations. Large sets of data obtained from measurements performed directly on the processes would likely result in more realistic predictions. In addition, the validation of novel methods, such as exentropy, could also benefit of a larger number of case studies in order to identify whether there are specific circumstances in which these may not provide reasonable outcomes. The work hereby presented is thus a contribution to the understanding and implementation of exentropy as a circularity parameter.

CRedit authorship contribution statement

Minerva Vierunketo: Writing – original draft, Methodology, Investigation, Conceptualization. **Anna Klemettinen:** Writing – review & editing, Validation, Formal analysis. **Markus A. Reuter:** Methodology, Conceptualization. **Annukka Santasalo-Aarnio:** Writing – review & editing, Funding acquisition. **Rodrigo Serna-Guerrero:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2024.143435>.

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