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Simulation-based life cycle assessment for hydrometallurgical recycling of mixed LIB and NiMH waste

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ABSTRACT

The sustainable and competitive recovery of materials from spent batteries is becoming an urgent issue due to the increasing popularity of hybrid and fully electric vehicles. In this present study, flowsheet simulation was combined with life cycle assessment to investigate the environmental impacts of a conceptual, experimentally proven hydrometallurgical battery recycling process, where nickel metal hydride (NiMH) battery waste is used as reductant for lithium-ion battery (LIB) waste, synergistically improving the extraction of valuable metals from both waste types. Various options for sodium circulation in the precipitation of rare earths were considered in different scenarios. The results showed that the main benefit of the process was the reduced consumption of leaching chemicals. Of the investigated sodium management scenarios, crystallization of sodium sulfate was found to be the most environmentally feasible option, allowing the use of Na as a precipitation chemical for rare earth recovery. Significant potential reductions in climate change, acidification, freshwater eutrophication, and human toxicity were also achievable when compared to the life cycle impacts of the primary production of battery metals, mainly due to the high environmental footprint of primary nickel and cobalt sulfate production. Although further improvements to the process were found to be possible, the future availability of waste NiMH batteries may limit the application of the described process concept on an industrial scale.

1. Introduction

The rapid adoption of electric vehicles (EVs) is projected to radically increase the demand for battery metals, such as lithium, nickel, and cobalt. The recovery of these metals from EVs is necessary not only to improve the availability of strategic and critical elements, but also to mitigate the problems caused by battery disposal in landfills (Harper et al., 2019). The recycling of lithium-ion batteries (LIBs) is currently driven by the high economic value of cobalt, but the high costs and ethical issues associated with cobalt have led to the development and increased use of low-cobalt cathode chemistries (Alves Dias et al., 2018; Mayyas et al., 2018). To minimize the environmental burden of batteries, the EU has provided targets for battery collection and recycling in the member countries in the Batteries Directive 2006/66/EC. However, this has been found to be inadequate in promoting a high level of material recovery from waste batteries (amount of recovered elements, as well as their recovery level) and the targets are to be critically reviewed in the near future (European Commission, 2019). Furthermore, lithium was defined as a critical element in the 2020 revision of the EU’s list of critical raw materials together with cobalt, which has been on the list since the beginning (European Commission, 2020). To meet future sustainability targets and to secure access to critical metals, it is imperative to develop more efficient processes that are also capable of recovering elements previously lost in waste streams, such as lithium and graphite.

Currently, several commercial processes are operating on industrial scale, typically consisting of one or several pyrometallurgical or hydrometallurgical units. One of the better known industrially operating processes, the Umicore process, combines both hydrometallurgical and pyrometallurgical unit processes to recover mainly nickel, cobalt, and copper from nickel metal hydride (NiMH) and LIB cells without the need for further mechanical pretreatment (Al-Thyabat et al., 2013; Pinegar and Smith, 2019). In a pyrometallurgical process, lithium, manganese, aluminum, and rare earth elements (REEs) from NiMH batteries are lost into the slag, without economically feasible ways to recover them (Elwert et al., 2015; Meshram et al., 2014). The method is also highly

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energy intensive and requires gas cleaning systems to prevent the release of toxic halogen compounds (Pinegar and Smith, 2019; Gaines, 2014). In contrast, hydrometallurgical processes, such as the commercial Recupyl process, appear promising in terms of material efficiency, but the indirect environmental impacts from the production of chemical reagents could be significant, particularly if the chemical consumption is high (Dunn et al., 2012). Additionally, hydrometallurgical processes produce significant quantities of wastewater, which has to be managed to prevent environmental disasters (Al-Thyabat et al., 2013).

A number of studies have addressed the environmental effects of battery recycling (Dunn et al., 2012; Amarakoon et al., 2013; Hendrickson et al., 2015; Ciez and Whitacre, 2019; Gaines, 2018); however, much uncertainty remains about the end-of-life phase. Ciez et al. (2019) estimated that while no significant mitigation is possible through hydrometallurgical and pyrometallurgical methods, direct recycling could be viable for lithium nickel manganese cobalt oxide (NMC) and lithium nickel cobalt aluminum oxide (NCA) chemistries. On the other hand, Hendrickson et al. (2015) concluded that both pyrometallurgical and hydrometallurgical recycling methods lead to decreased environmental impacts in most categories in comparison to the use of virgin raw materials. Amarakoon et al. (2013) modeled hydrometallurgical, pyrometallurgical, and direct physical recycling methods and presented the environmental mitigation as an average of the three processes; the greenhouse gas (GHG) savings obtained by recycling were only 3.6% on average compared to primary production, depending on the battery chemistry. The results calculated by Gaines (2018), on the other hand, would suggest that increasing the amount of recycled material in battery cells decreases the overall energy consumption significantly, especially when aluminum is also recovered.

Life cycle assessment (LCA) is a standardized and widely utilized method to quantify the impacts of a process or a product (ISO 14040; ISO 14044). Despite the standardization efforts, LCA studies in the metallurgical and mineral processing sector suffer from several methodological issues. One of the major sources of uncertainty in LCA studies is that metallurgical processes are usually reduced into simple black boxes with very little detail (Reuter, 1998; Pell et al., 2019; Segura-Salazar et al., 2019). Process simulation has been suggested as a powerful way of compiling more detailed, internally consistent life cycle inventories and can also increase the resolution in LCA studies. This helps in identifying the problem areas of the described processes (Reuter, 1998). In metals processing, the simulation-based approach has been demonstrated in several studies for different processes, such as primary copper (Abadiás Llamas et al., 2019), zinc (Abadiás Llamas et al., 2020), cyanide-free gold (Elomaa et al., 2020), and rare earths (Pell et al., 2019), as well as in selected processes in secondary production (Ghodrat et al., 2017; Reuter et al., 2015).

In the current study, the synergistic battery recycling process described by Liu et al. (2019), where nickel metal hydride (NiMH) battery waste is recycled together with LIB waste, was simulated with the SIM module of HSC Chemistry 10.0 (Outotec, 2020). The mass and energy balances from the model were used in compiling the life cycle inventory (LCI) with which the environmental impacts of the process were calculated in GaBi software (Sphera, 2020). The goal of the study was to critically assess both the technical and environmental merits of a hypothetical hydrometallurgical processing route for mixed battery waste using simulation and LCA as tools. The experimental data from Liu et al. (2019) was adapted in the model and the process was studied from several perspectives and suggestion were made for further development, wherein lies the novelty of this study.

2. Materials and methods

The experimental results from the laboratory scale proven process were used to conduct a process simulation with the simulation module in Outotec’s HSC Chemistry 10 (Outotec, 2020). The mass and energy balances from the simulation were then used to compile a consistent LCI of the described process. The environmental impact indicators were calculated with Sphera’s GaBi software.

2.1. Description of the case study

The availability of raw material for recycling was evaluated based on the forecasted volume of EOL Li-ion and NiMH batteries in the European market, with focus only on vehicle batteries. The recycling potential of these batteries is greatly reduced by the long average lifetime, which is estimated at 8–10 years (Alves Dias et al., 2018), making large-scale recycling feasible at the earliest during 2030. NiMHs have been the dominant battery type to date in hybrid electric vehicles (HEV), excluding plug-in hybrid vehicles. All commercial HEVs on the market had NiMH batteries in 2010; since then LIBs have taken an increasing share (Richa et al., 2014). Although NiMHs are a proven technology with a successful track record in HEVs, they have several shortcomings in comparison to LIBs, such as their lower energy density and higher rate of self-discharge (Manzetti and Mariasul, 2015). For these reasons, lithium ion is the only commercially applicable battery technology in electrically chargeable vehicles (ECV) (CEC, 2015). Although the share of NiMH-powered vehicles is on the decrease globally, the popularity of HEVs indicates that NiMH batteries will remain a considerable feedstock for the emerging recycling plants (CEC, 2015).

Only large vehicle batteries were considered in this estimation due to the uncertainties regarding the removal of the multiple small batteries in a vehicle and their low overall effect on the tonnages. Around 900 000 new HEVs and 460 000 ECVs were registered within the EU in 2019, which was an increase of approximately 50% for both types from 2018 (ACEA, 2020). Assuming a similar growth rate in 2020 and a lifetime of 10 years would give a rough estimate of 1.4 million waste LIBs and 670 000 waste NiMHs in 2030, when half of the HEV batteries are assumed to be Li-ion. The calculated number of waste ECVs (750 000) is in accordance with the predictions of Bobba et al. (2019), who did not take HEV batteries into account at all. HEV batteries were also excluded from the study by Dahllöf et al. (2019) due to their considerably smaller size in comparison with ECV batteries: HEV batteries weigh 50 kg on average, whereas ECV batteries weigh approximately 230 kg (CEC, 2015; Dahllöf et al., 2019). The popularity of HEVs, however, makes their batteries a significant feedstock for recycling. The annual volume of waste batteries was consequently calculated to be 205 900 tonnes of LIBs and 33 600 tonnes of NiMHs.

The throughput in the model was selected to be 10% of available EOL LIBs to ensure the availability of NiMHs. With 8 000 h of annual operational time, the maximum battery feed in the model was calculated as 3.0 t/h LIBs and 2.3 t/h NiMH. It is worth mentioning, however, that non-active components in the battery such as battery housing and management system already account for a considerable share of the weight, and the actual weight of the black mass would be considerably lower. Roughly a third of the cell weight was estimated to be active materials, meaning the throughput in the model was 908 kg/h LIBs and 681 kg/h NiMHs.

The raw materials used in the study of Liu et al. (2019) were industrially pretreated by crushing, magnetic separation, and sieving to obtain a <0.500 mm NiMH and <0.125 mm LIB black mass. The analysis is also not necessarily perfectly representative of the raw material fed into an industrial process as the raw material was very fine, and size classes of <0.500 mm can still contain significant quantities of valuable metals. It should also be noted that the content and behavior of Al and Zn were ignored in this study. Small quantities of both Zn and Al can be present on an NiMH anode and Zn alone on a NiMH cathode, both as fine powders. The analysis used for the raw material was the same as in the study by Liu et al. (2019), with the exclusion of Zn and Al. The
The composition of the battery waste raw material used for simulation was approximated based on the analyses to represent the heat balance and leaching chemistry in the simulation software with reasonable accuracy, and the analysis is included in the supplementary material.

One of the challenges in finding suitable recycling schemes for lithium-ion batteries is the heterogeneity and variability of the waste. The cathode materials of LIBs mainly consist of lithiated metal oxides, such as LiCoO$_2$ (LCO). Due to the cost of cobalt, high-cobalt formulations are being replaced by newer chemistries such as NMC (LiNi$_x$Mn$_y$Co$_{3-x}$O$_2$), various stoichiometric ratios such as xy = 111, 532, 622, and 811), which is becoming increasingly popular in electric vehicles. Manganese (LiMn$_2$O$_4$, LMO) and lithium iron phosphate-based chemistries (LiFePO$_4$, LFP) are also commercially available. In addition to the variability in the active materials alone, industrial black masses are also impure and contain residues of current collectors, electrolyte, and separator.

Nickel metal hydride batteries contain a hydride-forming metal alloy on the anode. In this paper, the materials are assumed to mostly contain of AB$_5$ type alloys where A= (La, Ce, Pr, Nd, Y) and B= (Ni, Co, Mn, Al, Zn), as supported by prior analysis (Hakola et al., 1999). On the cathode, the batteries contain Ni(OH)$_2$, which during charging is transformed to NiOOH. In this study, the behavior of REEs was modeled as an aggregate through the compound LaNi$_5$. La substituted for other REEs in the aggregate. Furthermore, by calculation, some of the Ni$_5$ was substituted by other transition elements.

2.2.2. Flowsheet

The modeled flowsheet was constructed based on the hydrometallurgical process suggested by Liu et al. (2019). A comprehensive description of the flowsheet and the model construction is presented in the supplementary material. The leaching media used is sulfuric acid solution due to its economic advantages over other commonly used leaching chemicals, such as hydrochloric acid (Porvali et al., 2019) and organic acids (Golmohammadzadeh et al., 2018). After leaching, rare earth elements are selectively recovered as alkaline double sulfates by precipitation with Na$_2$SO$_4$ and manganese is oxidatively precipitated as MnO$_2$ using KMnO$_4$. Sodium hydroxide is added in the following step to increase the pH to 5.5, removing iron as Fe(OH)$_3$ from the solution. Cobalt and nickel are purified by solvent extraction (SX) using Cyanex 272 and D2EHPA, respectively, and water is evaporated under vacuum from the solutions to crystallize CoSO$_4$·7H$_2$O and NiSO$_4$·6H$_2$O. Lithium is recovered as Li$_2$PO$_4$ at pH 11 with sodium phosphate. The filtrate from lithium recovery may be crystallized to produce sodium sulfate (Na$_2$SO$_4$·10H$_2$O), which may be recycled to REE precipitation. The wash waters and effluents are neutralized to produce neutral wastewater and to precipitate the remaining metals as hydroxides.

2.2.3. Investigated scenarios

The synergistic nature of NiMH and LIB processing together arose from two factors: the oxidative nature of NiMHs and reductive nature of NiMHS, and the circulation of sodium in the process (Liu et al., 2019). Sodium was introduced in the process due to the use of NaOH, which was needed to precipitate dissolved iron from LIB waste and adjust pH for lithium precipitation, and Na$_2$PO$_4$ for lithium precipitation, while the precipitation of rare earths consumed Na in the form of Na$_2$SO$_4$. Since the effluent from Li precipitation is high in dissolved sodium and sulfate, the crystallization of sodium sulfate could be an option for decreasing the consumption of chemicals. On the other hand, sodium sulfate is highly soluble, which makes its crystallization energy intensive. Furthermore, sodium sulfate is an inexpensive chemical. The exact execution of sodium circulation to REE precipitation was not considered in the conceptual study of Liu et al. (2019), but it can be addressed by process modeling. Some options for sodium and sulfate management were investigated in the following scenarios:

**SCE1, Na recycling as crystallized sulfate:** The first option for obtaining REE precipitation chemicals was the vacuum crystallization of sodium sulfate from the Li-barren brine. This has also been applied industrially in the management of industrial brines despite the expenses (Randall et al., 2011). Although vacuum evaporation process is energy consuming, it allows excess water, sulfate and sodium to be removed from the process. This may be beneficial in areas where sulfate and sodium containing wastewater can regulations.

**SCE2, Na recycling in dilute solution:** Second sodium management option circulates part of the Na containing solution (filtrate from lithium precipitation) to REE precipitation and the rest of the solution to neutralization. This way, the energy-consuming crystallization step can be completely avoided and sodium circulated in liquid form to REE recovery, however, the circulation of solution affects the water balance and may dilute the PLS and accumulate impurities in the system, which could affect the efficiency and recovery rates in the process.

**SCE3, no Na recycling:** In the third option, sodium sulfate is not crystallized and the alkaline solution from lithium phosphate precipitation is pumped directly to neutralization. In this option, Na in the process cannot be reused, but commercial technical grade sodium sulfate is required for the process to allow REE precipitation. Less energy is consumed as evaporation can be avoided, but more water needs to be processed in neutralization.

2.2.4. Simulation assumptions

The building of the models and the theory behind them is discussed in detail in the supplementary material. The main assumptions and data gaps in the model are presented in this section. The leaching data of Liu et al. (2019) was reanalyzed to be used in the leaching model and problems with the experimental design were identified, such as the use of fixed leaching time (40 min) and single parameter variation. The optimization of one variable at a time makes it difficult to evaluate the interaction between the parameters, which could have been prevented with simple acid consumption measurements. The data was analyzed so that the extraction was calculated as the function of calculated proton consumption per proton. In solution to avoid the highlighted problems, which presumes that acid is the limiting factor controlling the leaching process. It was assumed that NiMH/LIB ratio has to be 0.75:1 or above, but never lower to ensure sufficient reductive power for the complete dissolution of LIB active materials, i.e. the quantity of reductant is not the limiting factor in leaching. The progress of leaching reactions could thus be calculated based on the amount of acid in the system. The process was simulated assuming an initially slurry with 91 g/L solids and 0.75:1 NiMH/LIB ratio, where the “optimal” initial sulfuric acid content was calculated to be 123 g/L.

Solvent extraction steps were simulated with a black box approach in a single step without the organics, which were Cyanex 272 and D2EHPA. Both are cation exchangers, meaning that the pH of the solution decreases when the extractant is loaded, and the valuables are stripped into solution when the loaded organic is contacted with acid. The black box interface distributes each solution species between the raffinate and the pure solution based on experimental results, but the distribution of protons needed to be calculated separately to simulate the balance between the solution and the organic. A similar control was put in place for sulfate ions, which are not loaded into the extractant. The equilibrium pH of the raffinate was controlled by feeding NaOH into the SX units. This approach is reliant on experimental data on the extraction efficiency of each metal and is poorly suited to study complex SX processes in detail. Organic scrubbing, for instance, is not possible to model without additional steps. The advantage of the black box approach is that HSC database currently contains only a limited amount of data on organic extractants and organic-metal complexes. However, it is possible for the user to add missing species for personal use. A more thorough description of the SX model is provided in the supporting material.

The crystallization units for cobalt and nickel sulfate were modeled with literature data on the solubility of metal sulfates alone. The solubility of a suitable impurity metal present in the solution was used to
control the amount of evaporated water, while the solubility of the target metal controlled the progress of crystallization. It was observed that copper sulfate is the only impurity likely present in the solution to be used as the marker impurity, although cobalt sulfate could be suitable for use in nickel sulfate crystallization. Data for copper sulfate was obtained from the publication of de Juan et al. (1999), nickel sulfate from Kobylin et al. (2013), and cobalt sulfate from Charykova et al. (2010). Although this approach is likely an oversimplification of a complex unit process, the crystallization units have a limited effect on the balances of other units. The data gap could be addressed by thermodynamic studies on multi-compound systems, which are more lacking for aqueous solutions than systems relevant to pyrometallurgy.

Further model improvements could be made particularly for thickeners and filters, which were modeled with the constants embedded in HSC Sim. Although the sedimentation behavior of leaching slurries is easy to study with a very simple setup, this is scarcely done in literature despite the importance of thickeners for the feasibility of industrial operation. Rough estimations on filter cake moisture before washing, washing water consumption, and washing efficiency would also be invaluable based on simple measurements. The use of ready constants leads to errors in the water balance and the electricity consumption calculations, but possibly also the recovery rates of valuables and the purity of the end products.

2.3. Life cycle assessment

2.3.1. Scope and functional unit

The aim of this study was to conduct a gate-to-gate LCA study to determine the environmental impacts of a conceptual battery recycling process in Europe. GaBi software was used to conduct the LCIA. The functional unit was defined as the treatment of 1 kg of crushed waste batteries and the analysis was conducted gate-to-gate.

2.3.2. System boundary

The waste batteries were considered as post-consumer waste in the study, and the production and use of the batteries were not included in the system. Mechanical pretreatment such as dismantling, crushing, and screening were excluded from the system boundary limit, but the impacts from these steps were assumed to be small in comparison to the hydrometallurgical process due to the low temperatures used in the pretreatment. Steel from casings and aluminum and copper from the current collector foils are recovered already during the mechanical treatment steps, however, and the scope of this study is consequently only the recovery of the active materials in the batteries: lithium, cobalt, nickel, rare earths, and manganese. The recovery of copper and aluminum in the pretreatment steps are evaluated with sensitivity analysis, however. The boundary and a schematic of the process is provided in Fig. 1.

Substitution approach was used to credit recycling with a 1:1 ratio for equivalent virgin raw materials. Data for primary nickel sulfate and manganese dioxide production was obtained from the used databases, and the LCI data for cobalt sulfate reported by Dai et al. (2018) was used to estimate virgin cobalt sulfate production. Lithium phosphate and REE double sulfate were not in the databases, and lithium carbonate and rare earth oxide concentrate were used at stoichiometric ratios were used instead. Based on the system boundary, negative impacts would imply environmental benefits from recycling (credit) and positive values disadvantages (debit).

The study focused on Europe, and average European values were used to model the production of chemicals and utilities where

Fig. 1. Technical boundary used in the study, the possible scenarios highlighted with a blue dashed line and the expanded system with a red dashed line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
applicable. Average transport distances embedded in the ecoinvent database were also used for the chemicals and utilities, including the avoided primary products. The effect of the energy profile in the results is evaluated in the sensitivity analysis.

2.3.4. Inventory analysis

Sb-eq), and fossil depletion (ADPf, MJ), photochemical ozone creation (POCP, kg Ethylene-eq), human toxicity potential (GWP, measured in CO₂-eq), terrestrial acidification potential (AP, unit SO₂-eq), freshwater eutrophication potential (EF, unit Phosphate-eq), stratospheric ozone depletion (ODP, kg R11-eq), photochemical ozone creation (POCP, kg Ethylene-eq), human toxicity potential (HTP, unit DCB-eq), abiotic depletion of elements (ADPe, kg Sb-eq), and fossil depletion (ADPf, MJ).

2.3.4. Inventory analysis

Table 1

The life cycle inventories of each scenario, normalized for 1 kg of mixed feed.

| INPUTS | SCE1 | SCE2 | SCE3 | Unit |
|--------|------|------|------|------|
| Spent NiMHs | 0.43 | 0.43 | 0.43 | kg |
| Spent LIBs | 0.57 | 0.57 | 0.57 | kg |
| Process water | 26.49 | 23.84 | 18.22 | kg |
| Electrical power | 0.36 | 0.30 | 0.29 | kWh |
| H₂SO₄ | 3.15 | 3.36 | 3.15 | kg |
| Na₂SO₄ | 0.00 | 0.00 | 0.00 | kg |
| KMnO₄ | 0.05 | 0.05 | 0.05 | kg |
| NaOH | 2.10 | 2.27 | 2.10 | kg |
| Na₃PO₄ | 0.11 | 0.11 | 0.11 | kg |
| Ca(OH)₂ | 0.02 | 0.00 | 0.00 | kg |
| OUTPUTS | SCE1 | SCE2 | SCE3 | Unit |
| NiSO₄·6H₂O | 1.12 | 1.12 | 1.12 | kg |
| CoSO₄·7H₂O | 0.68 | 0.68 | 0.68 | kg |
| Li₂PO₄ | 0.08 | 0.08 | 0.08 | kg |
| Na₂REE(SO₄)₂ | 0.17 | 0.17 | 0.17 | kg |
| MnO₂ | 0.06 | 0.06 | 0.06 | kg |
| Solid waste | 3.45 | 0.34 | 0.54 | kg |
| Waste water | 17.31 | 19.72 | 19.33 | kg |
| Oxygen | 0.02 | 0.02 | 0.02 | kg |
| Hydrogen | 0.01 | 0.01 | 0.01 | kg |
| Water vapor | 10.34 | 3.35 | 3.08 | kg |

The compiled LCI normalized for 1 kg of mixed battery feed is presented in Table 1, and the flows and upstream processes along with the GUID codes used in GaBi are presented in the supporting information. For instance, no equivalent flows were present in the database for lithium phosphate and rare earth double sulphate, which is why lithium carbonate and lanthanum oxide were assigned instead. The residues from leaching, iron precipitation, and neutralization were mapped as solid waste. In the table, it can be seen that the differences between the scenarios were very minor. Differences are visible in the consumption of sulfuric acid, neutralizing chemicals, water and electricity, and the amount of water vapor and wastewater. SCE3 is also the only investigated scenario with sodium sulfate input, while excess is produced in SCE1.

3. Results

3.1. Process performance in simulation

3.1.1. Products and recovery rates

The products recovered from the process in all scenarios were nickel sulfate hexahydrate, cobalt sulfate heptahydrate, lithium phosphate, rare earth salt, and manganese oxide. Assuming 8000 h of annual operation, the annual production rate of the plant would be 1020 t lithium phosphate, 8650 t cobalt sulfate, 14 200 t nickel sulfate, 2200 t rare earth product and 760 t manganese dioxide. Impure sodium sulfate was also produced in SCE1 in excess, but the high NaOH content in the solid waste. In the table, it can be seen that the differences between the scenarios were very minor. Differences are visible in the consumption of sulfuric acid, neutralizing chemicals, water and electricity, and the amount of water vapor and wastewater. SCE3 is also the only investigated scenario with sodium sulfate input, while excess is produced in SCE1.

3.1.2. Wastewater and solid residues

One of the major challenges in developing sustainable hydrometallurgical processes is the sound management of contaminated wastewaters and the stabilization of harmful species. The primary concern here is the release of acidic solutions containing copper, nickel, and cobalt into the environment. Neutralization of the effluent and thus the removal of most metals was conducted in the simulation, but the bleed waters contain species such as sulfate and alkali metals, which may be harmful to sensitive aquatic ecosystems despite their lower toxicity. In addition, the behavior of F or electrolyte residues could potentially challenge the wastewater treatment, if present, but was excluded from the process consideration (Sun and Qiu, 2011). Sulfate and Na concentrations in the bleed were 6 g/L and 2 g/L respectively, while the values in the other scenarios were >20 g/L and >6 g/L in SCE2 and 3. The water balance was also affected: the washing of crystallized Na₂SO₄ salt resulted in 12% more freshwater use than in SCE2 and 47% more than in SCE3. The condensate from the crystallizers could, however, possibly be used to replace some of the water in SCE1.

The leach residue consisted mainly of the acid-insoluble graphite (96.6%) found in the lithium-ion battery anodes and residual metals from both battery types, mainly LaNi₅ (0.9%), LiCoO₂ (1.0%) and Ni (OH)₂ (1.1%). Since graphite is deemed a critical raw material in the EU, recovering and regenerating it as an anode material would be highly desirable. Approximately 0.32 tonnes of carbon-rich leaching residue is produced for each tonne of treated batteries and 0.55 tonnes for each tonne of lithium ion batteries, making the graphite-rich residue a significant waste stream.

The solubility of heavy metals, mainly nickel and cobalt, from the solid process residues would need to be confirmed experimentally to determine suitable methods for their disposal. Further washing especially of the leach residue is recommended to remove the easily soluble nickel, cobalt, and copper sulfates (270 mg, 150 mg, and 9 mg/kg, respectively) contained in the moisture after filtration. The residual nickel-bearing active materials are of particular concern due to the strict limits imposed by the EU in Directive 1999/31/EC. The residue contains approximately 1290 mg/kg of nickel in the active materials, while the limit for non-hazardous waste in the leaching tests (L/S ratio 10 L/kg) is 10 mg for 1 kg of dry substance. The same is true particularly for the neutralization residue, which contains mainly nickel, cobalt, and manganese hydroxides in addition to gypsum (CaSO₄·2H₂O) in SCE1.

The iron-rich sludge, on the other hand, is considerably more benign...
in terms of its environmental properties, although the large surface area of iron hydroxide precipitates may, in truth, promote the adsorption of other dissolved metals (Monhemius, 2016), which was not accounted for in the model. However, the main issue in this iron control method lies in its gel-like consistency, which makes its dewatering and washing particularly challenging (Monhemius, 2016). The rejection of iron as hematite (Fe₂O₃) would be preferable to the other industrial alternatives such as sodium iron oxihydroxide, not only due to its easier filterability but also because sufficiently pure hematite can be utilized by the steel or pigment industries (Masambi et al., 2016).

3.2. Environmental impacts

The consumption of chemicals and utilities is presented in Table 2 for 1 kg of mixed feed batteries. Lime slaking was assumed to be done onsite into a milk-of-lime slurry with a high solids content, while the rest of the chemicals are commercial grade. The consumption of the extractants in solvent extraction was also not accounted for due to the use of the black box approach in the simulation.

It can be surmised from Table 2 that the highest consumption of leaching and neutralizing chemicals is associated with SCE2, where sodium was circulated in solution. The reason for this is the larger volume of solution in the solvent extraction steps, where the stripping acid feed was controlled by the ratio of aqueous feed to purified solutions, and the higher solution volume also increased the need for pH control chemicals. However, subjecting the alkaline filtrate from lime precipitation to neutralization minimized the need for lime, in both SCE2 and SCE3. In SCE1, the increased water and electricity feeds were directly due to the Na₂SO₄·10H₂O crystallization step, as a considerable amount of water was needed to wash the salt.

Despite the relatively high consumption especially of acid and NaOH solutions, overall the results are encouraging when it comes to novel battery recycling processes. The leaching chemical consumption in the optimal conditions described by Swain et al. (2007): 2 M H₂SO₄, 5 vol% H₂O₂, 100 g/L solids, would be approx. 2 kg/kg of 98% sulfuric acid and over 1.6 kg/kg of 35 vol% peroxide solution. In the study by Shin et al. (2005), the optimal conditions were 2 M H₂SO₄, 50 g/L solids, and 15 vol%, which corresponds to 4 kg/kg of H₂SO₄ and 9.6 kg/kg of 35% H₂O₂. This highlights the importance of finding ways to decrease the reductant consumption in hydrometallurgical battery recycling processes, such as by using the reductive power in other waste types. The main difference between the studied process and reductive leaching with H₂O₂ was in the reductant consumption, but the sulfuric acid consumption in leaching alone was also smaller in leaching.

3.2. Environmental impacts

The results for the evaluated environmental indicators are presented in Fig. 2, together with the estimated burdens for the production of an equivalent amount of virgin raw materials. It was seen in the analysis that the crystallization of hydrated sodium sulfate (SCE1) was the most beneficial in terms of environmental impacts in all of the investigated categories. The circulation of dilute solution to precipitate REEs (SCE2) had the highest impacts in impact categories other than human toxicity (HTP) and abiotic depletion of elements (ADPe), where the consumption of Na₂SO₄ made SCE3 (no precipitation chemical circulation) the least environmentally viable option. The impacts in recycling were mostly indirect emissions from background processes, and sodium hydroxide and sulfuric acid production were the most significant contributors (Fig. 2). Although the differences are very small on the LCA, larger differences were observed in the simulation in terms of discharge salt (Na⁺, SO₄²⁻) contents and the overall water balance, which would affect the surrounding environment.

In impact categories other than ODP, the impacts from the process were smaller than the assumed avoided impacts from primary production. The environmental gains from recycling were observed to be mainly from the recovery of nickel and cobalt, which is consistent with earlier studies considering only a single battery chemistry at a time (Ciez et al., 2019; Hendrickson et al., 2015). The finding is explained both by the fact that the treated batteries were high in cobalt and nickel, and that the metals have comparably intensive primary production routes. The environmental profile of the process is also affected by the variability in the feed composition: for instance, high Mn content in the raw materials increases the consumption of permanganate. Although the reclamation of lithium, manganese and rare earths have limited benefits in terms of the measured impacts, their recovery is needed to address potential raw material scarcity, and also to minimize the other impacts from mining and brine processing, such as water pollution and loss of biodiversity.

The comparison between recycling and virgin production impacts is also shown in Fig 3. For SCE1, the treatment of the batteries reduced GHG emissions by 37.7%, acidifying emission by 94.5%, phosphate by 76.5%, photochemical ozone precursors by 93.2%, toxic emissions by 81.2%, abiotic resource depletion by 78.2% and fossil fuel depletion by 13.8%. At the same time, ozone depleting substances increased by 288.3%.

The impacts were calculated based on process parameters obtained from laboratory scale results and are only indicative of the hypothetical industrial process. Some of the aspects of the experimentally verified process are unlikely to be feasible in industrial scale. Instead of expensive and intensive sodium hydroxide, limestone and its derivatives or ammonia are usually used in hydrometallurgical processes for increasing pH. Although their use would likely have a positive effect on the environmental impacts, the introduction of calcium into the solution would result in the precipitation of gypsum, which would need to be removed from the process. The adsorption of valuables on gypsum could result in metal losses and thus also negatively affect the environmental impacts to an unknown extent. Ammonia is often used in solvent extraction units due to their sensitivity to solid matter, but ammonium would also need to be removed from the wastewaters. Ammonia is commonly crystallized as ammonium sulfate, which could be a sellable byproduct. At the same time, the synergistic effect of using the sodium-containing side streams for RREE recovery would likely be lost and virgin Na₂SO₄ would be needed, such as in SCE3.

Although manganese precipitation using potassium permanganate is both selective and results in high manganese recoveries, it is very unlikely to be feasible. Other presented options for manganese recovery include oxidative precipitation with other oxidants, such as SO₂/0₂ mixtures, ammonium persulfate or Caro’s acid (Zhang et al., 2002; Zhang and Chen, 2007), but the selectivity and the resulting purity of the product is not known in battery leaching solutions. Manganese carbonate precipitation has also been suggested after Ni and Co extraction, but this method is likely to result in significant Li losses (Wang and Friedrich, 2015). It was shown by Peng et al. (2019) that Mn, Al and Fe can be extracted using D2EHPA, from which Mn can be selectively stripped in sulfuric acid solution for the recovery of pure Mn product. The removal of aluminum and iron from the organic could then be achieved with strong acid solutions, which would also prevent valuable losses due to adsorption on amorphous Fe and Al residues.

| Table 2 | The consumption of chemicals in all of the scenarios (kg/kg mixed feed). |
|---------|---------------------------------|
|         | Consumption | SCE1 | SCE2 | SCE3 |
| H₂SO₄ (98% solution), leaching | 1.48 | 1.48 | 1.48 | kg/kg feed |
| H₂O₂ (98% solution), SX | 1.56 | 1.56 | 1.56 | kg/kg feed |
| Na₂SO₄·10H₂O (97% solid) | – | 0.25 | 0.25 | kg/kg feed |
| K₂MnO₄ (99% solid) | 0.04 | 0.04 | 0.04 | kg/kg feed |
| NaOH (50% solution), Fe precipitation | 0.98 | 0.95 | 0.98 | kg/kg feed |
| NaOH (50% solution), SX | 2.47 | 2.78 | 2.47 | kg/kg feed |
| NaOH (50% solution), Li precipitation | 0.51 | 0.55 | 0.51 | kg/kg feed |
| Na₂PO₄·12H₂O (98% solid) | 0.11 | 0.11 | 0.11 | kg/kg feed |
| Ca(OH)₂ (20% solid suspension) | 0.08 | – | – | kg/kg feed |
Fig. 2. The calculated environmental impacts for treating 1 kg of mixed batteries in each investigated scenario, including the contributions of upstream processes, and the negative impacts from valuable recovery. a) Global warming (GWP, kg CO$_2$-eq) b) Acidification (AP, kg SO$_2$-eq) c) Eutrophication (EP, kg Phosphate-eq) d) Ozone depletion (ODP, kg R11-eq) e) Photochemical ozone creation (kg Ethylene-eq) f) Human toxicity (HTP, kg DCB-eq) g) Abiotic depletion of elements (ADPe, kg Sb-eq) h) Abiotic depletion of fossil fuels (ADPF, MJ).

Fig. 3. Comparison of recycling impacts (SCE1) to virgin impacts.
The fundamental issue with the synergistic leaching of NiMH battery and LIB waste is the long-term availability of waste NiMH batteries. In Section 2.1, it was predicted that by 2030, the mass of EOL LIBs would be over six times larger than the mass of EOL NiMH batteries and the difference would be increasing fast. Although the share of NiMH-powered vehicles is on the decrease globally, the popularity of HEVs indicates that NiMH batteries will remain a considerable feedstock for emerging recycling plants (CEC, 2015). Although the reductive power in NiMHs can likely be used in smaller recycling operations, the feasibility of the studied recycling process is put into question.

3.3. Sensitivity analysis

One of the largest sources of uncertainty when considering future scenarios is the effect of energy on the environmental profile of prospective processes. The decarbonization of the energy industry will also inevitably affect the environmental footprint of the power intensive chemical, mining, and metallurgical industries particularly in Europe, where the transfer to renewable energy has so far been rapid. Therefore, the sensitivity of the results in terms of future power generation was evaluated by changing the electricity profile of the recycling process and the upstream processes.

As of 2020, the previous target of 40% GHG reduction within the EU was increased to 55%, and the share of renewable energy sources (RES) would increase to 65% or more in electricity production (European Commission, 2020). Several studies have addressed the pathways for the decarbonization of European energy industry and the associated challenges, such as cost effectiveness and uncertainty in future demand (Spiecker and Weber, 2014; Knopf et al., 2015; Gerbaulet et al., 2019), and Knopf et al. (2015) and Gerbaulet et al. (2019) both predicted that onshore wind power is likely the most important renewable energy technology in 2030, and natural gas and nuclear would dominate the fossil fuel use in the scenarios where nuclear power is not phased out. Therefore, the results for the sensitivity analyses, based on the scenarios presented by Knopf et al. (2015), are presented in Fig. 4a.

The effect of including the pretreatment stages, where mainly Cu and Al are recovered, was investigated, assuming that Cu and Al occupy approximately 12% and 20% of LIB cell weight respectively (Dunn et al., 2012) and normalized for 1 kg feed to the hydrometallurgical process. It was estimated that the mechanical processing consumes mainly electricity and the effects are predominantly from the recovery of current collector materials, of which aluminum is lost in the slag in smelting processes. Although sieving has been shown useful in the separation of different fractions (Porvali et al., 2019), much of the valuables are lost in other streams. Low (30%) and moderate (80%) Al and Cu recoveries were selected thus for the analysis. The results are shown in Fig. 4b.

As can be surmised from Fig. 4a, clean sourcing of chemicals and utilities has a large impact on the overall process: GHG emissions could decrease by 26.9–40.0% (to 2.25–2.74 kg CO₂-eq for 1 kg batteries). The sensitivity of the recycling credits were not addressed due to the uncertainty related to the globally limited primary production in the EU, but it is possible that intensive primary production is more sensitive to the energy shift as a whole, which would decrease the difference.

Fig. 4b indicates that the recovery of even a small fraction of the current collector foils has a significant effect on the process. Particularly the reclamation of energy-intensive aluminum would have a massive positive impact on the process: recovering 30% aluminum in the waste decreases the baseline GHG emissions from 61% against virgin production to 46%, while recovering 30% of copper decreases the value to 58%. The analysis supports the hypothesis that the recovery of aluminum foil in addition to copper is critical for the environmentally sound end-of-life management of waste batteries.

4. Discussion

Some of the limitations in the current study are discussed in this section. One of the major limitations is the lack of proper data for battery pretreatment and the representability of the data used for the raw materials. Mechanical pretreatment has been shown to have a significant impact on the subsequent processing steps and the overall recovery rates. For instance, cathode materials may be lost with the aluminum foils due to the polymeric binders, which may be decomposed by thermal pretreatment and thus liberate the active material (Kim et al., 2021). Efficient pretreatment is consequently paramount for the hydrometallurgical process, and the model does not predict final recovery rates for the valuable metals in the active materials.

Error and uncertainty also arise from the limitations in the used databases for both the simulation and the LCA steps. Although HSC databases for both the simulation and the LCA steps. Although HSC databases for both the simulation and the LCA steps.
Chemistry software contains an extensive thermochemical database for different species, predicting solution properties is difficult, which leads to error in the heat balance and solution density. Solvent extraction steps were modeled as black boxes in single units based on mass balance alone, and the heat balance of solvent extraction and consecutive units contains error as a result. Upstream data for the impact analysis was obtained from ecoinvent and GaBi Professional databases.

It is also worth acknowledging that process parameters determined in laboratory batch experiments may not be directly applicable in industrial scale due to the differences in equipment, such as agitators. Most of the process would be presumed to be operated continuously in the industry instead of batch due to the higher efficiency, which would affect the retention times and possibly also the valuable levels in solution. Lower or higher than predicted retention times may be necessary in larger scale to reach the determined extractions at a given process unit, which is reflected on the electricity consumption of the process. Necessary buffer tanks were also not accounted for in the model, which affects the water balance in addition to the energy consumption. The contribution analysis (Fig. 2) indicates that moderate variation in the electricity consumption from the predicted value would have a limited effect on the environmental impacts.

5. Conclusions

The goal of the study was to conduct an early evaluation of the environmental impacts of a conceptual hydrometallurgical battery recycling process, where the complementary chemical properties of NiMH and Li-ion battery wastes are used in the recycling of batteries. The environmental feasibility of sodium salt circulation to precipitate rare earth metals was also investigated by comparing different technical ways to implement it using process simulation. The life cycle inventory was compiled from the process model. Although the simulation-based LCA methodological is useful in studying prospective processes with little or no industrial data behind them, some experimental data is needed. Problems with the previous experimental design of Liu et al. (2019) were recognized and the data was re-analyzed. It was also determined that data on slurry sedimentation behavior and filterability would be valuable for flowsheet modeling, but such data is scarcely presented in experimental literature.

In the study it was demonstrated that the chemical consumption and by extension, the environmental impacts, of hydrometallurgical battery recycling can be significantly decreased by using the waste itself as a reductant. The year 2030 was used as the basis for estimating the availability of waste NiMHs. Finding large enough quantities of these batteries was shown to be a significant obstacle for the widespread implementation of the process concept. On the other hand, in smaller recycling operations, the treatment of mixed battery streams could be used as a means to reduce the consumption of expensive and energy intensive reducing chemicals such as hydrogen peroxide. The process has several merits when compared to pyrometallurgical processes where NiMH and Li-ion batteries are treated together: the mechanical pre-treatment allows the recovery of aluminum current collectors in addition to copper, which was determined to greatly affect the environmental footprint of the process. Furthermore, REEs, Mn and Li, which would traditionally be lost to slag, may be recovered hydrometallurgically.

In comparison to the virgin production of manganese, lithium, nickel, cobalt, and rare earths, the GWP savings in the recycling process were calculated to be 38%. Significant savings were also seen in the other investigated categories, whereas ODP increased by 288%. The environmental benefits of recycling derive from the primary production of nickel and cobalt, attributed in part to their high content in the raw material but also to their comparably intensive primary production. The sensitivity analysis indicates that the recovery of aluminum is even more beneficial in environmental terms. The recycling of low Ni and Co battery mixtures would likely therefore not be as favorable in terms of the environmental footprint of the process.

CRediT authorship contribution statement

Marja Rinne: Conceptualization, Methodology, Software, Investigation, Formal analysis, Visualization, Writing – original draft. Heinu Elomaa: Conceptualization, Methodology, Software, Investigation, Writing – review & editing, Supervision. Antti Porvali: Conceptualization, Methodology, Software, Formal analysis, Writing – original draft. Mari Lundstrom: Conceptualization, Methodology, Supervision, Writing – review & editing, Funding acquisition, Resources, Project administration.

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.

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Supplementary materials

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