



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

# Liu, Fupeng; Peng, Chao; Porvali, Antti; Wang, Zulin; Wilson, Benjamin P.; Lundström, Mari Synergistic Recovery of Valuable Metals from Spent Nickel–Metal Hydride Batteries and Lithium-Ion Batteries

Published in: ACS Sustainable Chemistry and Engineering

DOI: 10.1021/acssuschemeng.9b02863

Published: 29/08/2019

Document Version Publisher's PDF, also known as Version of record

Published under the following license: CC BY

Please cite the original version:

Liu, F., Peng, C., Porvali, A., Wang, Z., Wilson, B. P., & Lundström, M. (2019). Synergistic Recovery of Valuable Metals from Spent Nickel–Metal Hydride Batteries and Lithium-Ion Batteries. *ACS Sustainable Chemistry and Engineering*. https://doi.org/10.1021/acssuschemeng.9b02863

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.





pubs.acs.org/iournal/asceco

# Synergistic Recovery of Valuable Metals from Spent Nickel-Metal Hydride Batteries and Lithium-Ion Batteries

Cite This: ACS Sustainable Chem. Eng. XXXX, XXX, XXX–XXX

Fupeng Liu,<sup>†,‡</sup> Chao Peng,<sup>‡</sup> Antti Porvali,<sup>‡</sup> Zulin Wang,<sup>‡</sup> Benjamin P. Wilson,<sup>‡</sup> and Mari Lundström\*,<sup>‡</sup>

<sup>†</sup>Institute of Engineering Research, Jiangxi University of Science and Technology, 341000 Ganzhou, China <sup>‡</sup>Hydrometallurgy and Corrosion, Department of Chemical and Metallurgical Engineering (CMET), School of Chemical Engineering, Aalto University, Espoo 02150, Finland

Supporting Information

Süstalnable

Chemistry& Engineering

ABSTRACT: This research presents a sustainable approach for the simultaneous recycling of spent lithium-ion batteries (LIBs) and nickel-metal hydride batteries (NiMHs). First, dissolution of LIBs and NiMHs were found to be mutually copromoted, resulting in above 98% extraction of Li, Co, Ni, and rare-earth elements (REEs) without the need for any oxidant or reductant additions. After leaching, >97% of REEs were recovered as a REEs-alkali double sulfate precipitate with the addition of NaOH and Na2SO4 precipitants. This REEs-free solution was then further processed to separate and recover the battery metals present: Mn, Co, Ni, and Li. The resultant residual solution (rich in NaOH and Na<sub>2</sub>SO<sub>4</sub>) was redirected to the REEs precipitation step, decreasing both the need of



precipitants (e.g., Na2SO4) as well as the costs related to the treatment of the high-Na waste solution. Moreover, the Li remaining in the waste solution can be circulated back into the main process, resulting in an exceptionally high Li recovery of >93% in the form of high-purity Li<sub>3</sub>PO<sub>4</sub> (99.95%). This is a marked improvement over the previously reported Li recovery levels of 60-80%. Overall, this newly developed process has considerable environmental and economic advantages for the recovery of valuable metals from mixed LIBs and NiMHs wastes.

**KEYWORDS:** Synergistic leaching, Metals circular economy, Sustainable recycling, Lithium, Rare-earth elements

# INTRODUCTION

Nickel-metal hydride batteries (NiMHs) and lithium ion batteries (LIBs) are the most widely used secondary consumer batteries in the world, both because of their excellent electrochemical performance and their environmental acceptability when compared to lead-acid and nickel cadmium batteries.<sup>1,2</sup> Currently, NiMHs and LIBs represent ca. 28% and 37%, respectively, of the world rechargeable batteries market and their consumption is increasing as a result of the worldwide growth of electronic devices.<sup>3</sup> On average, the maximum life cycle of these batteries is ca. 1000 cycles, which means that large quantities of spent NiMHs and LIBs are discarded after 3-5 years of useful life.<sup>4</sup> These wastes are considered to be a significant environmental pollutant risk, primarily as a result of their heavy-metal content.<sup>5</sup> Moreover, the tremendous growth in demand, increasingly strict mining regulations, and fragilities within the supply chain are predicted to lead to a shortage of both rare-earth elements (REEs) and lithium (Li), which are critical for preparation of NiMHs and LIBs, within only a few decades.<sup>6,7</sup> Considering that spent LIBs contain valuable metals like cobalt (5-20%), nickel (5-10%), and lithium (5-8%) and the NiMHs are rich in nickel (36-

42%), cobalt (3-5%), and REEs (5-25%), these waste streams are increasingly being investigated as important potential resources for Ni, Co, Li, and REEs.<sup>8-10</sup>

Nowadays, hydrometallurgical processes offer a promising alternative for the sustainable recycling of spent batteries in preference to pyrometallurgical routes-which are often associated with high energy consumption, significant valuable metals loss, and hazardous gas emissions.<sup>11</sup> Typically, the hydrometallurgical technologies suggested for spent LIBs involve the combination of reductive acid leaching, sequential solvent extraction of Ni/Co/Mn, and preparation of lithium carbonate.<sup>12</sup> Recently, Gao et al.<sup>13</sup> made a comprehensive evaluation related to the acid leaching of LIBs waste using both mineral (HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>) and organic acids (ascorbic acid, citric acid, tartaric acid, etc.). This review found that the acid species is the most important parameter that influences the leaching kinetics and recovery of target Co and Li elements. Generally, sulfuric acid is most commonly used for

Received: May 21, 2019 August 27, 2019 **Revised:** Published: August 29, 2019

<b>Fab</b>	le 1.	C	hemical	Ana	lysis o	of	Spent	Li-Ion	Battery	and	NiMH	Raw	Material	s (mg	/g	)
------------	-------	---	---------	-----	---------	----	-------	--------	---------	-----	------	-----	----------	-------	----	---

materials	Li	Co	Ni	Cu	Mn	Fe	La	Ce	Pr	Nd	K	Na
LIBs	39.7	207.9	29.9	4.0	18.7	3.7	0.0	0.0	0.0	0.0	0.0	0.0
NiMH	0.0	55.9	432.5	1.0	30.2	3.9	88.2	79.7	12.4	37.2	0.2	0.1

leaching—in preference to hydrochloric acid, nitric acid, and other organic acids—because of its economic advantages. Nevertheless, because the acid dissolution of active materials is a reductive process, addition of reducing agent like  $H_2O_2$ , NaHSO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, D-glucose, or ascorbic acid is often a necessity,  $H_2O_2$  being the most commonly used one.<sup>14</sup> For example, research by Swain et al.<sup>15</sup> revealed that  $H_2O_2$  addition (0–5 vol %) can improve Li extraction from 75% to 94% and Co extraction from 35% to 93% (2 M  $H_2SO_4$ , liquid-to-solid (*L/S*) ratios of 100 g/L, 75 °C). This finding suggests that around 1.6 tonnes of  $H_2O_2$  (35 wt %) would be required by the leaching process per tonne of LIBs waste treated, which would lead to a significant increase in the processing costs.

Another challenge for the comprehensive recycling of spent LIBs by hydrometallurgical methods lies in the difficulty of treating the high-Na-low-Li sulfate raffinate that is produced after the recovery of target metals (Co, Ni, Mn, and Li). It is well-known that, after the acid leaching process, the leachates obtained are usually treated by conventional neutralization, precipitation, and solvent extraction processes to recover Mn, Co, and Ni, which leave a Li-rich raffinate (3-7 g/L).<sup>16</sup> This Li-rich raffinate can then be subjected to Li recovery by evaporation-carbonation or precipitation with phosphate under alkaline conditions.<sup>17</sup> As a consequence of these steps, large quantities of Na are introduced in the system, resulting in the production of large quantities of high-Na-low-Li sulfate raffinate or, in the case of crystallization, a low-value byproduct  $(Na_2SO_4 \cdot xH_2O)$  with coprecipitated impurities. Treatment of both the sodium-containing wastewater and the reuse of lowvalue, impure sodium sulfate byproducts needs to be performed to ensure the clean and economical recycling of spent LIBs.<sup>18</sup>

In contrast to Li-ion batteries, the active anode materials of NiMHs are more akin to hydrogen storage materials and tend to consist of highly reductive substances like hydrogenabsorbing alloys that are commonly based on misch metal (La, Ce, Pr, and Nd), Ni, Co, and Mn. Typical technologies utilized for the recycling of spent NiMHs involve H<sub>2</sub>SO<sub>4</sub> leaching followed by REEs precipitation<sup>19</sup> and then solvent extraction to separate the other metals.<sup>20</sup> Previous research of the acid leaching of NiMHs clearly demonstrate that the presence of an additional oxidant during leaching enhances both metal extraction and reaction kinetics. Rabah et al.<sup>21</sup> investigated the leaching of spent NiMHs in a sulfuric acid system and their results showed that the maximum Ni dissolution was only 93.5% with 3 mol/L H<sub>2</sub>SO<sub>4</sub> after 3 h without any additional oxidant, while >99% Ni dissolution was achieved within 1 h in the presence of 10% (v/v)  $H_2O_2$ . After the leaching process, the sodium double sulfate precipitation method is a straightforward approach for REEs recovery.<sup>19,22</sup> To achieve the high recovery of REEs (e.g., >99%), 6-12 times the stoichiometric amount of Na2SO4 needs to be consumed, that is, 0.4-0.8 tonnes of Na<sub>2</sub>SO<sub>4</sub> per 1 tonne of spent NiMHs. This large consumption for the oxidant  $(H_2O_2)$ and precipitant  $(Na_2SO_4)$  would add to the recycling cost for spent NiMHs considerably.

Overall, to greatly improve the recycling efficiency of spent lithium batteries and reduce operational costs, the following processing aspects must be improved: (1) supply of a reagent with high reduction performance and low cost; (2) effective use of subsequent byproducts (NaOH and Na<sub>2</sub>SO<sub>4</sub>). On the other hand, processing of spent NiMHs requires the introduction of a reagent with excellent oxidation performance as well as a precipitation reagent (Na<sub>2</sub>SO<sub>4</sub>) to capture the REEs. In this regard, simultaneous recycling of both types of spent batteries is synergistic: NiMHs waste provides the reductive power required for LIBs recycling, whereas LIB processing generates large quantities of reusable sodium sulfate for REEs precipitation.

On the basis of the complementary chemical properties of these raw materials, this paper outlines the development of a more economical and environmentally attractive methodology for the reprocessing of NiMHs and LIBs wastes through their synergistic recycling based on green chemistry principles. The proposed methodology not only avoids the use of an expensive oxidant (e.g., H2O2) for spent NiMHs and reducing agent (e.g.,  $H_2O_2$ ) for LIBs but also utilizes the value-added use of the byproducts (NaOH and  $Na_2SO_4$ ) as neutralization and precipitation reagents within the process, which reduces the recycling cost while avoiding the adverse effect of byproducts on the environment. Moreover, the comprehensive recovery of valuable metals is significantly improved by the synergistic recycling of these two spent battery types, demonstrating the environmental and economic viability of the process and further highlighting the significant potential for industrial application. Comprehensive recovery of Li can also be increased by 20-30% by adopting the phosphate precipitation method and by returning the low-lithium-containing sidestream back to the process.

#### EXPERIMENTAL SECTION

**Materials and Characterization.** The collected spent LIBs and NiMHs were industrially pretreated by mechanical processing which included crushing, magnetic separation, and sieving to produce NiMHs (<0.500 mm) and LIBs (<0.125 mm) wastes.<sup>8,19</sup> The NiMHs battery waste was first prewashed with distilled water (L/S = 15 mL/g) for 1 h at 30 °C to remove any potential alkali metals (e.g., Na and K) from the electrolyte, which can act as an initiator for the double sulfate precipitation of REEs and lead to the loss of REEs during the sulfuric acid leaching.<sup>19</sup> The chemical compositions of the LIBs and prewashed NiMHs battery waste are presented in Table 1, which shows that these two battery wastes are both rich in Co, Ni, and Mn; additionally, the LIBs material contains ca. 4% Li, whereas NiMH contains ca. 22% REEs (La, Ce, Pr, and Nd).

Characterization of the raw materials, leaching residues, and products formed were carried out using a number of different spectroscopic techniques. First, chemical composition of the solid samples were measured based on aqua regia digestion and ICP-OES determination (inductively coupled plasma-optical emission spectroscopy, PerkinElmer Optima 7100 DV, USA). The main mineral phases within the solid samples were identified by XRD (X-ray diffractometry, PANalytical X'Pert Pro Powder, Almelo, The Netherlands) using a Co K $\alpha$  radiation source with a 40 kV acceleration potential and current of 40 mA. XRD patterns were analyzed by using HighScore 4.0 Plus software. Additional chemical identification and elemental distribution were also performed with EDS (energy dispersive spectrometer, Link Inca X-sight 7366, Oxfordshire, UK). The morphology of the products (REEs double sulfates and lithium phosphate) were determined by scanning electron microscope (SEM, A LEO 1450, Carl Zeiss Microscopy GmbH, Jena, Germany). All the other chemicals used in the leaching, precipitation, and solvent extraction were of analytical grade.

Acid Leaching with Mixed Battery Wastes. The acid leaching experiments were performed in a 300 mL cylindrical reactor with magnetic stirring (300 rpm) and the temperature was controlled by a water bath (Thermo Haake, DC10). Initially, separate acid leaching experiments with either LIBs or NiMHs waste only as the starting material were investigated as a function of time and then compared to the mixed battery leaching process-the other type of battery waste, depending on the initial starting material, was added at t = 90 min. Further leaching experiments where the two battery wastes were mixed prior to experimentation were also conducted to study the influence of the mass ratio of NiMHs:LIBs (1:0.25-1.5:1, N/L), leaching time (10-120 min), acid concentration (0.5-3 mol/L), and liquid-to-solid (L/S) ratios (5-15 mL/g). After a predetermined duration, the resultant slurry was filtered and the obtained leaching residues were washed with hot distilled water (70-80 °C) before being dried at 80 °C for 12 h. The filtrate and washing solutions were then subjected to chemical analysis to calculate the leaching efficiency (%*E*) via eq 1:

$$\%E = (C_{\rm M1}V_1 + C_{\rm M2}V_2) / (m_1w_{\rm M}^1 + m_2w_{\rm M}^2) \times 100\%$$
(1)

where  $C_{M1}$  and  $C_{M2}$  are the concentration of metals in the leachate and washing water (g/L),  $V_1$  and  $V_2$  are the volume of leachate and washing water (L),  $m_1$  and  $m_2$  are the mass of input NiMHs and LIBs waste (g), and  $w_M^1$  and  $w_M^2$  are the composition of metals in NiMHs and LIBs wastes, respectively. To ensure the accuracy of the leaching results, the residual contents of elements in leaching residues were also analyzed to further verify the results. Some key experiments were repeated three times and the variations of the results were presented—where appropriate—as error bars.

**Recovery of REEs by Alkali Double Sulfate Precipitation.** The precipitation of REEs experiments were performed in a 250 mL conical flask, which was placed in a constant-temperature water bath (Thermo Haake, DC10). Precipitation efficiency of REEs and purity of the products as a function of pH and  $Na_2SO_4$  dosage were investigated at 70 °C with magnetic stirring of 200 rpm for 1 h. In experiments, to determine the influence of pH, we selected Ni(OH)<sub>2</sub> rather than NaOH to adjust pH to avoid the introduction of alkaline ions (Na<sup>+</sup>), which coprecipitate with REEs in sulfate systems. The stoichiometric amount of sodium sulfate was determined by eq 2, where REE stands for rare-earth elements.

$$\operatorname{REE}_{2}(\operatorname{SO}_{4})_{3} + \operatorname{Na}_{2}\operatorname{SO}_{4} + n\operatorname{H}_{2}\operatorname{O} \to 2\operatorname{Na}\operatorname{REE}(\operatorname{SO}_{4})_{2} \cdot n\operatorname{H}_{2}\operatorname{O}\downarrow$$
(2)

The resultant precipitate was filtered, washed with distilled water, and then dried at 100  $^{\circ}$ C for 12 h. Precipitation efficiencies of the REEs (%*P*) were calculated on the basis of the concentration of REEs in leachate and washing solution:

$$%P = \left[ \left( 1 - \left( V_1 C_1 + V_2 C_2 \right) / \left( V_0 C_0 \right) \right] \times 100\%$$
(3)

where  $C_0$  and  $C_1$  represent the initial and final concentration of REEs before and after precipitation procedure,  $V_0$  and  $V_1$  are the volume of solution before and after precipitation,  $C_2$  represents the concentration of REEs in washing solution, and  $V_2$  is the volume of washing water.

After REEs precipitation, the REEs-free solution was then subjected to the separation and recovery of Mn, Co, Ni, and Li, further details of which can be found in the Supporting Information.

# RESULTS AND DISCUSSION

**Synergistic Leaching of NiMHs and LIBs.** The effect of leaching time (10–90 min) on the recovery of the main metals

of interest from spent LIBs (Li and Co) and spent NiMHs (Ni and REEs) were initially investigated separately to provide a benchmark for the kinetics of the respective leaching processes. After 90 min of reaction time, either LIBs (25 g/L) or NiMHs (50 g/L) were introduced as an additive to the reactor bath—depending on the initial starting material—to ascertain any synergistic effects. Results shown in Figure 1 indicate that the



**Figure 1.** Leaching kinetics of LIBs and NiMHs wastes without additional agents and the synergistic effect of LIBs and NiMHs wastes in mixed leaching (2 mol/L  $H_2SO_4$ , T = 75 °C, liquid-to-solid ratio of 10:1).

acid dissolution of spent LIBs and NiMHs both increase as a function of time and reach equilibrium at around 60 min. For the acid dissolution of spent NiMHs in the absence of any additives, Ni and REEs extraction exhibit similar behaviors, increasing with time, and reach the equilibrium of around 90% after 45 min. Nevetheless, Ni extraction is observed to be slightly higher than REEs. This may result from the fact that part of Ni in NiMHs exists as Ni<sub>2</sub>(OH)—which is readily dissolved under acidic conditions, whereas the majority of REEs are present in the form of alloys like LaNi<sub>5</sub> and Ce<sub>2</sub>Ni<sub>7</sub> (Figure 2a). XRD results of the leaching residue in Figure 2b further illustrate that the peaks corresponding to Ni(OH)<sub>2</sub> in



Figure 2. XRD diffractograms of (a) NiMH battery waste, (b) leaching residue with only NiMH battery waste, (c) Li-ion battery waste, (d) leaching residue with only LIBs waste, and (e) leaching residue with mixed batteries.



# Table 2. Proposed Reactions in the Acid Dissolution Process of Mixed LIBs and NiMHs Waste (HSC Chemistry 9, 353.15 K)

**Figure 3.** Influence of (a) mass ratio of NiMHs and LIBs (1.25 mol/L  $H_2SO_4$ , T = 75 °C, t = 40 min, L/S = 10:1), (b) leaching time (N/L = 0.75, 1.25 mol/L  $H_2SO_4$ , T = 75 °C, L/S = 10:1), (c) acid concentration (T = 75 °C, t = 40 min, N/L = 0.75) and (d) liquid-to-solid ratio (1.25 mol/L  $H_2SO_4$ , T = 75 °C, t = 40 min, N/L = 0.75) and (d) liquid-to-solid ratio (1.25 mol/L  $H_2SO_4$ , T = 75 °C, t = 40 min, N/L = 0.75) and (d) liquid-to-solid ratio (1.25 mol/L  $H_2SO_4$ , T = 75 °C, t = 40 min, N/L = 0.75) on the leaching of valuable metals.

Figure 2a cannot be observed and Ni is present only in alloy phases like NiFe<sub>3</sub>, AlNi<sub>3</sub>, and LaNi<sub>5</sub>. In the case of spent LIBs, the maximum leaching efficiency of Li was only 80% and for Co, 63%. According to previous research by Ferreira et al.,<sup>23</sup> the limited acid dissolution of LIBs is mainly a result of the formation of intermediate products like Co<sub>3</sub>O<sub>4</sub> that hinder further dissolution of active materials. Additionally, the results also show that Li dissolution reaches equilibrium faster than Co and that the leaching efficiency of Li is consistently 15-25% higher than that of Co. This can be attributed to the fact that Li ions, which lie between layers of the octahedra formed by cobalt and oxygen atoms, can readily transfer to the electrolyte solution.<sup>24</sup> It is therefore comparatively much easier for Li to be dissolved than Co, resulting in a range of compounds  $\text{Li}_x \text{CoO}_2$  (0 < x < 1), which is consistent with the XRD results of the leaching residue (shown in Figure 2d) where Li<sub>0.6</sub>CoO<sub>2</sub> compounds can be clearly identified. According to previous research,<sup>25</sup> to dissolve these residual Co-bearing compounds (e.g., Li<sub>0.6</sub>CoO<sub>2</sub>), one must utilize additional reducing agents such as H<sub>2</sub>O<sub>2</sub> and ascorbic acid.

Interestingly, after the introduction of NiMHs materials into the LIBs leaching process, Li and Co leaching efficiency increases significantly and reaches almost 100% for both Li and Co within 30 min of the addition. A similar observation for the addition of LIBs to the NiMHs leaching process is also seen, as the leaching efficiencies of Ni and REEs increase markedly to above 98%. XRD results of the related leaching residue with mixed battery wastes (Figure 2e) show that the only main phase that could be identified was carbon from spent LIBs, whereas diffraction peaks corresponding to undissolved Li<sub>0.6</sub>CoO<sub>2</sub> (Figure 2d) and alloys of Ni and REEs (e.g., Ni<sub>3</sub>Fe, LaNi<sub>5</sub>, and AlNi<sub>3</sub>, Figure 2b) all disappear after the introduction of the other type of battery waste as reductant or oxidant. Further SEM morphologies and mapping analysis of the mixed battery leaching residue in Figure S1 verified that, in the leaching residue, no REEs metals can be detected and that the material is comprised primarily of C and trace alloy particles that contain Ni, Co, Fe, and Ti (Figure S1C).

These findings suggest that spent NiMHs and LIBs materials can copromote the acidic dissolution of one another. Such a synergistic leaching of LIBs and NiMHs wastes can be



**Figure 4.** Influence of (a) the final pH (T = 70 °C, t = 60 min, Na<sup>+</sup>/REE<sup>3+</sup> = 4) and (b) the amount of Na<sub>2</sub>SO<sub>4</sub> added (pH = 1.4, t = 60 min, T = 70 °C) on the recovery of rare earth. (c) and (d) are the XRD diffractogram pattern and SEM micrograph of the white REEs double sulfate precipitate, respectively.

assumed, at least partly, to result from the complementary oxidation-reduction properties of their main components. It is evident from the data presented in Table S1 that the alloy materials in NiMHs such as LaNi<sub>5</sub>, AlNi<sub>3</sub>, and AlCe<sub>2</sub> have reasonably strong reductive capabilities on the basis of their negative half-reaction potentials, whereas the half-reaction potential of LiCoO<sub>2</sub> in LIBs is up to 2.1 V (vs SHE). This suggests that the alloys present in NiMHs battery waste and the active materials in LIBs can act as electron donors and acceptors in the leaching system. This idea is further corroborated by the measured changes in the redox potentials of the LIBs waste leaching system, which clearly reduce from ca. 910 to 300 mV (vs SHE) with the addition of NiMHs waste after 90 min. This confirms the reductive nature of the materials present in the NiMHs waste. Taking LaNi5 and LiCoO<sub>2</sub> as examples, the acid dissolution of LIBs, NiMHs, and mixed battery wastes can be described via reactions 4-6, outlined in Table 2. The mechanism by which the electrons are transferred between the reductant (LaNi<sub>5</sub>, Ce<sub>2</sub>Ni<sub>7</sub>, and AlNi<sub>3</sub>) and oxidant (LiCoO<sub>2</sub>) can be considered to occur via a number of different pathways. One option is through the combination of reactions 7 and 8, wherein the  $Fe^{2+}/Fe^{3+}$  ions act as a charge mediator in the solution. Thermodynamically, ferrous ions have the potential to reduce LiCoO<sub>2</sub>, whereas ferric ions can act as an oxidant through the reaction with the metallic alloys present (reaction 8) as highlighted by our previous research.<sup>26</sup> Furthermore, an alternative dissolution

pathway for the acid-resistant phases that involves galvanic interactions between  $LiCoO_2$  and  $LaNi_5$  in the acidic medium (reaction 6) is theoretically possible. However, the probability and the extent to which this reaction occurs remain debatable.

To optimize the conditions for the synergistic leaching of NiMHs and LIBs, we performed further experiments to study the effect of the NiMHs-to-LIBs (N/L) mass ratios (Figure 3a), leaching time (Figure 3b), acid concentration (Figure 3c), and liquid-to-solid ratio (L/S) (Figure 3d) on the leaching of Li, Co, Ni, and REEs during mixed batteries leaching. In these experiments, LIBs and NiMHs battery wastes were mixed together in different proportions prior to initiation of the leaching process.

As observed in Figure 3a, the leaching efficiencies of Ni and REEs maintain a high level of around 99% over the N/L mass ratio range of 0.25:1–0.75:1, whereas further increases of N/L ratios to 1.5:1 result in a marked drop of Ni and REEs leaching efficiencies to approximately 94%. In contrast, extraction of Li and Co exihibit the opposite behavior, which increase substantially as the N/L mass ratios increased from 0.25:1 to 0.75:1 and then level off at above 98% with further increasing of the N/L ratio. The converse dissolution behavior of LIBs and NiMHs as a function of the NiMHs-to-LIBs (N/L) mass ratios further support the idea that LIBs and NiMHs wastes have complementary properties for each other; that is, they can act as reciprocal oxidizing (LIBs) and reducing (NiMHs) agents. Moreover, it can be observed that as the of N/L ratios

Table 3. Composition of the Sulfate Solution before	(PLS1	) and after	(PLS2	) pH Adj	justment	with NaOH	(g/L	,)
---	-------	-------------	-------	----------	----------	-----------	------	----

			concentration (g/L)										
no.	pН	Li	Co	Ni	La	Ce	Pr	Nd	Fe	Mn			
PLS1	1.18	2.29	14.58	20.30	3.39	3.79	0.53	1.58	0.31	2.21			
PLS2	1.40	2.28	14.53	20.26	1.56	1.81	0.30	0.86	0.28	2.20			

Table 4	L	Concentration	of	Flements	in	Fach	Subsec	ment	Solution	in	the	Metals	Recovery	Process	a
I able 4	•	Concentration	01	Liements	ш	Lacii	Subsec	uent	Solution	ш	une	wictais	Recovery	FIUCESS	

				_						
					cor	ncentration (g/I	L)			
no.	pН	Li	Co	Ni	Mn	Fe	REEs	Na	SO4 <sup>2-</sup>	PO4 <sup>3-</sup>
PLS3	1.5	2.28	14.53	20.26	2.20	0.28	< 0.01			
PLS4	6.7	2.18	0.13	0.21	0.075	< 0.01	< 0.01	48.4	126.2	
PLS5	12.0	2.17	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	56.8	125.7	
PLS6	12.0	0.11	< 0.01	<0.01	< 0.01	< 0.01	< 0.01	63.2	122.0	< 0.01
<sup>a</sup> Before (PLS	3) and after	(PLS4) th	e recovery of	Ni. Mn. and	Co. followed u	in by the reco	overv of Li be	fore (PLS5)	and after (P	LS6) Li-PO

"Before (PLS3) and after (PLS4) the recovery of Ni, Mn, and Co, followed up by the recovery of Li before (PLS5) and after (PLS6)  $Li_3PO_4$  precipitation.

increase from 0.75:1 to 1.5:1, Co leaching efficiency decreases slightly from ca. 99.5% to 98.5%, whereas Li extraction remains above 99.5%. This "abnormal" behavior of Co is hypothesized to result from the incomplete dissolution of Co from NiMHs. From these results, it can be concluded that the optimum mass ratio of NiMHs and LIBs is 0.75:1 and this ratio was subsequently used for further studies.

The results shown in Figure 3b demonstrate that leaching of Li, Co, Ni, and REEs is rapid with >95% dissolved within 30 min and their maximum efficiencies of over 98% achieved after only 40 min. Compared to the separate leaching of spent LIBs or NiMHs waste in Figure 1, it is clear that the synergistic mixed leaching of LIBs and NiMHs is much more efficient in terms of both leaching kinetics and efficiency. Further studies into the effect of acid concentration and L/S ratios in Figure 3c,d show that the leaching efficiency of Li, Co, Ni, and REEs all increase with increasing acid concentration and L/S ratios before reaching the maximum efficiency of >98% under optimum conditions of N/L = 0.75:1, t = 40 min,  $[H_2SO_4] = 1.25$  mol/L, and L/S = 10 mL/g.

It is clear from these findings that through this synergistic leaching of LIBs and NiMHs wastes, over 98% of the valuable metals could be extracted with no consumption of external additives such as  $H_2O_2$ . According to previous research, the consumption of  $H_2O_2$  in acid leaching of LIBs waste (2 M  $H_2SO_4$ , L/S = 10 mL/g) is at least 2.0–6.0 v/v %.<sup>15,27</sup> By calculation, around 0.6–1.8 tonnes of  $H_2O_2$  (35 wt %) can be saved when treating 1 tonne of spent LIBs. The resultant pregnant leaching solution (PLS) with a pH ~ 1 contains 2.3 g/L Li, 14.6 g/L Co, 20.3 g/L Ni, 3.4 g/L La, 3.8 g/L Ce, 0.5 g/L Pr ,and 1.6 g/L Nd, which can then be subjected to the subsequent REEs precipitation process.

**Recovery of REEs by Alkali Double Sulfate Precipitation.** The selective extraction of REEs by forming alkali double sulfate precipitate—NaREE(SO<sub>4</sub>)<sub>2</sub>. $nH_2O$ —in a sulfuric acid system has been widely reported.<sup>28</sup> According to eq 2, the precipitation of REEs can be promoted with the addition of Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup>, which can be derived from the impure byproducts (NaOH and Na<sub>2</sub>SO<sub>4</sub>) of the Li recovery process. To determine the optimum consumption of the precipitants (NaOH and Na<sub>2</sub>SO<sub>4</sub>) during the REEs precipitation, we performed a detailed investigation related to the effect of pH and Na<sub>2</sub>SO<sub>4</sub> dosage. The results shown in Figure 4a indicate that the change in pH has a minor effect on the precipitation when the solution containing REEs was mixed with 4 times the stoichiometric amount of Na<sub>2</sub>SO<sub>4</sub> and heated at 70 °C for 60 min. In contrast, the contents of REEs in the double sulfate precipitation decline from 36% to 34% as the pH increases from 0.6 to 2.2, with a marked decrease in purity recorded when pH increased above 1.4. The changes in purity might be a result of the coprecipitation of other metals like Fe at higher pH values as it has been shown by Pietrelli et al.<sup>22</sup> that iron can start to precipitate at a low pH of 1.0–1.5 (depending on the concentration of iron). As the subsequent solvent extractions of Co and Ni are normally performed at higher pH (5.5–6.5), a pH of 1.4 was selected as the optimum level for REEs recovery in this study.

On the basis of these results, the acid leaching solution (PLS1) obtained was first adjusted to pH 1.4 by the addition of 300 g/L NaOH solution. During this process, ~54% of REEs was recovered in the form of double sulfate precipitate because of the introduction of Na<sup>+</sup>, resulting in PLS2 (Table 3). Nevertheless, as NaOH alone is insufficient to completely recover the REEs from the PLS, Na<sub>2</sub>SO<sub>4</sub> was used as an additional precipitation agent.

As can be observed from Figure 4b, the percentage of REEs precipitation increases significantly from ca. 70% to almost 100% as the Na2SO4 addition increases from 1 to above 4 times the stoichiometric amount. The corresponding concentration of residual REEs decreases appreciably and reaches a low level of <10 mg/L for each element (La, Ce, Pr, and Nd) when 4 times the stoichiometric amount of  $Na_2SO_4$  is consumed. The comprehensive recovery efficiency of REEs can reach 97% once pH is adjusted and Na<sub>2</sub>SO<sub>4</sub> is introduced into the system. XRD (Figure 4c) and SEM (Figure 4d) analysis of the main phases present within the precipitate shows that it comprises NaREE(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O structures with a hexagonal crystal configuration. Furthermore, the REEs (La, Ce, Pr, and Nd) can be separated and recovered from the REEs double sulfate precipitates by a process based on NaOH treatment—to form REE(OH)<sub>3</sub>—followed by acid dissolution and solvent extraction.<sup>29,30</sup>

From these results, the optimum consumption of NaOH and Na<sub>2</sub>SO<sub>4</sub> for nearly complete recovery of REEs was calculated to be 1.5 g/L (NaOH) and 9.5 g/L (Na<sub>2</sub>SO<sub>4</sub>), which would equate to an industrial precipitation reagent that consists of 14% NaOH and 86% Na<sub>2</sub>SO<sub>4</sub>.

**Separation and Recovery of Mn, Co, Ni, and Li.** After the precipitation of REEs, the resultant filtrate (PLS3) is rich in valuable metals (Mn, Co, Ni, Li) and trace Fe impurities

(Table 4). Subsequent separation and recovery of Mn, Co, Ni, and Li from PLS3 were conducted as outlined previously,<sup>12,31,32</sup> including Mn recovery by oxidative precipitation with KMnO<sub>4</sub> (at pH 1.5), Fe removal by neutralization precipitation (at pH ca. 5.6), Co recovery by Cynaex 272 at pH 5.2–5.5, Ni recovery by D2EHPA at pH 6, and Li recovery by phosphate precipitation at pH 12. Futher details related to the separation and recovery of Mn, Co, Ni, and Li are outlined in the Supporting Information.

Table 4 summarizes the concentration of elements in the resultant solutions following REEs recovery (PLS3), Mn, Fe, Co, and Ni separation (PLS4), and solutions before (PLS5) and after Li recovery (PLS6). It can be observed that all target metals are almost completely recovered and the final remnants of the process solution consist of 0.11 g/L Li<sup>+</sup>, 63.2 g/L Na<sup>+</sup>, and 122 g/L SO<sub>4</sub><sup>2-</sup> (pH 12). By evaporation and crystallization, byproducts containing ~5% NaOH and ~94% Na<sub>2</sub>SO<sub>4</sub> can be produced from this type of waste solution and these can be subsequently utilized as a precipitant within the REEs double salt precipitation step. Calculation shows that almost 1.2 tonnes of byproducts (Na<sub>2</sub>SO<sub>4</sub> and NaOH) can be produced per tonne of mixed batteries materials (NiMHs-to-LIBs ratio of 0.75:1). This byproduct material can readily fulfill the required levels of precipitants for REEs (0.4-0.8 tonnes per 1 tonne of spent NiMHs). The circular utilization of these sodium salts is a significant improvement when compared to existing methodologies. In current processes, the sodium ions end up as a major component of industrial wastewaters, which then require further treatment steps to allow safe disposal. Moreover, the protocols outlined here also allow the residual Li in the high-salt solution to be recirculated back into the main process along this Na-rich byproduct stream, meaning that the losses of Li can be effectively minimized.

**Outline of the Proposed Flow Sheet.** From the above results, a new process for the recovery of valuable metals (REEs, Co, Ni, Mn, and Li) based on the combination of synergistic leaching of spent LIBs and NiMHs, REEs recovery using double sulfate precipitation, Ni and Co separation by solvent extraction, and Li recovery by lithium phosphate precipitation is outlined in Figure 5. The mass balance and chemical compositions of these various products can be found in Figure S3 and Table S2.

Through this original process, up to 97% REEs, 96% Mn, 96% Co, 96% Ni, and 93% Li can be recovered in the following form and purities: REEs sulfate precipitate (>99%), MnO2 (~97%), CoSO<sub>4</sub>·7H<sub>2</sub>O (>99%), NiSO<sub>4</sub>·6H<sub>2</sub>O (>99%), and  $Li_3PO_4$  (~100% purity), respectively. By taking advantage of the complementary chemical properties of LIBs and NiMHs wastes, no additives like H<sub>2</sub>O<sub>2</sub> need to be consumed during this copromoted leaching process. Compared to the published acid leaching process in the presence of  $H_2O_2$  (2-6%, v/v), this distinctive process can save 0.6-1.8 tonnes of  $H_2O_2$  (35%) purity) for per 1 tonne of spent LIBs. In addition, the circular utilization of high sodium content byproducts-Na<sub>2</sub>SO<sub>4</sub> and NaOH—can also save the Na<sub>2</sub>SO<sub>4</sub> consumption of 0.4–0.8 tonnes per 1 tonne of spent NiMHs. Furthermore, there are no additional costs and ecological pressures resulting from the need to treat wastewater due to the recirculation of the raffinate; therefore, the new process outlined is advantageous from both an economical and environmental point of view.



Figure 5. Proposed flow sheet for the recovery of REEs, Li, Ni, and Co.

# CONCLUSIONS

This research outlines a sulfuric acid battery leaching process that minimizes the external reagent consumption by utilizing the inherent properties of the LIBs and NiMH wastes as the reduction or oxidation reagents. This route requires no additional high-cost reagents (such as  $H_2O_2$ ) in the leaching stage. In addition, the circulation of the impure Na-rich byproducts (NaOH and Na<sub>2</sub>SO<sub>4</sub>) for REEs precipitation enhances the overall economic feasibility for the process since 0.4–0.8 tonnes of Na<sub>2</sub>SO<sub>4</sub> per 1 tonne of spent NiMH batteries can be saved by recycling. Moreover, this methodology has the added advantage that the Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> which enter the process does not increase the environmental load as the associated process wastewaters are recirculated for REEs recovery and end up in the final precipitate, while the residual Li in the effluent is returned back to the process.

Overall, the application of this new process would not only significantly improve the recovery of REEs, Ni, Co, and Li but also produce economic and environmental benefits through recirculation of the reagents and innovative use of the different waste fractions. Therefore, the process has great industrial application potential. Nevertheless, since the main components of lithium batteries and nickel—hydrogen batteries are constantly changing, the optimal mass ratio of these two waste batteries would need adjustment based on the raw materials specific composition. What is more, the potential application of the mixed leaching residues—which mainly are comprised of carbon—requires further study to fully realize its value-added utilization in wastewater treatment and further enhance the sustainability of this new process.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b02863.

SEM morphologies and mapping analysis of raw materials and the leaching residue with mixed battery waste; standard reduction potentials of target elements related compounds found in LIBs and NiMH wastes; detailed results about the separation and recovery of Mn, Co, Ni, and Li; mass balance of the recycling process and chemical composition of the products (PDF)

# AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: mari.lundstrom@aalto.fi. Mailing address: Hydrometallurgy and Corrosion, Department of Chemical and Metallurgical Engineering, Aalto University, P.O. Box 12200, 00076 Aalto, Finland.

### ORCID 🔍

Chao Peng: 0000-0003-2347-2556

Benjamin P. Wilson: 0000-0002-2874-6475

#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

This paper has been financially supported by the Strategic Research Council of the Academy of Finland (Closeloop project, Grant Number 303454). The authors also acknowledge the collaboration with Business Finland supported projects (CMEco and BATCircle, Grant Numbers 7405/31/2016 and 4853/31/2018), and the Academy of Finland's RawMatTERS Finland Infrastructure (RAMI) based at Aalto University. The authors also acknowledge the financial support from the National Nature Science Foundation of China (No. 51804141) as well as the Science and Technology Project of the Education Department of Jiangxi Province (GJJ170533). Special thanks also go to AkkuSer Ltd. for providing the spent battery waste used in this study.

#### REFERENCES

(1) Al-Thyabat, S.; Nakamura, T.; Shibata, E.; Iizuka, A. Adaptation of Minerals Processing Operations for Lithium-Ion (LiBs) and Nickel Metal Hydride (NiMH) Batteries Recycling: Critical Review. *Miner. Eng.* **2013**, *45*, 4–17.

(2) Lv, W.; Wang, Z.; Cao, H.; Sun, Y.; Zhang, Y.; Sun, Z. A Critical Review and Analysis on the Recycling of Spent Lithium-Ion Batteries. *ACS Sustainable Chem. Eng.* **2018**, *6* (2), 1504–1521.

(3) Rodrigues, L. E. O. C.; Mansur, M. B. Hydrometallurgical Separation of Rare Earth Elements, Cobalt and Nickel from Spent Nickel–Metal–Hydride Batteries. *J. Power Sources* **2010**, *195* (11), 3735–3741.

(4) Zhao, S.; You, F. Comparative Life-Cycle Assessment of Li-Ion Batteries through Process-Based and Integrated Hybrid Approaches. *ACS Sustainable Chem. Eng.* **2019**, 7 (5), 5082–5094.

(5) Kang, D. H. P.; Chen, M.; Ogunseitan, O. A. Potential Environmental and Human Health Impacts of Rechargeable Lithium Batteries in Electronic Waste. *Environ. Sci. Technol.* **2013**, 47 (10), 5495–5503. (6) Habib, K.; Wenzel, H. Exploring Rare Earths Supply Constraints for the Emerging Clean Energy Technologies and the Role of Recycling. J. Cleaner Prod. **2014**, 84, 348–359.

(7) Eftekhari, A. Lithium Batteries for Electric Vehicles: From Economy to Research Strategy. ACS Sustain. ACS Sustainable Chem. Eng. 2019, 7 (6), 5602–5613.

(8) Peng, C.; Hamuyuni, J.; Wilson, B. P.; Lundström, M. Selective Reductive Leaching of Cobalt and Lithium from Industrially Crushed Waste Li-Ion Batteries in Sulfuric Acid System. *Waste Manage.* **2018**, *76*, 582–590.

(9) Müller, T.; Friedrich, B. Development of a Recycling Process for Nickel-Metal Hydride Batteries. *J. Power Sources* **2006**, *158* (2), 1498–1509.

(10) Wang, M.-M.; Zhang, C.-C.; Zhang, F.-S. Recycling of Spent Lithium-Ion Battery with Polyvinyl Chloride by Mechanochemical Process. *Waste Manage*. **2017**, *67*, 232–239.

(11) Tirronen, T.; Sukhomlinov, D.; O'Brien, H.; Taskinen, P.; Lundström, M. Distributions of Lithium-Ion and Nickel-Metal Hydride Battery Elements in Copper Converting. *J. Cleaner Prod.* **2017**, *168* (Suppl C), 399–409.

(12) Yao, Y.; Zhu, M.; Zhao, Z.; Tong, B.; Fan, Y.; Hua, Z. Hydrometallurgical Processes for Recycling Spent Lithium-Ion Batteries: A Critical Review. ACS Sustainable Chem. Eng. 2018, 6 (11), 13611–13627.

(13) Gao, W.; Liu, C.; Cao, H.; Zheng, X.; Lin, X.; Wang, H.; Zhang, Y.; Sun, Z. Comprehensive evaluation on effective leaching of critical metals from spent lithium-ion batteries. *Waste Manage*. **2018**, *75*, 477–485.

(14) He, L.-P.; Sun, S.-Y.; Mu, Y.-Y.; Song, X.-F.; Yu, J.-G. Recovery of Lithium, Nickel, Cobalt, and Manganese from Spent Lithium-Ion Batteries Using I-Tartaric Acid as a Leachant. ACS Sustain. ACS Sustainable Chem. Eng. 2017, 5 (1), 714–721.

(15) Swain, B.; Jeong, J.; Lee, J.; Lee, G.-H.; Sohn, J.-S. Hydrometallurgical Process for Recovery of Cobalt from Waste Cathodic Active Material Generated during Manufacturing of Lithium Ion Batteries. J. Power Sources **2007**, *167* (2), 536–544.

(16) Dhiman, S.; Gupta, B. Partition Studies on Cobalt and Recycling of Valuable Metals from Waste Li-Ion Batteries via Solvent Extraction and Chemical Precipitation. *J. Cleaner Prod.* **2019**, *225*, 820–832.

(17) Zhang, J.; Hu, J.; Liu, Y.; Jing, Q.; Yang, C.; Chen, Y.; Wang, C. Sustainable and Facile Method for the Selective Recovery of Lithium from Cathode Scrap of Spent LiFePO4 Batteries. *ACS Sustainable Chem. Eng.* **2019**, 7 (6), 5626–5631.

(18) Song, Y.; Zhao, Z. Recovery of Lithium from Spent Lithium-Ion Batteries Using Precipitation and Electrodialysis Techniques. *Sep. Purif. Technol.* **2018**, *206*, 335–342.

(19) Porvali, A.; Wilson, B. P.; Lundström, M. Lanthanide-Alkali Double Sulfate Precipitation from Strong Sulfuric Acid NiMH Battery Waste Leachate. *Waste Manage.* **2018**, *71*, 381–389.

(20) Swain, N.; Mishra, S. A Review on the Recovery and Separation of Rare Earths and Transition Metals from Secondary Resources. *J. Cleaner Prod.* **2019**, *220*, 884–898.

(21) Rabah, M. A.; Farghaly, F. E.; Abd-El Motaleb, M. A. Recovery of Nickel, Cobalt and Some Salts from Spent Ni-MH Batteries. *Waste Manage*. **2008**, *28* (7), 1159–1167.

(22) Pietrelli, L.; Bellomo, B.; Fontana, D.; Montereali, M. R. Rare Earths Recovery from NiMH Spent Batteries. *Hydrometallurgy* **2002**, *66* (1), 135–139.

(23) Ferreira, D. A.; Prados, L. M. Z.; Majuste, D.; Mansur, M. B. Hydrometallurgical Separation of Aluminium, Cobalt, Copper and Lithium from Spent Li-Ion Batteries. *J. Power Sources* **2009**, *187* (1), 238–246.

(24) Jankovský, O.; Kovařík, J.; Leitner, J.; Růžička, K.; Sedmidubský, D. Thermodynamic Properties of Stoichiometric Lithium Cobaltite LiCoO2. *Thermochim. Acta* **2016**, 634, 26–30.

(25) Chen, X.; Guo, C.; Ma, H.; Li, J.; Zhou, T.; Cao, L.; Kang, D. Organic Reductants Based Leaching: A Sustainable Process for the

н

Recovery of Valuable Metals from Spent Lithium Ion Batteries. *Waste Manage*. **2018**, *75*, 459–468.

(26) Peng, C.; Liu, F.; Aji, A. T.; Wilson, B. P.; Lundström, M. Extraction of Li and Co from Industrially Produced Li-Ion Battery Waste – Using the Reductive Power of Waste Itself. *Waste Manage.* **2019**, *95*, 604–611.

(27) Zhu, S.; He, W.-Z.; Li, G.-M.; Zhou, X.; Zhang, X.; Huang, J.-W. Recovery of Co and Li from Spent Lithium-Ion Batteries by Combination Method of Acid Leaching and Chemical Precipitation. *Trans. Nonferrous Met. Soc. China* **2012**, *22* (9), 2274–2281.

(28) Lokshin, E. P.; Tareeva, O. A.; Ivlev, K. G.; Kashulina, T. G. Solubility of Double Alkali Metal (Na, K) Rare-Earth (La, Ce) Sulfates in Sulfuric-Phosphoric Acid Solutions at 20°C. *Russ. J. Appl. Chem.* **2005**, 78 (7), 1058–1063.

(29) Xie, F.; Zhang, T.; Dreisinger, D.; Doyle, F. A critical review on solvent extraction of rare earths from aqueous solutions. *Miner. Eng.* **2014**, *56*, 10–28.

(30) Abreu, R.; Morais, C. Purification of rare earth elements from monazite sulphuric acid leach liquor and the production of high-purity ceric oxide. *Miner. Eng.* **2010**, *23*, 536–540.

(31) Chen, X.; Chen, Y.; Zhou, T.; Liu, D.; Hu, H.; Fan, S. Hydrometallurgical Recovery of Metal Values from Sulfuric Acid Leaching Liquor of Spent Lithium-Ion Batteries. *Waste Manage*. **2015**, 38, 349–356.

(32) Chen, X.; Xu, B.; Zhou, T.; Liu, D.; Hu, H.; Fan, S. Separation and Recovery of Metal Values from Leaching Liquor of Mixed-Type of Spent Lithium-Ion Batteries. *Sep. Purif. Technol.* **2015**, *144*, 197–205.