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Lanthanide-alkali double sulfate precipitation from strong sulfuric acid NiMH battery waste leachate

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ABSTRACT

In NiMH battery leaching, rare earth element (REE) precipitation from sulfate media is often reported as being a result of increasing pH of the pregnant leach solution (PLS). Here we demonstrate that this precipitation is a phenomenon that depends on both Na^+ and SO_4^{2-} concentrations and not solely on pH. A two-stage leaching for industrially crushed NiMH waste is performed: The first stage consists of H_2SO_4 leaching (2 M H_2SO_4, $L/S = 10.4$, $V = 104$ ml, $T = 30$ °C) and the second stage of H_2O leaching ($V = 100$ ml, $T = 25$ °C). Moreover, precipitation experiments are separately performed as a function of added Na_2SO_4 and H_2SO_4. During the precipitation, higher than stoichiometric quantities of Na to REE are utilized and this increase in both precipitation reagent concentrations results in an improved double sulfate precipitation efficiency. The best REE precipitation efficiencies (98–99%) – achieved by increasing concentrations of H_2SO_4 and Na_2SO_4 by 1.59 M and 0.35 M, respectively – results in a 21.8 times Na (as Na_2SO_4) and 58.3 times SO_4 change in stoichiometric ratio to REE. Results strongly indicate a straightforward approach for REE recovery from NiMH battery waste without the need to increase the pH of PLS.

1. Introduction

The challenge in metal circular economy is that the consumables are not designed for recycling. From the collected battery waste, base metals such as Fe, Al, Cu, Ni, Co are recovered with high recovery efficiency whereas rare earth elements (REE) and lithium (Li) commonly end up into slag or other waste streams, with typically <1% of REEs present in waste being recovered (Reuter et al., 2013). Such low rates of reclamation highlights the importance of finding a straightforward method for REE recovery from secondary raw materials. It has been estimated that by the 2020s, ca. 20–35% of NiMH batteries could be recycled (Binnemans et al., 2013). It is also of increasing importance to develop the circular economy of metals as REEs especially, are critical to modern societies using advanced technologies, e.g. electrical vehicles and renewable energy (Tunsu et al., 2015). In addition, REEs are difficult and costly to produce as well as being hard to substitute due to their unique chemical properties. Furthermore, Europe as a whole lacks its own REE primary production (Rollat et al., 2016) and is thus almost totally reliant on the import of these critical materials. As a consequence, it is imperative that the European-wide circulation of REEs be improved, in order to reduce the dependency on REE imports.

NiMH batteries have several applications, which range in dimension from thumb-sized consumer batteries to large hybrid-electric vehicle batteries. In contrast to Li-ion systems, NiMH battery based systems have remained popular, in countries like Brazil, due to their cheaper price (Bertuol et al., 2006). NiMH batteries are composed of variety of metals: Outer casings are typically made of plastics or environment resistant metal alloys, whereas the electrolytes commonly contain a mix of sodium hydroxide (NaOH) and potassium hydroxide (KOH) – although some researchers claim that lithium hydroxide (LiOH) (Ye and Noréus, 2012) can also be used as a part of the electrolyte. Moreover, the current collector plates are comprised of nickel-plated steel metal alloy, upon which the active electrode powder is deposited using adhesives. The battery system also features electrodes that are isolated by a polymer separator, made of e.g., nylon, in order to avoid short circuit. On the cathode, a nickel hydroxide/nickel oxyhydroxide mix ($Ni(OH)_2$/NiOOH) is present depending on the charge state of the battery. The active anode powder is composed of hydride-forming metal alloy, which can consist of a varying mixture of metals, such as lanthanum (La), cerium (Ce), praseodymium (Pr) and neodymium (Nd), cobalt (Co), manganese (Mn), aluminum (Al) and zinc (Zn), nickel (Ni) being the primary element. (Larsson et al., 2013) The fact whether a NiMH battery contains REEs depends on which hydride forming metal alloy has been used on the anode. Other more uncommon options include titanium (Ti) or zirconium (Zr) alloys. (Ying et al., 2006) Such a varied and complex battery

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structure inevitably makes them difficult to process such that a vast majority of all the metal value contained within can be recycled.

The recovery and purification of rare earth elements (REE) via precipitation is an old technique. In the early years of REE recovery and purification, fractional crystallization and precipitation were used (Lucas et al., 2015); however, these have been subsequently abandoned in favor of solvent extraction and ion-exchange chromatography. Solvent extraction, in particular, is well-suited to continuous operation, as it is a fast process that offers suitable selectivity for REEs (Zhang et al., 2016). In contrast, ion-exchange chromatography is utilized when ultrapure compound separation is desired (Tunsu et al., 2015). Nevertheless, the precipitation of REEs from complex solution can still provide advantages, especially in the case of double sulfates, as it allows the separation of entire group of REEs from impure bulk solution at relatively high purity (Pietrelli et al., 2002). Generally, rare earth double sulfates can written to be of form $LnM(SO_4)_2$, where Ln = REE and typically in fractional precipitation M = Na^+, K^+, or NH_4^+ (Wickleder, 2002). Too often alkali lanthanide double sulfates are reported unclearly as just simple sulfates which are distinct compounds with different chemical compositions (Innocenzi et al., 2017). Distinction must be made as the compounds have remarkably different solubility properties ($NaLa(SO_4)_2$ = 2.34 g l^{-1}) vs. ($La_2(SO_4)_3$ = soluble) in H_2O (Lokshin et al., 2005; Perry, 2016).

Commonly REE recovery by precipitation from sulfuric NiMH battery leachates has been reported as a result of increasing pH of the pregnant leach solution (PLS), however there are contradictory reports as to whether the precipitates formed by pH adjustment are sulfates or double sulfates (Wu et al., 2009; Rodrigues and Mansur, 2010). Bertuol et al. (2009) reported that they determined the precipitates to be double sulfates, but assumed the precipitation was connected to the increase of pH of the solution. The assumption that the precipitation is connected to increasing pH is evident in several papers reporting optimal precipitation conditions as a function of pH as outlined in Table 1. The desire to increase pH and simultaneously precipitate REEs can be understood as a necessity to prepare REE-free leachate for solvent extraction (Rodrigues and Mansur, 2010) which often requires higher pH (Wilson et al., 2014) than that used in the H_2SO_4 leaching of NiMH battery waste. In some papers (Pietrelli et al., 2002; Provazi et al., 2011) the precipitation is logically investigated as a function of pH as it is the effect of the activity of hydronium and hydroxide ions specifically that is being investigated. However in some papers even when precipitation products have been presented as double sulfate, no consideration has been given to how the change of precipitating agent contents affect the efficiency of precipitation. In contrast, this study focuses on demonstrating that the REE precipitation from sulfuric acid NiMH battery waste leachate is more a phenomenon that depends on Na^+ and SO_4^{2-} concentration, rather than being related to a decrease in acidity as is often stated in the current published literature.

In this study, H_2SO_4 leaching of industrially crushed, manually sieved and unwashed nickel metal hydride (NiMH) battery waste was investigated to determine whether double sulfates form during the acidic leaching of NiMH battery waste without pH increase or alkali hydroxide adjustment. This is done in order to provide information on the applicability of the leaching method by investigating the effect of impurities and precipitation of double sulfates during and after leaching.

Double sulfate precipitation was investigated from sulfuric acid NiMH battery leachate as it has been shown by multiple authors that H_2SO_4 is an efficient lixiviant for REE leaching (Tunsu et al., 2015; Bertuol et al., 2009), and additionally double sulfate precipitation of alkaline-lanthanides to separate light rare earth elements (LREE) from metal sulfate rich sulfuric acid (H_2SO_4) solution has also been suggested (Kikuta and Asano, 2016). Precipitation efficiencies were investigated as a function of added H_2SO_4 and Na_2SO_4 in leachate, as both are low cost and commonly available chemicals. Additionally, H_2SO_4 is widely applied in industrial metal processing, including Ni processing and Cu electrorefining (Honey et al., 1997; Casas et al., 2000) and thus can provide a selective precipitation media for LREEs as a group of alkali-lanthanide double sulfates by sodium (Na) and potassium (K) addition (Bertuol et al., 2009).

1.1. Management of NiMH battery waste

It is not viable to manually sort and open small batteries on industrial scale. However, car batteries are already sorted in a sense. Additionally, they are large which can enable viable dismantling in order to obtain cleaner and more specific waste fractions for further processing (Larsson et al., 2013). This is exemplified how Honda is recycling its own NiMH HEV batteries. It is viable to dismantle them by hand as they are easier to open and can contain large quantities (up to over 2 kg) of the valuable electrode powder (Honda Motor et al., 2017). However, in the case of smaller batteries, reliable, efficient mechanical processing becomes challenging as their compactness removes the ease of opening the batteries and the separation of components.

Currently, nickel can be satisfactorily recovered from NiMH batteries. These batteries can be fed into primary process smelters

Table 1
Double sulfate precipitation yields from Waste NiMH leached in sulfuric acid. Data compiled from various literature sources. *N/U* = not used. *N/A* = not available.

La Leaching efficiency (%)	Ce Leaching efficiency (%)	Pr Leaching efficiency (%)	Nd Leaching efficiency (%)	Average REE Leaching efficiency (%)	Initial Conc. M (H_2SO_4)	L/S Ratio	Optimal ppt. pH	Conc. (NaOH)	Conc. (KOH)	Conc. (Na_2CO_3)	Average REE ppt. yield	Ref.
92.5	93	91.8	95.6	93.2	2	10	1–2	*N/A*	*N/U*	*N/U*	>70%	Pietrelli et al. (2002)
N/A	*N/A*	*N/A*	*N/A*	99.5	3	15	≤1.6	6.5 wt%	*N/U*	3.5 wt%	>94%	Nan et al. (2006)
N/A	*N/A*	*N/A*	*N/A*	>96	3	10	1.5–1.7	6.5 wt%	*N/U*	3.5 wt%	>94%	Nan et al. (2006)
69.5	89.4	95.5	98.1	88.1	2	10	1.8	3 M	*N/U*	*N/U*	*N/A*	Meshram et al. (2016)
N/A	*N/A*	*N/A*	*N/A*	30–35, 99	2	7.5	<2	5 M	*N/U*	*N/U*	99%	Innocenzi and Vegliò (2012)
N/A	*N/A*	*N/A*	*N/A*	98	2	20	0.8–1.2	5 M	5 M	*N/U*	>98%	Bertuol et al. (2009)
N/A	*N/A*	*N/A*	*N/A*	87.3	8% v/v	10	2.5	*N/A*	*N/U*	*N/U*	50%	Rodrigues and Mansur (2010)

after mechanical treatment (Sommer et al., 2015). However, major faction of the minor metals are lost to the slag fraction (Tirronen et al., 2017), including rare earths. One advantage of the pyrometallurgical processing is that appropriate temperatures can be used in order to achieve pyrolysis with which it is possible to bypass the difficult and laborious mechanical separation of plastics. In this way, adhesives and plastics are burnt, and some hazardous heavy metals such as cadmium are vaporized and subsequently the toxic gases are scrubbed. In practice, this is exemplified in the Umicore's ultra-high temperature process (Binnemans et al., 2013) utilizing high temperatures in producing matte of valuable base metals for recovery.

Mechano-hydrometallurgical routes especially suffer from the extreme heterogeneity of waste raw material. For chemical processes, the quality and consistency of raw material can be important. However as the current batteries within a category are not necessarily similar in their chemistry there is no way to guarantee that the material feed is consistent. Battery chemistries are not always obvious via superficial inspection, making optimal sorting and separation impossible. Therefore chemical processes must be robust and flexible, able to adapt to changing raw material feed.

Cyanex 272 is a commonly used extractant in nickel and cobalt separation hydrometallurgy, both which are present in NiMH battery waste. Cyanex 272 is a cation exchanger extractant and its extraction reactions are controlled by pH adjustment, commonly with NaOH, generating large amounts of sodium sulfate waste waters (Cytec, 2017). Application of old fractional precipitation to battery waste leachate can provide benefits which are investigated in this paper.

2. Materials and methods

2.1. Raw material

Industrially crushed NiMH battery waste was used as raw material. The raw material was sized by 1.4 mm sieve, and the underflow accounting for approximately 50 wt% of the original weight used as the raw material for leaching experiments. The chemical analysis of the raw material and precipitates formed was conducted by total leaching (aqua regia). Solution analyses were conducted by ICP-OES (inductively coupled plasma optical emission spectroscopy, Perkin Elmer Optima 7100 DV, USA) for REEs, Zr, V and Ti and by flame AAS (Varian AA240) for the remaining elements. The chemical composition of the NiMH raw material (underflow of 1.4 mm sieve) used in the leaching tests is presented in Table 2. No Zr, V and Ti was detected.

2.2. Leaching experiments

Leaching experiments were performed in a glass beakers under magnetic stirring with the parameters outlined in Table 3. The first leaching experiment, Exp. 1 (Table 3), was performed to determine the presence of any water soluble REEs (La, Ce, Pr), any double sulfate precipitation elements (Na, K) or other water soluble impurities (S, Fe) present in the battery waste. Experiments 2L1, 2L2 and 3L1 were conducted in order to investigate both (i) the metal extraction into the solution as well as (ii) in-situ double sulfate formation and further dissolution into the water (2L2 and 3L1). The residue of experiment 2L1 was filtered and leached with water (2L2). Solutions were analyzed for elemental concentrations. Initial L/S ratio and total slurry volume remained unchanged in 1L1, 2L1 and 3L1. All solution samples were drawn by glass pipette and filtered with a 0.45 μm syringe filter. Sample solutions were subsequently analyzed for metals content.

Table 3
Parameters for water leaching (Exp. 1, 1L1), sulfuric acid leaching (Exp. 2, 2L1 and 3L1) and leach residue leaching with water (2L2).

Exp. 1	
1L1	NiMH Leaching with H_2O, *T* = 25 °C, *L/S* = 10.4 *V* = 100 ml water + residue, *t* = 2 h
Exp. 2	
2L1	NiMH Leaching with *T* = 30 °C, L/S = 10.4, 2 M H_2SO_4, *V* = 104 ml, *t* = 3 h
2L2	Leach Residue (from 2L1) leaching with T = 25 °C, distilled H_2O, *V* = 100 ml, *t* = 1.5 h
3L1	NiMH Leaching with *T* = 30 °C, *L/S* = 10, 2 M H_2SO_4, *V* = 100 ml and 0.16 M Na_2SO_4, *t* = 3 h
Exp. 3 & 4	
4L & 5L	NiMH Leaching with *T* = 70 °C, L/S = 10, 2 M H_2SO_4, *V* = 800 ml, *t* = 3 h

Table 4
Design of Exp. 3. PLS (4L) was used. Second column shows the increase in of H_2SO_4 molar concentration.

Exp. 3	+H_2SO_4 (M)	Added SO_4 (SO_4/REE, mol mol^{-1})	Added Na (Na/REE, mol mol^{-1})
1E0	0	0	0
1E1	0.89	30.92	14.1
1E2	0.89	30.92	14.1
1E3	0	10.60	21.2
1E4	1.8	51.24	7.07
1E5	1.59	58.31	21.2
1E6	0	3.53	7.07
P9	0	21.20	42.4

Table 5
Design of Exp. 4. PLS (5L) was used. Second column shows the increase in H_2SO_4 molar concentration in the experiment.

Exp. 4	+H_2SO_4 (M)	Added SO_4 (SO_4/REE, mol mol^{-1})	Added Na (Na/REE, mol mol^{-1})
2E0	0	0	0
2E1	0	5.31	10.6
2E2	1.33	47.8	0
2E3	1.16	53.1	10.6
2E4	0.69	23.9	0
2E5	0.60	29.2	10.6
2E6	0	2.66	5.31
2E7	1.24	50.5	5.31
2E8	0.64	26.6	5.31
2E9	0.64	26.6	5.31
2E10	0.64	26.6	5.31

2.3. Precipitation experiments

The precipitation of REEs from PLS were investigated by two different experimental series, presented in Table 5 (Exp. 3) and Table 6 (Exp. 4). For all precipitation experiments two different

Table 2
Chemical analysis of NiMH waste raw material. * =analysis by ICP-OES, ** = analysis by FAAS.

Ni** (mg g^{-1})	Co** (mg g^{-1})	Fe** (mg g^{-1})	La* (mg g^{-1})	Ce* (mg g^{-1})	Pr* (mg g^{-1})
433.8	55.1	17.6	40.4	41.4	12.4

Table 6
Dissolved metal concentrations after water leaching of NiMH battery waste (Exp. 1, Table 3).

Exp. 1	La (mg l^{-1})	Ce (mg l^{-1})	Pr (mg l^{-1})	Na (mg l^{-1})	K (mg l^{-1})	S (mg l^{-1})	Fe (mg l^{-1})
1L1	6.3	9.7	3.7	317	1394	31.8	< 0.1

PLS were prepared by leaching industrially crushed NiMH battery waste, leaching parameters being presented in Table 3.

The precipitation chemicals investigated were H_2SO_4 (18 M) and Na_2SO_4 (2 M in Exp. 3 and 1 M in Exp. 4). In both Exp. 3 and 4 initial sample size of 50 ml was used. The chemical additions resulted in changes of Na/REE and SO_4/REE stoichiometric ratio and change of H_2SO_4 molarity of the modified solution, all presented in Table 4 (Exp. 3) and Table 5 (Exp. 4). In Exp. 4, the experimental series was designed to gain knowledge of the precipitation at a lower precipitation chemical concentrations (both H_2SO_4 and Na_2SO_4) compared to the first experimental precipitation series, Exp. 3.

REE extraction was determined based on solution analysis. In the precipitation experiments H_2SO_4 chemical was always applied first to the PLS. After that Na_2SO_4 solution was added. The volumetric flasks were manually shaken for 30 s each, sealed with plastic corks and allowed to stand for 25 h. After 25 h, the samples were shaken for 30 s each, then solution samples were drawn from the flasks, filtered and subjected to analysis. All precipitation experiments were performed at the room temperature. Experiments 1E0 and 2E0 signify the analysis of unmodified PLS. Additionally in order to observe REE precipitation at even higher Na/REE ratio, sample P9 was prepared. For each experiment, precipitation efficiency was calculated. The computational formula is presented, where C_e and V_e are concentration and volume after reaction and C_i and V_i the initial concentration and volume, respectively:

$$Yield = 100 - \frac{C_e \cdot V_e}{C_i \cdot V_i} * 100 \tag{1}$$

2.4. Precipitate characterization

Precipitate crystal structure characterization was performed by XRD (PANalytical X'Pert Pro Powder, Almelo, the Netherlands) and it was done with CuKα radiation source at a continuous scan rate of 0.54° min^{-1} with acceleration potential 45 kV, current 40 mA. The XRD pattern was analyzed by using HighScore 4.0 Plus software. Phase identification was performed. Supporting crystal structure and chemical identification was performed with EDS-analysis (LEO 1450 VP attached with Oxford Instruments INCA analyzer). Finally, supporting chemical composition analysis was performed with ICP-OES.

Precipitate was produced by using 4L & 5L leaching parameters (Table 3) and subsequently using methods described in Section 2.3. 1 M Na_2SO_4 and 18 M H_2SO_4 were used in achieving supersaturation at room temperature. Precipitate was filtered and washed with 1 M sodium sulfate solution and dried.

3. Results and discussion

3.1. Leaching results

The results of the first leaching experiment (Exp. 1), outlined in Table 6, indicate that the raw material sample contains a significant quantity of Na and K that originates from the battery electrolyte residues. Consequently, we hypothesize that based on the solubility data (Lokshin et al., 2005) the presence of these residual Na and K in the NiMH waste can affect the precipitation of double sulfates by acting as an initiator of double sulfate precipitation, thus decreasing REE extraction into solution during sulfuric acid leaching. As a result, water washing prior to NiMH battery leaching has been performed in numerous papers in order to wash water-solvable compounds from the raw material (Nan et al., 2006; Innocenzi and Vegliò, 2012). However, in prior literature no consideration has been directly given to the effect of alkali electrolytes on REE extraction. In addition, there is also water soluble sulfur (S) in the leachate, which is likely a contamination originating from industrial crushing stage, as the same processing equipment is used to treat materials other than NiMH battery wastes. Moreover, it was found that a minor amount of REEs also dissolved, indicating the presence of unknown, water soluble compounds within the raw material.

In the sulfuric acid leaching of NiMH waste (2L1 and 3L1), temperature is shown to increase from initial temperature of 30 °C up to 47 °C (2L1) and up to 42.5 °C (3L1) after the exposure of the NiMH sample to the H_2SO_4 solution. This is most likely due to the exothermic reactions of the metallic elements and hydroxides present in the sample with the sulfuric acid medium: Such an exothermic reaction may be beneficial during the leaching process at low temperature as it has been suggested that an increase in temperature increases metal extraction into the solution from NiMH wastes (Tzanetakis and Scott, 2004; Meshram et al., 2017). We also observed strong gas evolution during the leaching experiments, indicating reduction of hydrogen as e.g. per Reaction (2):

$$2LaNi_5 + 13H_2SO_4 \rightarrow La_2(SO_4)_3 + 10NiSO_4 + 13H_2(g) \tag{2}$$

Results of each leaching experiment are presented in Table 7, respectively. These results demonstrate that the dissolution lanthanides is inadequate during H_2SO_4 leaching (2L1), with REE extraction of 66.4% La, 88.8% Ce and 59.3% Pr, whereas base metal leaching efficiencies are excellent and similar to others found in the literature (Pietrelli et al., 2002). The extraction for REEs in sample 2L1 is relatively poor (66.4% La). However, into the authors' knowledge here we show for the first time that a relatively significant amount of lanthanides in the water leaching of leach residue (2L2) are water soluble as compared to the in-situ precipitation experiment 3L1, test 2L2 has a much higher concentration of lanthanides in solution. Water leaching provided extractions of 13.7% La, 18% Ce and 12.7% Pr. This suggests double sulfate formation due to the presence of alkali electrolytes during sulfuric acid leaching (2L1) and dissolution from the leach residue into the water as double sulfates are known to be sparingly soluble (Lokshin et al., 2005).

It is likely that a part of the lanthanide concentration in 2L2 is due to leachate residues as it is expected that base metals do not form water soluble compounds during leaching, as indicated by test 1L1. Nevertheless, La, Ce and Pr concentrations of 2L2 in relation to 2L1 are La = 23.9%, Ce = 23.6%, Pr = 24.7%, whereas base metals Ni and Co are Ni = 3.90% and Co = 4.67% only, although the level of Fe was found to be higher at 11.9%. These findings indicate that some of the La, Ce and Pr content comes from the retained moisture in the leach residue, however, the results clearly show REE concentrations increase significantly more than those of the base metals in relation to the leachate concentrations of the first stage. Moisture content is estimated based on the relative difference of Ni and Co concentration and based on this relative difference, the moisture content was calculated to be ca. 4.05 ml,

Table 7
Dissolved metal concentrations in leaching experiments (Table 3).

Exp. 2	La (mg l^{-1})	Ce (mg l^{-1})	Pr (mg l^{-1})	Fe (mg l^{-1})	Ni (mg l^{-1})	Co (mg l^{-1})
2L1 (H_2SO_4)	2658	3636	725	1787	38,750	5173
2L2 (H_2O)	635	858	179	213	1510	241
3L1 (H_2SO_4 + Na_2SO_4)	138	154	30	1172	38,013	4908

resulting in overestimated extraction of between 2.38 and 3.56% for the REEs investigated in the water leaching (2L2). The reported extractions have been subsequently corrected using these moisture calculations.

The total leaching efficiency of La, Ce and Pr when the recoveries into the PLS and water (tests 2L1 and 2L2) are combined are 80.1%, 106.8% and 72%, respectively. These results are similar in magnitude to those obtained previously by Pietrelli et al. (2002), with hand separated unwashed active powders from manually dismantled batteries. Fig. 1 presents the combined leaching extractions which show that extraction is relatively good with test 2L1 alone and that when combined with a second step (test 2L2) there are further improvements. It has been previously reported that a two-stage leaching with 3 M H_2SO_4 and then subsequently with 1 M H_2SO_4 solution leads to an almost total dissolution of REEs in NiMH leaching (Innocenzi and Vegliò, 2012). In contrast the results presented here clearly demonstrate that the second sulfuric acid leaching is not necessary, assuming either sulfate or double sulfate precipitation is occurring due to low REE double sulfate solubility products. In this way, water leaching can be exploited in REE recovery from unwashed battery waste. In addition, the Ce and Fe leaching efficiencies were found to slightly exceed 100% which is most likely a result of the inhomogeneous nature of the industrially crushed and sieved NiMH raw material. In test 3L1, leaching of raw material with sulfuric-sodium medium, the extractions of REEs are extremely low (<3.5%), suggesting the formation of double sulfates in-situ due to the low solubility of lanthanide alkali double sulfates in strong sulfuric acid solutions (Lokshin et al., 2005).

3.2. Precipitation results

Separate PLS for both Exp. 3 and 4 is produced by leaching NiMH battery waste in order to investigate precipitation phenomenon indicated by the leaching experiments 2L1 and 2L2.

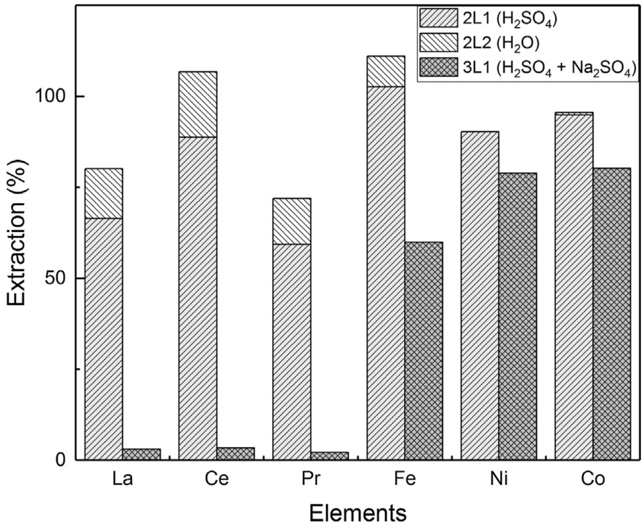

Fig. 1. Metal extraction into the PLS. 2-stage leaching, 2L1 and 2L2, are presented as stacked columns. Parameters are presented in Table 3.

The analysis results of Exp. 3 are presented in Table 8. The reference sample (1E0) demonstrates clearly that residual Na and K still remains in the PLS even after sulfuric acid leaching. Nonetheless, when compared to the leachate from water leaching (3L1 and Table 6), the K concentration is lower in the reference sample (1E0) whereas Na concentration remains unchanged.

The decrease of K content after precipitation experiments, in relation to reference sample (1E0), amounts to 23–38 wt%, depending on the solution sample (1E1–1E6, P9). This loss of dissolved K indicates precipitation of potassium REE double sulfates, when their solubility limits as determined by Lokshin et al. (2005) are taken into account. The formation of potassium double sulfates has been indicated by others but not confirmed by XRD (Bertuol et al., 2009).

After the Exp. 3 the precipitation phenomenon was systematically investigated at lower precipitation reagent concentrations in Exp. 4 and the resultant metal contents in solutions after precipitation are displayed in Table 9. The differences observed between the analyses of Exp. 1–3 and Exp. 4 suggest there exists some inhomogeneity related to the initial raw material in particular. The content of Na is remarkably lower than that previously determined in Exp. 3 (Table 8), indicating that either less electrolyte residues were present in the waste or that efficient precipitation might occur during the leaching of waste. However, the REE contents in reference samples 1E0 and 2E0 were also noticeably lower (La: 121.9 vs. 81 mg; Ce: 153.5 vs. 107.7 mg; Pr: 42 vs. 21.7 mg), which signifies that the raw material used in Exp. 4 contains less valuable

Table 8
Solution analysis of non-REEs after precipitation series Exp. 3. 2 M Na_2SO_4 and 18 M H_2SO_4 solutions were used as precipitation agents. 1E0 was the reference sample of PLS.

Exp. 3	Fe (mg)	K (mg)	Na (mg)
1E0	70.0	42.0	17
1E1	76.9	26.1	323
1E2	78.6	26.9	346
1E3	73.7	26.0	619
1E4	83.3	28.0	117
1E5	75.8	29.2	593
1E6	76.5	32.0	122
P9	80.1	25.9	1364

Table 9
Solution analysis of non-REEs after precipitation series Exp. 4. 1 M Na_2SO_4 and 18 M H_2SO_4 solutions were used as precipitation agents. 2E0 was the reference sample of PLS.

Exp. 4	Fe (mg)	Na (mg)	K (mg)
2E0	81.8	1.4	28.0
2E1	81.6	144.3	18.5
2E2	80.2	3.6	27.7
2E3	78.9	160.0	20.3
2E4	79.0	4.1	27.4
2E5	78.3	158.8	19.7
2E6	80.0	68.0	18.4
2E7	77.8	58.0	20.0
2E8	75.8	58.9	18.2
2E9	77.2	60.9	19.0
2E10	79.9	60.3	18.3

material overall, which in turn indicates a notable variation in the metal content of the raw material, as could be expected from a crushed mixed NiMH battery waste stream. Overall, these results highlight the challenges of performing small scale experiments on industrially crushed battery waste, an issue that would need to be taken into account when undertaking process design to accommodate the variations in elemental concentrations.

Direct comparison of the results of Exp. 3 and Exp. 4 is, in general, relatively complicated due to the fact that the reference solution 2E0 in Exp. 4 has lower initial REE, Na and K concentrations than reference solution 1E0 in Exp. 3. The precipitation efficiencies for REEs in Exp. 3 are presented in Fig. 2a, c and e and for Exp. 4 in Fig. 2b, d and f. Precipitation efficiencies in Exp. 4 are similar to ones obtained in Exp. 3. As the initial alkali and REE concentration

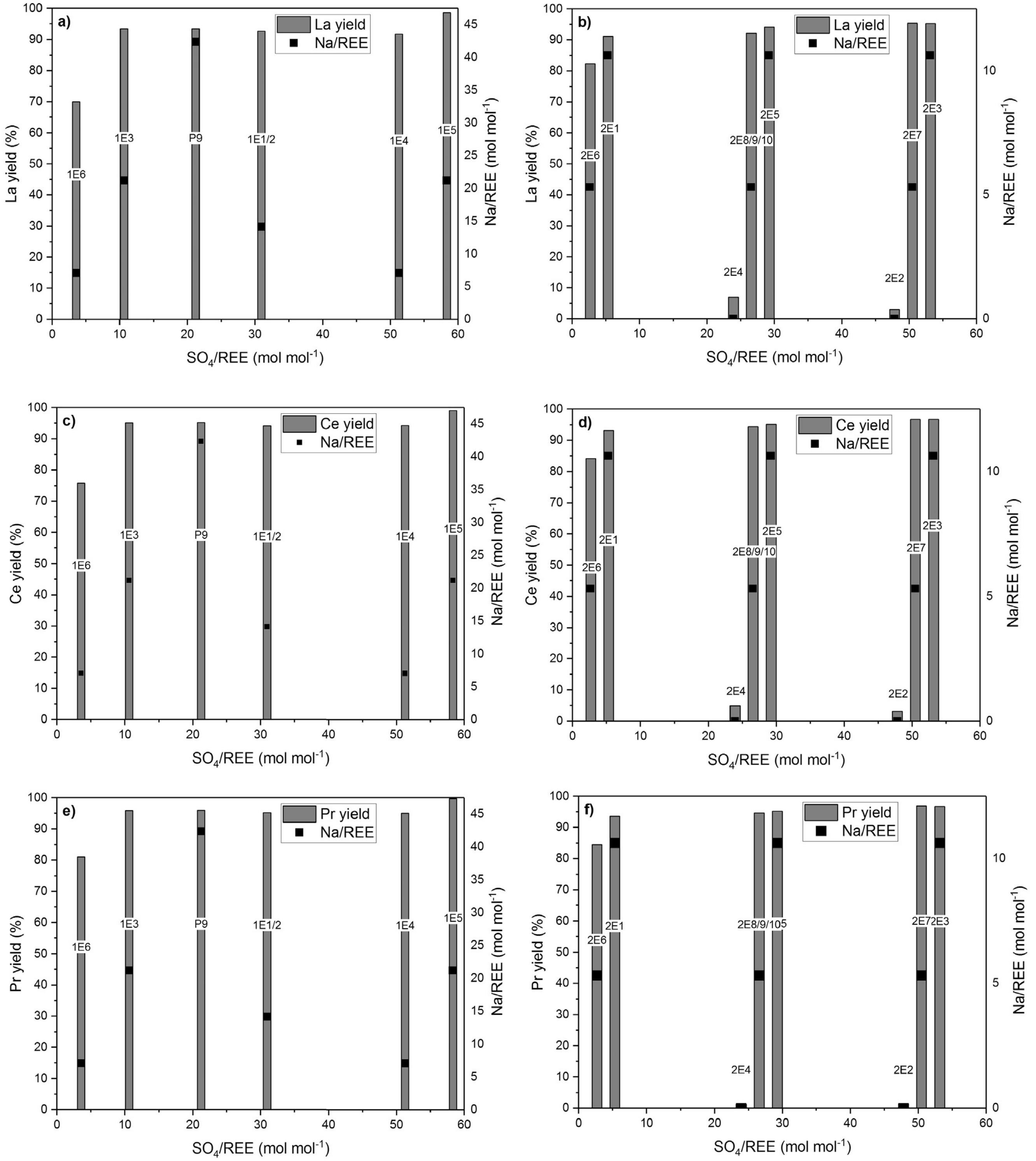

Fig. 2. (a) Exp. 3 and (b) Exp. 4 results of La precipitation efficiency (left y-axis) as a function of added total SO_4 in molar relation to REE from sodium sulfate and sulfuric acid (x-axis). Black squares signify the added Na in Na to REE molar relation (right y-axis). Tests 1E1/2 and 2E8/9/10 are the average of experimental center points.

is already low in Exp. 4, it initially appears that there is no significant effect on the precipitation of REEs due to sulfuric acid alone. Nevertheless, once the yields are plotted as a function of added SO_4/REE, with special consideration given to added Na/REE, a similar effect is observed in both experiments. The calculated precipitation efficiencies of Exp. 3 and Exp. 4 are plotted as a function of both SO_4 (x-axis) and Na addition (right y-axis) the results of which are presented Fig. 2. As can be clearly seen, the results demonstrate that either sulfate and sodium ion concentration significantly influences the precipitation yields achieved. The main differences between Exp. 3 and Exp. 4 could result – at least in part – from the PLS having different elemental concentrations as a result of raw material inhomogeneity. Consequently, due to the smaller metal concentrations, the results of Exp. 4 would be dissimilar to Exp. 3.

The best precipitation efficiency (>98% La) is achieved with 1E5, which has a high level of added sulfuric acid and sodium sulfate (3.19 M H^+, SO_4/REE 58.31 mol mol^{-1}, Na/REE 21.2, mol mol^{-1}), which unambiguously demonstrates their co-effect on precipitation. The lowest precipitation efficiency is obtained with 1E6 that features both a low Na/REE ratio of addition (Na/REE 7.07, mol mol^{-1}) and no added H_2SO_4. In contrast, the precipitation efficiencies of samples 1E1–1E4 are observed to be comparable to those outlined previously in the literature, as shown in Table 1. The precipitation efficiency obtained with the P9 experimental parameters is much less than those of test 1E5 parameters. This demonstrates that a higher H_2SO_4 concentration has a clear positive effect on double sulfate precipitation as the sample P9 had no added H_2SO_4 in the solution.

The results gained from the parameters used in test 1E5 show excellent precipitation efficiencies, which confirms the hypothesis that use of concentrated H_2SO_4 solutions in leaching enhances the precipitation of REE double sulfates. A comparison of the results from 1E4 and 1E6 further confirms this finding where the addition of H_2SO_4 enhances precipitation efficiency > 90% (1E4) *cf.* > 70% (1E6). The results most probably indicate that the common ion effect is a major factor in determining precipitation efficiency (Lokshin et al., 2005). However, the addition of sulfate from both sulfuric acid and sodium sulfate make the effect of sulfate less persuasive. Never the less, sulfuric acid concentration seems to affect the REE recovery efficiency (1E4 vs. 1E6 and 2E6 vs. 2E1)

The results from Exp. 3 outlined here, clearly show that the current convention of reporting precipitation efficiencies solely as a function of pH is disingenuous as precipitation occurs in concentrated H_2SO_4 solutions with high Na/REE and SO_4/REE ratios more readily than in higher pH solutions. Notably in a recent review article (Tunsu et al., 2015) hydroxide formation was incorrectly referred to have occurred, highlighting the importance of having clear understanding of the effect of the pH on precipitation.

These findings also show that a Na/REE molar ratio of = 0 results in only very low La yields (<10%), even at high sulfate concentrations (SO_4/REE ratio = 47.8). In addition, an SO_4/REE molar ratio of <6 can result in >90% La yield in the presence of excess Na (Na/REE ratio = 10.6) although an increased SO_4/REE can also can enhance the yield of La (e.g. an increase from 4 to 50 can increase La yield ca. 20%-units with enough Na present).

3.3. Precipitate characterization

XRD analysis showed that the crystals are of form sodium cerium sulfate hydrate ($NaCe(SO_4)_2 \cdot H_2O$) and sodium lanthanum sulfate hydrate ($NaLa(SO_4)_2 \cdot H_2O$) as shown in Fig. 3. These crystals are known to exist as a hexagonal structure (HighScore 4.0 Plus). The signals conform well with the reference patterns. Potassium compounds cannot be discerned by XRD as the crystals are not distinct but both Na and K can be found in a single crystal. All the data which were recognized as peaks in the measured pattern matched to the reference patterns of lanthanum sodium sulfate, cerium sodium sulfate or both lanthanum and cerium sodium sulfate. Only three peaks were identified as exclusively sodium lanthanum sulfate and one as sodium cerium sulfate as differences are small between the two reference patterns. Precipitation Reaction (3) has been presented in the literature (Abreu and Morais, 2010):

$$Ln_2(SO_4)_3 + Na_2SO_4 + H_2O \rightarrow 2NaLn(SO_4)_2 \cdot H_2O \quad (3)$$

The conclusions drawn from XRD are supported by SEM-EDS analysis which indicated that the crystals were chemically composed of La, Ce, Pr, Nd, Na, K, S and O, Table 10. Additionally, it

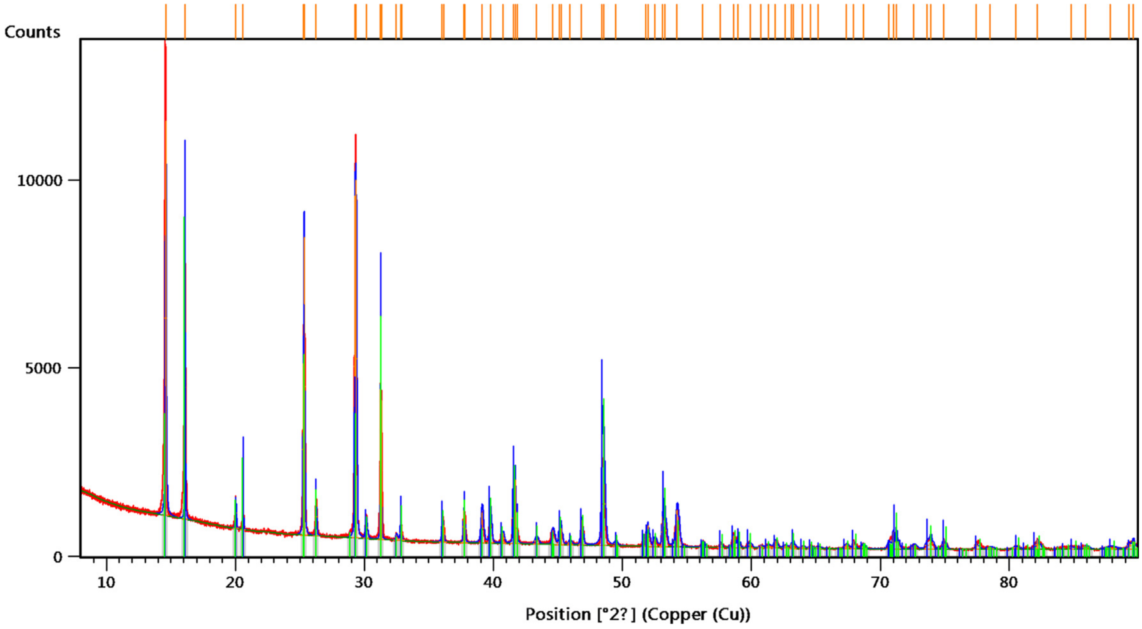

Fig. 3. Measured XRD pattern of white precipitate superimposed on reference patterns. Lines above graph indicate data points identified as peaks which match the reference pattern.

Table 10
SEM-EDS-recognized elements and their mass fractions.

Spectrum	O	Na	S	K	La	Ce	Pr	Nd	Total
Spectrum 1	43.98	6.60	15.14	0.81	19.24	11.99	1.21	4.51	103.48
Spectrum 2	27.83	4.86	13.38	0.86	17.15	10.57	1.09	4.31	80.06
Spectrum 3	43.36	6.71	15.60	1.24	18.65	12.26	1.43	4.67	103.92
Mean	38.39	6.06	14.71	0.97	18.35	11.61	1.24	4.50	95.82
Std. dev.	9.15	1.03	1.17	0.23	1.08	0.91	0.17	0.18	

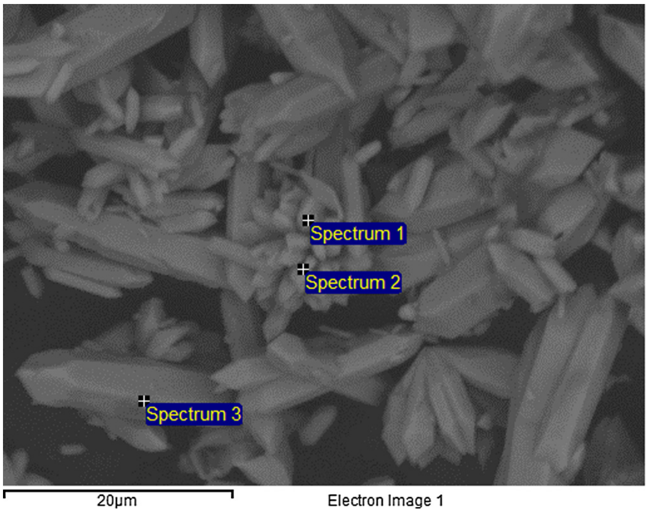

Fig. 4. SEM picture of white precipitates from which EDS results were derived.

can be seen from Fig. 4 that the crystals are hexagonal in form. Pure alkali lanthanide double sulfates are known to exist as three different crystal structures and it is also known that nonstoichiometric and other compositions of double sulfates exist (Wickleder, 2002). Therefore it is not possible to conclusively say which composition or compositions exist in the crystals of this study, other than that the results strongly indicate the presence of sodium and potassium containing double sulfates of some form. These results of mixed crystal composition partly explain why the detected XRD pattern is not a perfect match with reference patterns. Perles et al. discovered that the associated M ion in $MLn(SO_4)_2$ affects the degree of hydration in the crystal and for M = Na the monohydrate is the most prevalent (Perles et al., 2005).

ICP-OES analysis of the white precipitate indicate presence of elements typical to alkali lanthanide double sulfate, shown in Table 11. The washed powder is mostly composed of lanthanides, alkalis and sulfur and as such the findings support the analysis results of SEM-EDS and XRD. Taken together the results prove that powder is composed of relatively pure rare earth compounds.

The results presented in this study can be advantageous in rethinking the process design of Ni and Co recovery from the sulfuric acid battery waste leachate after REE recovery by double sulfate precipitation. This approach, with proper precipitate washing with e.g. with a hot sodium sulfate solution, might efficiently reduce the potential for iron hydroxide impurity in the precipitate, for example, due to the reduced solubility of double sulfates at high temperatures (Kul et al., 2008).

4. Conclusions

The current paper reveals phenomena related to direct and high purity double-sulfate precipitation from heterogeneous industrially crushed NiMH battery waste. It was shown that the sulfate concentration can have major impact on precipitation efficiency in addition to Na concentration, both during leaching process and during precipitation process. Therefore it is disingenuous to report precipitation efficiencies as function of pH when using alkali hydroxides as precipitating agents as initial state of experiments can greatly differ between experiments. Emphasis should be given to the fact that precipitates are alkali lanthanide double sulfates, not simple rare earth sulfates.

It was ascertained that during the sulfuric acid leaching of industrially crushed NiMH battery waste, REE extraction in leaching was significantly less than that of the investigated transition metals, for example, during sulfuric acid leaching of NiMH waste (test 2L1), La extraction into the solution was 66.4%, whereas Ni extraction was 90.3% Ni. In contrast, water leaching (test 1L1) of NiMH waste, NaOH (Na = 317 mg l^{-1}) and KOH (K = 1394 mg l^{-1}) were found to dissolve from the waste into the solution, which suggests that Na^+ and K^+ ions inherent in the raw material can result in REE double sulfate precipitation during the leaching of NiMH waste. As a consequence a two stage leaching process for NiMH waste was investigated, firstly dissolution in sulfuric acid media followed by leaching in water media. Both sulfuric acid leaching resulted in REE extraction of La = 66.4%, Ce = 88.8% and Pr = 59.3% (2 M H_2SO_4, L/S = 10.4, t = 3 h and T = 30 °C) and the subsequent water leaching of the leach residue at room temperature resulted in REE extraction of La = 16.3%, Ce = 21.6% and Pr = 15.1%. This suggests that during the sulfuric acid leaching precipitation of sparingly water soluble double sulfate occurs, most likely due to the alkali electrolyte residues. Overall the total extraction of REEs achieved by leaching was La = 80.1%, Ce = 106.8%, Pr = 72%. The finding of the effect of alkali electrolyte is further enhanced by the fact that during water leaching of crushed NiMH waste only (1L1) no REE extraction into the solution could be observed. Additionally, during sulfuric acid leaching with initial 0.16 M sodium sulfate content (3L1) REE extraction into the solution was extremely limited (<3.5%), indicating in-situ precipitation.

In our research it was found that precipitation is dependent on both H_2SO_4 and Na_2SO_4 concentration. In Exp. 3, the best precipitation efficiency achieved was La > 98%, Ce > 99% and Pr > 99% (1E5), by adjusting initial solution concentration by adjusting the ratios to 21.2 Na^+/REE and 58.3 SO_4^{2-}/REE, which also corresponds to 1.59 M change in H_2SO_4 concentration. Notably extraction was weaker when 21.2 Na^+/REE was added without additional sulfuric acid. In Exp. 4, the precipitation efficiency of 93–95% was achieved with multiple samples (2E3, 2E5 and 2E7).

Table 11
Results of ICP-OES analysis of white precipitate.

La (mg g^{-1})	Ce (mg g^{-1})	Pr (mg g^{-1})	Na (mg g^{-1})	K (mg g^{-1})	Ni (mg g^{-1})	Co (mg g^{-1})	Mn (mg g^{-1})	Al (mg g^{-1})	Fe (mg g^{-1})	Zn (mg g^{-1})	S (mg g^{-1})
168	98	23	61	11	0.75	0.13	0.19	0.16	0.07	0.05	177

Characterization revealed formation of sodium lanthanum sulfate and cerium lanthanum sulfate by XRD. Due to the use of low pH during double sulfate precipitation the accumulation of Fe or other transition metals into the precipitate was limited, as shown by SEM-EDS and ICP-OES, producing a relatively pure (>98%) alkali lanthanide double sulfate, highlighting the advantage of performing the precipitation at low pH.

Based on the results, a whole REE recovery process from complex sulfuric acid leachate can be performed with relatively straightforward hydrometallurgical setup comprised of leaching reactor and filter. These REE-rich precipitates in turn could be further processed with traditional hydrometallurgical methods of REE separation and purification. Furthermore, the associated REE-free leachate could be processed with traditional hydrometallurgical methods that are currently used in Ni and Co production.

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References

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

Bertuol, D.A., Bernardes, A.M., Tenório, J.A.S., 2006. Spent NiMH batteries: characterization and metal recovery through mechanical processing. J. Power Sources 160, 1465–1470.

Bertuol, D.A., Bernardes, A.M., Tenório, J.A.S., 2009. Spent NiMH batteries—the role of selective precipitation in the recovery of valuable metals. J. Power Sources 193, 914–923.

Binnemans, K., Jones, P.T., Blanpain, B., Van Gerven, T., Yang, Y., Walton, A., Buchert, M., 2013. Recycling of rare earths: a critical review. J. Clean. Prod. 51, 1–22.

Casas, J.M., Alvarez, F., Cifuentes, L., 2000. Aqueous speciation of sulfuric acid–cupric sulfate solutions. Chem. Eng. Sci. 55, 6223–6234.

Cytec. CYANEX 272 Extractant. 2008; Available at: <http://www.cytec.com/sites/default/files/datasheets/CYANEX%20272%20Brochure.pdf> (Accessed 9/25, 2017).

Honda Motor Co., Japan Metals and Chemicals Co. World's First Commercialization of Rare Earth Elements Recycling. 2013; Available at: <http://world.honda.com/environment/face/2013/case17/episode/episode01.html> (Accessed 9/25, 2017).

Honey, D.J., Muir, D.M., Hunt, P.R., 1997. Hydrometallurgical processing options for nickel sulphide concentrates. Proc Nickel-Cobalt Int. Sympos. I, 15–29.

Innocenzi, V., Vegliò, F., 2012. Recovery of rare earths and base metals from spent nickel-metal hydride batteries by sequential sulphuric acid leaching and selective precipitations. J. Power Sources 211, 184–191.

Innocenzi, V., Ippolito, N.M., De Michelis, I., Prisciandaro, M., Medici, F., Vegliò, F., 2017. A review of the processes and lab-scale techniques for the treatment of spent rechargeable NiMH batteries. J. Power Sources 362, 202–218.

Kikuta, N., Asano, S., Takano, M., 2016. Method for separating nikel and cobalt from active materials contained in spent nickel-hydrogen battery US8888892B2.

Kul, M., Topkaya, Y., Karakaya, İ., 2008. Rare earth double sulfates from pre-concentrated bastnasite. Hydrometallurgy 93, 129–135.

Larsson, K., Ekberg, C., Ødegaard-Jensen, A., 2013. Dissolution and characterization of HEV NiMH batteries. Waste Manage. 33, 689–698.

Lucas, J., Lucas, P., Mercier, T.L., Rollat, A., Davenport, W., 2015. Rare Earths – Science, Technology, Production and Use, Elsevier, pp. 407.

Lokshin, E.P., Tareeva, O.A., Ivlev, K.G., Kashulina, T.G., 2005. Solubility of double alkali metal (Na, K) rare-earth (La, Ce) sulfates in sulfuric-phosphoric acid solutions at 20 C, Russian. J. Appl. Chem. 78, 1058–1063.

Meshram, P., Pandey, B.D., Mankhand, T.R., 2016. Process optimization and kinetics for leaching of rare earth metals from the spent Ni–metal hydride batteries. Waste Manage. 51, 196–203.

Meshram, P., Somani, H., Pandey, B.D., Mankhand, T.R., Deveci, H., 2017. Two stage leaching process for selective metal extraction from spent nickel metal hydride batteries. J. Clean. Prod. 157, 322–332.

Nan, J., Han, D., Yang, M., Cui, M., Hou, X., 2006. Recovery of metal values from a mixture of spent lithium-ion batteries and nickel-metal hydride batteries. Hydrometallurgy 84, 75–80.

Nan, J., Han, D., Yang, M., Cui, M., 2006. Dismantling, recovery, and reuse of spent nickel-metal hydride batteries. J. Electrochem. Soc. 153, A101–A105.

Perles, J., Fortes-Revilla, C., Gutiérrez-Puebla, E., Iglesias, M., Monge, M.Ã., Ruiz-Valero, C., Snejko, N., 2005. Synthesis, structure, and catalytic properties of rare-earth ternary sulfates. Chem. Mater. 17, 2701–2706.

Perry, D.L., 2016. Handbook of Inorganic Compounds. CRC Press.

Pietrelli, L., Bellomo, B., Fontana, D., Montereali, M.R., 2002. Rare earths recovery from NiMH spent batteries. Hydrometallurgy 66, 135–139.

Provazi, K., Campos, B.A., Espinosa, D.C.R., Tenório, J.A.S., 2011. Metal separation from mixed types of batteries using selective precipitation and liquid–liquid extraction techniques. Waste Manage. 31, 59–64.

Reuter, M.A., Hudson, C., Van Schaik, A., Heiskanen, K., Meskers, C., Hagelüken, C., 2013. Metal Recycling: Opportunities, Limits, Infrastructure, A Report of the Working Group on the Global Metal Flows to the International Resource Panel. UNEP.

Rodrigues, L.E.O.C., Mansur, M.B., 2010. Hydrometallurgical separation of rare earth elements, cobalt and nickel from spent nickel–metal–hydride batteries. J. Power Sources 195, 3735–3741.

Rollat, A., Guyonnet, D., Planchon, M., Tuduri, J., 2016. Prospective analysis of the flows of certain rare earths in Europe at the 2020 horizon. Waste Manage. 49, 427–436.

Sommer, P., Rotter, V.S., Ueberschaar, M., 2015. Battery related cobalt and REE flows in WEEE treatment. Waste Manage. 45, 298–305.

Tirronen, T., Sukhomlinov, D., O'Brien, H., Taskinen, P., Lundström, M., 2017. Distributions of lithium-ion and nickel-metal hydride battery elements in copper converting. J. Clean. Prod. 168, 399–409.

Tunsu, C., Petranikova, M., Gergorić, M., Ekberg, C., Retegan, T., 2015. Reclaiming rare earth elements from end-of-life products: a review of the perspectives for urban mining using hydrometallurgical unit operations. Hydrometallurgy 156, 239–258.

Tzanetakis, N., Scott, K., 2004. Recycling of nickel-metal hydride batteries. I: Dissolution and solvent extraction of metals. J. Chem. Technol. Biotechnol. 79, 919–926.

Wickleder, M.S., 2002. Inorganic lanthanide compounds with complex anions. Chem. Rev. 102, 2011–2088.

Wilson, A.M., Bailey, P.J., Tasker, P.A., Turkington, J.R., Grant, R.A., Love, J.B., 2014. Solvent extraction: the coordination chemistry behind extractive metallurgy. Chem. Soc. Rev. 43, 123–135.

Wu, F., Xu, S., Li, L., Chen, S., Xu, G., Xu, J., 2009. Recovery of valuable metals from anode material of hydrogen-nickel battery. Trans. Nonferrous Met. Soc. China. 19, 468–473.

Ye, Z., Noréus, D., 2012. Oxygen and hydrogen gas recombination in NiMH cells. J. Power Sources 208, 232–236.

Ying, T.K., Gao, X.P., Hu, W.K., Wu, F., Noréus, D., 2006. Studies on rechargeable NiMH batteries. Int. J. Hydrogen Energ. 31, 525–530.

Zhang, J., Zhao, B., Schreiner, B., 2016. Separation Hydrometallurgy of Rare Earth Elements. Springer, Canada, p. 259.