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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 | $\leq$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) |

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