Chemical processes for the recovery of valuable metals from spent nickel metal hydride batteries: A review

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Chemical processes for the recovery of valuable metals from spent Nickel Metal Hydride batteries: a review

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Abstract

This work proposes a review of the various unit operations described in the literature for the specific recycling of nickel metal hydride batteries, with a large focus on the chemical reactions and processes. After a brief presentation of the characteristics of spent nickel metal hydride batteries and their composition, this review first describes the physical pretreatment methods, followed by the main principles and challenges of element separation by pyrometallurgy. Then, the main steps of hydrometallurgical processes (leaching, selective precipitation, solvent extraction, electrowinning) are analyzed, focusing on explaining the main difficulties and the most promising solutions. In addition, when available, recent thermodynamic models have been used to calculate equilibria for both pyrometallurgical and hydrometallurgical systems, with a view to provide elements of understanding in the choice of operating conditions for unit operations.

Keywords: nickel metal hydride batteries, hydrometallurgy, pyrometallurgy, rare earth elements, recycling, leaching, selective precipitation, solvent extraction, electrowining

Highlights

- Spent nickel metal hydride batteries are secondary source of nickel and rare earths
- Efficient element separation remains a challenge due to the battery complexity
- Conventional pyrometallurgical routes and alternative thermal treatment are reviewed
- Hydrometallurgical operations (leaching and separation methods) are reviewed
- Recent thermodynamic models are powerful tools to better understand these processes

List of abreviations

BM	Black mass
HEV	Hybrid electric vehicles
LiBs	Lithium batteries
M	mol/L
NiMH	Nickel metal hydride
PLS	Pregnant leach solution
REEs	Rare earths elements
T	Temperature

1. Introduction

With rapidly increasing environmental changes, more sustainable energy supplies are being developed, in particular in the field of transport, resulting in increasing number of electric and HEV in replacement of internal-combustion-engine cars. Since their commercialization in the 2000s, the HEV sales have exceeded 4.5 million units per year in 2018. As a result, in 2020, more than 80% of global battery industry was devoted to electric mobility, with an expected growth of 25% per year [1].

The NiMH batteries were introduced in 1991 as a replacement of hazardous Ni-Cd batteries, and constituted the majority of the batteries used in HEV at the beginning of the 21st century [2]. NiMH market peaked at about 1.5 million HEV packs in 2012-2013 and is now slowly dropping due to replacing by higher performance LiBs [1]. In 2013, more than half of HEVs used NiMH batteries and the quantity of NiMH batteries on the market is still large [3–5]. Accordingly, important amounts of spent NiMH batteries are discarded and represent hazardous wastes that need to be correctly disposed. Besides, spent NiMH batteries contain specific metal elements that represent valuable secondary resources: for example, each Toyota Prius HEV contains 10-15 kg of REEs [6] whose large scale recovery could account for significant resources for new battery manufacturing [7]. REEs are also among the most critical raw material groups in several regions (especially Europe [8]), while the recovery of nickel is made attractive due to its high sales price.

However, NiMH batteries, as well as LiBs, are highly complex products that may contain up to 15 chemical elements (see section 2.3), and advanced recycling processes are required to recover and separate the majority of the valuable metal content. Intense research efforts have been developed since the end of the 1990's for this purpose, but, as recently pointed out by Wang [9], industrialized waste Ni-based battery recovery processes still require further developments. Specifically, pyrometallurgical processes suffer from poor separation capabilities, while, as pointed out by Silvestri [3] in 2020 based on a life cycle assessment, hydrometallurgical processes present a large negative environmental impact of both production and end-of-life of NiMH batteries due to the massive chemical consumption and the generation of wastes that require reprocessing stages. The development of versatile and economically profitable processes thus remains a challenge for the years to come.

In relation to these research activities, in the last decade several review papers have focused on establishing the status of research in the field of metal recovery from secondary sources such as batteries and other electronic devices. Among them, the recycling of REEs from various secondary sources (phosphors, permanent NdFeB magnets and NiMH batteries) was described in 2013 by Binnemans [10], while Tunsu [11] focused in 2015 on hydrometallurgical unit operations. Al-Thyabat [12] established in 2013 an analysis of NiMH and LiBs recovery through the prism of the adaptation of minerals processing operations. Wang [9] and Pradhan [13] focused very recently on the overall available routes for the recovery of valuable elements from Ni-based batteries. Most of these reviews were devoted either to the recycling of various types of batteries (LiBs, NiMH, Ni-Cd), or to the recovery of specific elements (e.g. REEs) from electronic wastes. However, the recycling of NiMH batteries has specificities related to their composition, namely high REEs and nickel contents, and a low cobalt content, which affects the development of separation processes. To the knowledge of the authors, the only literature review that is entirely dedicated to NiMH battery recycling processes was established in 2017 by Innocenzi [14]. Since then, more than 60 technical articles exploring various operating conditions or proposing new recycling ways have been published.

The present work proposes an in-depth litterature investigation of the various unit operations that have been reported in the literature for the specific recycling of NiMH batteries, with a main focus on the chemical reactions and processes. After a brief presentation of the characteristics of spent NiMH batteries, this review describes the physical pretreatment methods, followed by pyrometallurgical processes and then hydrometallurgical methods. In addition, thermodynamic calculations have been performed for both pyrometallurgical and hydrometallurgical systems (using the FactSage [15] and OLI Systems [16] commercial software, respectively), with the aim of understanding the influence of operating conditiong. Both software include recent and rigorous

models that allow to describe high temperature systems (e.g. liquid metals, slags) as well as concentrated aqueous electrolytes (e.g. REEs solubility in sulfuric acid [17]), which provides new insights on the various unit operations usually described solely from experimental results.

2. From spent NiMH batteries to Black Mass

2.1 Major battery components and electrode composition

The main characteristic of the active materials of NiMH batteries is their ability to intercalate or de-intercalate H^+ ions in a reversible manner, also called hydriding. The overall cell reaction is described in Eq. 1 [18,19]:

$$NiO(OH)_{(s)} + MH_{x(s)} \leftrightarrow Ni(OH)_{2(s)} + MH_{x-1(s)} \quad \text{Eq. 1}$$

where M is a hydrogen absorbing alloy and the forward direction is the discharge reaction.

As illustrated in Figure 1, the NiMH cells are composed of a positive electrode (cathode), a negative electrode (anode), and a KOH electrolyte that is contained in a gas permeable polymer separator [20]. These elements are placed in a protective steel based case. The batteries have mainly three geometrical configurations: prismatic/rectangular used in HEV, button and cylindrical cells [18,19]. Some typical compositions are gathered in Table 1 [21,22]: the mass of the electrodes represents about 50-60 wt.% of the total battery weight.

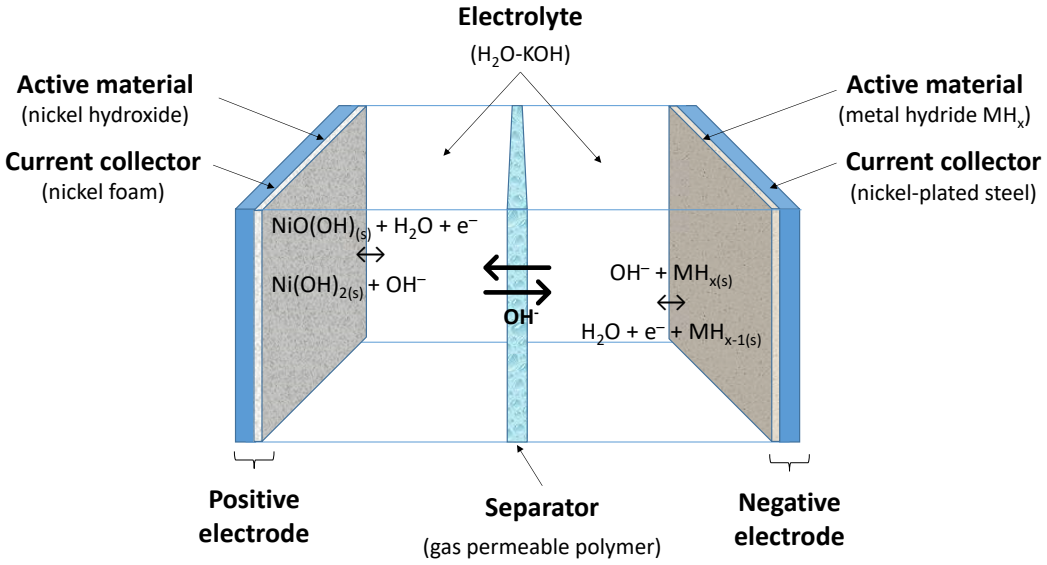


Figure 1: Operating principle of a NiMH battery

Table 1 – Overall component repartition in NiMH batteries (wt.%)

Component (wt.%)	[12]	[23] without casing and electrolyte	[24]	[25]
Type	cylindrical	Cylindrical	Mobile phone	Prismatic - HEV
Cathode materials	35	38	37	28
Steel cathode collector	-	21	-	21
Anode materials	22	33	30	23
Electrolyte	5	-	-	13
Separator	5	4.5	10	3
Case materials	33	-	27	13

The cathode active mass consists of spherical particles of β-$Ni(OH)_2$, which oxidize into β-NiOOH during battery charging. The current collector is a metallic nickel foam [18,19]. The anode active material is composed of metal hydride particles deposited on a nickel-plated steel current collector. Several alloys such as AB_5 and A_2B_7 have been developed, where A represents a mixture of rare earths elements and B is a mixture of transition metals [2]. The best performing alloy identified to date is the intermetallic compound $LaNi_5$, which allows hydrogen storage as $LaNi_5H_6$ hydride [10]. Mixtures of REEs and other transition metals, the so-called mischmetal, are usually used in order to reduce material costs.

Table 2 provides an overlook of the metal distribution in cathode and anode, which contain the high value metals, for various battery types: REEs are essentially found in anode materials, where Ce and La are the main elements, whith minor contents of Nd, Pr and Y. Iron is almost absent of the electrodes, and nickel is predominant in both anodes and cathodes. Thirteen chemical elements are listed in Table 2, which highlights the complexity of selective metal recovery.

Table 2 – Examples of NiMH electrodes elemental composition (wt%)

Ref.	[26]		[25]		[27]		[23]	
Type	Cell phone		Prismatic - HEV		Prismatic - HEV		Cylindrical	
Element	Cathode	Anode	Cathode	Anode	Cathode	Anode	Cathode	Anode
Ni	31.0	11.2	64.7	52.3	75.5	51.7	19.7	23.4
Co	27.9	18.4	5.7	3.6	6.1	4.7	2.1	7.3
Mn	1.7	9.1	0.2	5.6	0.5	4.1	0.5	4.0
Fe	0.7	1.5	-	0.1	0.1	0.1	0.3	0.6
Al	-	-	0.1	1.5	0.3	1.9	-	-
Zn	16.4	0.7	0.5	-	3.5	0.4	<0.1	<0.1
Mg	-	-	0.3	-	-			-
K	10.0	3.2	0.2	0.4	1.9	1.4	3.6	5.0
La	0.4	32	-	20.2	-	20.4	-	-
Ce	0.4	24	-	7.4	-	6.4	-	-
Nd	-	5.2	-	2.4	-	2.9	-	-
Pr	-	2.6	-	1.0	-	2.5	-	-
Y	-	-	0.9	0.7	0.7	0.7	-	-
$\sum REEs$	0.8	63.8	0.9	31.7	0.7	32.9	0.1	58.8

The lifetime of industrial NiMH batteries can typically extend up to 2000 charge-discharge cycles [19] before they fail due various degradation mechanisms [28]. Nevertheless, since NiMH batteries are closed systems, their overall chemical composition is not much affected by aging.

2.2 Pretreatment processes: physical based technologies

Pretreatment of discarded NiMH batteries, schematized in Figure 2, aims at volume reduction, separation into different fractions (ferrous, plastic, non-magnetic) and production of a black powder ready to be treated [29], the so-called black mass BM. Some early works on NiMH battery recycling envisaged the specific recovery of Ni-based alloys by minerals techniques only [30].

First, the batteries are often sorted manually to minimize mixing with other battery types. The automotive batteries are dismantled manually due to their larger size and weight compared to cylindrical batteries [31,32]. Next, at industrial scale, the materials proceed through a thermal treatment in order to inert the batteries, avoid short circuits and facilitate the phase liberation

during subsequent comminution operations [32–34]. Cryogenic freezing has been implemented at Retriev Technologies/Toxco to make the batteries fragile [31]. Tang [35] reported that liquid nitrogen (-196 °C) was to be preferred over liquid CO_2 (-78.5 °C) to separate the steel case. Moreover, heat treatment can be carried out at 250-550 °C with controlled atmospheric conditions (vacuum or low oxygen content). Various operation conditions are reported: at SNAM company the heat treatment is performed with low oxygen content [33], while Sumitomo Metal Mining uses a roasting operation with carbon in order to reduce nickel oxide and facilitate further Ni leaching [32]. Korkmaz [36] also investigated selective roasting of NiMH anode material after reaction into concentrated sulfuric acid.

Next, the material is crushed by hammer or knife mill, followed by separation operations. Tanabe [24] report that spouted bed elutriation after hammer milling and sieving allows to separate the NiMH materials into three different fluxes (plastics, iron-based metals and electrodes powder). Magnetic separation may also be implemented. The highly magnetic part (from the protective steel case) is recovered for the production of secondary steel. The weak magnetic fraction is sieved, and the resulting fine fraction, in the form of a black powder (the BM, see Figure 2), is finally recovered [12,26].

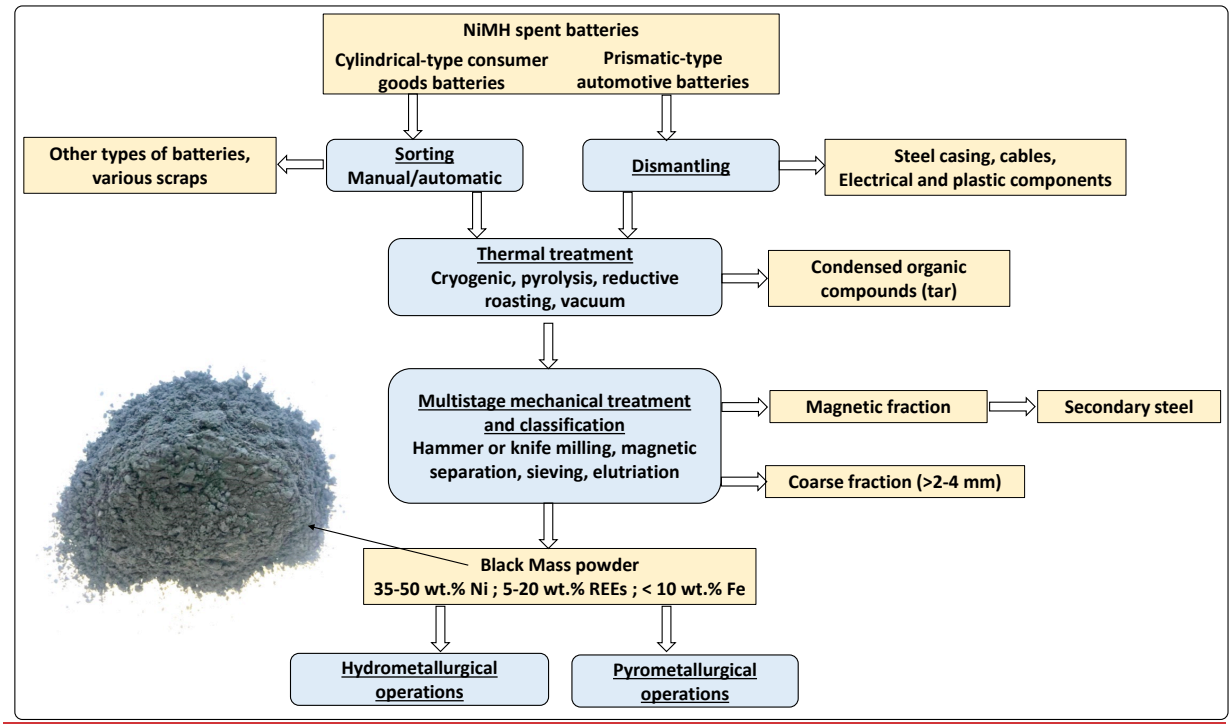


Figure 2 – Flow chart of typical physical based pretreatments of spent NiMH batteries, including a picture of a black mass sample (prepared at the SNAM facilities)

2.3 Black Mass elemental composition

An overview of BM powders chemical composition is compiled in Table 3. It first highlights that most of the academic studies did not characterize battery materials that have undergone thermal treatment or magnetic separation. Several studies [29,33,37,38] evidence the influence of the fraction size on the BM elemental composition for particle sizes from < 100 µm up to 4 mm. As shown in Figure 3, Ni and REEs contents are higher in the finest fraction of the BM while Fe follows the opposite trend, where the typical cut-off particle size is around 1 mm. The Ni content is between 35 and 50 wt% in fine particles, and below 20 wt% in large particles. The REEs content

is 5-20 wt% in fine particles, and almost zero in the coarse fraction. Fe content is typically lower than 10 wt% in fine particles, and becomes the major component in large particles.

The total carbon content represents a small part of the BM (2 – 5 wt%) [29,37]. It originates from residual organic compounds such as plastic, papers and graphite particles [29], and although it is chemically inert in aqueous solutions, the presence of fine carbon particles may cause filtration issues after leaching operations. K and Na elements are usually present in the BM due to the presence of residual electrolyte, resulting in high K contents (2-10 wt%) reported by several authors [33,37,39–41], while Na is usually low (< 1 wt%).

Table 3 – Composition (wt%) of different BM powders prepared from mixed (anode+cathode) elements

Type of battery	Thermal/ magnetic treatment	Sieving fraction (µm)	Element, wt%												Ref.
			Ni	Co	Mn	Fe	La	Ce	Nd	Pr	REEs	K	Na	C	
Unknown	no	3000 - 6000	5.9	0.0	na	37.8	0.0	na	na	na	na	na	na	na	[38]
		1500 – 3000	22.6	1.8	na	31.3	0.0	na	na	na	na	na	na	na	
		750 – 1500	41.2	2.6	na	15.2	0.6	na	na	na	na	na	na	na	
		375 – 750	48.1	4.8	na	6.9	3.4	na	na	na	na	na	na	na	
		187 – 375	45.1	5.3	na	0.8	4.0	na	na	na	na	na	na	na	
		88 – 187	48.5	5.5	na	1.0	4.4	na	na	na	na	na	na	na	
		< 88	42.0	6.1	na	0.0	4.4	na	na	na	na	na	na	na	
Cylindrical	no	1000 – 4000	13.7	0.5	0.3	66.2	0.7	0.2	0.0	0.0	0.9	0.2	bd	7.3	[37]
		500 – 1000	22.0	1.3	0.6	57.8	1.5	0.5	0.1	0.1	2.2	0.4	bd	1.9	
		250 – 500	39.9	2.7	0.8	27.8	3.2	1.0	0.3	0.4	4.9	0.7	0.03	4.7	
		125 – 250	45.8	4.4	1.2	6.9	5.3	1.6	0.6	0.7	8.2	1.3	0.1	3.4	
		63-125	42.7	5.5	1.7	4.3	7.3	2.3	0.9	1.0	11.5	1.1	0.1	2.9	
		0-63	48.6	6.9	2.5	1.9	9.1	2.9	1.3	1.2	14.5	1.4	0.1	2.9	
Cylindrical	no	2000 – 4000	8.1	bd	bd	91.6	bd	bd	bd	bd	bd	bd	na	na	[29]
		1000 – 2000	40.1	6.3	8.2	18.9	ns	ns	ns	ns	7.5	6.3	na	na	
		500 – 1000	39.8	3.7	6.2	22.8	ns	ns	ns	ns	7.6	8.8	na	na	
		< 500	37.7	5.1	9.6	13.2	ns	ns	ns	ns	6.8	4.9	na	na	
Cylindrical	300–500 °C	250 - 600	43.8	4.6	2.2	4.1	9.1	4.1	1.5	0.4	15.1	2.2	0.5	1.6	[33]
		100 - 250	42.4	4.6	2.1	4.4	8.8	3.9	1.8	0.4	14.9	2.4	0.6	3.2	
		< 100	44.9	5.5	2.4	2.9	8.7	5.0	1.7	0.5	15.9	2.2	bd	2.8	
Prismatic	300–500 °C	250 - 600	43.7	2.4	2.7	1.6	11.8	4.2	1.3	0.4	17.7	3.6	0.4	2.8	
		100 - 250	44.5	3.8	2.0	1.5	8.0	2.9	1.0	0.3	12.2	4.2	0.4	4.4	
		< 100	44.9	4.8	1.9	1.2	7.4	2.9	1.1	0.3	11.7	4.4	0.4	5.1	
Unknown	no	< 500	11.7	2.6	14.3	1.1	3.6	1.7	na	na	5.3	2.5	na	na	[39]
	105 °C; 24 h		22.7	5.0	26.2	1.7	5.8	2.6	na	na	8.4	5.7	na	na	
Unknown	no + magnetic separation	< 500	43.2	5.6	3.0	0.4	8.8	8.0	3.7	1.2	21.8	0.02	0.01	na	[42]
Unknown	80 °C; 24 h	< 45	58.9	4.6	2.9	2.8	2.7	2.6	4.5	2.3	12.1	na	na	na	[43, 44]
Unknown	no + magnetic separation	< 72	87.2	9.4	na	0.5	na	na	na	na	1.1	na	na	na	[45]

Cylindrical + prismatic	60 °C; 24 h	< 500	49.8	5.5	2.4	0.3	5.4	6.1	3.0	0.8	15.3	2.2	na	na	[46]
Unknown	no	< 1400	43.4	5.5	na	1.8	4.0	4.1	na	1.2	9.4	ns	ns	na	[47]
Prismatic	105 °C; 3 h	< 1000	26.4	3.2	1.3	2.9	8.9	2.3	na	0.7	11.9	10.4	3.7	na	[40]
Prismatic	Reduction roasting	no sieving	48	4.1	na	na	12	5.8	na	na	18.6	na	na	na	[32]

Mixed: all components of the battery are included in the Black Mass
na – element not analyzed
ns – element analyzed but data not specified (only the total concentration of REEs is provided)
bd – concentration below detection limit

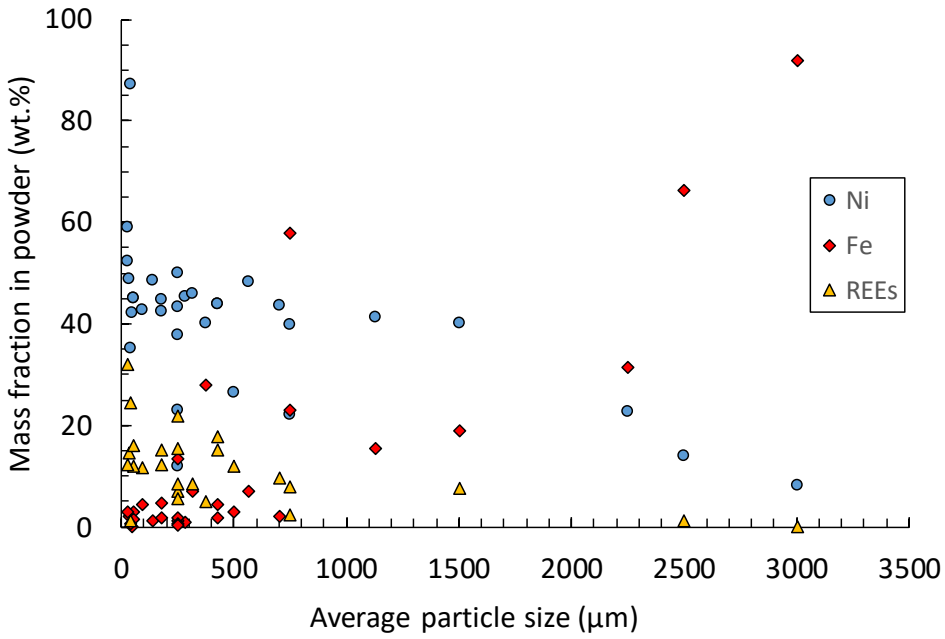


Figure 3 – Fe, Ni and REEs content (in wt%) in NiMH Black Mass powder as a function of particle size (based on references compiled in Table 3)

Grinding and sieving operations have a strong impact on the overall material balance, since a large amount of the initial material is likely to be discarded in the coarse fraction depending on the grinding technology. Ebin [37] showed that lab-scale sieving with a sieve size above 4 mm leads to the recovery of 85% of the initial mass, while Huang [29] recovered only 16% in the same size fraction. Granata [48] carried out medium scale mechanical pretreatment and recovered 44% of initial mass at 1000 µm sieving size. Porvali [38] recovered 38% of a batch material that had been crushed at industrial scale after sieving at 750 µm. In addition, the authors report that fiber from polymeric separators pass even through the smaller sieve size.

Compared to the elemental analyses, only few authors focused on determining the nature of the mineral phases present in the BM. Some works highlight that mischmetal alloys such as $LaNi_5$ are mainly oxidized into rare earth oxides [46,49]. Rodrigues [46] performed X-Ray diffraction on mischmetal treated at low temperature, and detected only rare earth oxides, while Ebin [37] identified mostly metal phases and $Ni(OH)_2$ on BM that did not go through any thermal treatment. Zielinski [33] provided an in-depth characterization of heterogeneous battery powder, where three types of BM particles were identified and quantified: Ni-NiO particles originating from the cathode, partially oxidized mischmetal from the anode active mass and iron oxide particles from the anode mesh. These particles have a core–shell structure resulting from the partial oxidation of the battery components during ageing and pretreatment operations. The whole picture highlights

the joint importance of battery ageing mechanisms, thermal deactivation and BM sieving steps on the final structure and composition of the BM particles.

3. Pyrometallurgical processes

As reported by Müller and Friedrich [50], in the early 2000's the "discarded NiMH batteries were used as a cheap nickel source in the steel industry, while cobalt was not considered and REEs were lost in the slags". More recently, Tirronen [51] have investigated the element distributions (Ni, Co, Mn, Nd) in copper converting process facilities. They concluded that the secondary copper smelting circuits are not effective for NiMH metals recovery, since a large fraction of the valuable elements is lost and diluted in the slag phases. Wang [52] studied in 2002 the direct smelting and re-use of dismantled bulk cathode materials but, even if good performances of the secondary alloys were obtained, this route has not been further mentioned nor put into application. With the exception of these publications, only a few works have been devoted to the valorization of Ni and Co on one side and REEs on the other side in the frame of a dedicated pyrometallurgical process [53]. The general principle of such operations, as established for instance by [35,50], is schematized in Figure 4. It consists in melting the battery material, either after pretreatments (Figure 2) in order to decrease the Fe content, or sometimes as a full piece including plastic elements. In contact with a slag (i.e. an oxide liquid phase), the process leads to the reduction of Ni and Co elements into a liquid Ni-Co alloy, while REEs oxidize and dissolve into the slag.

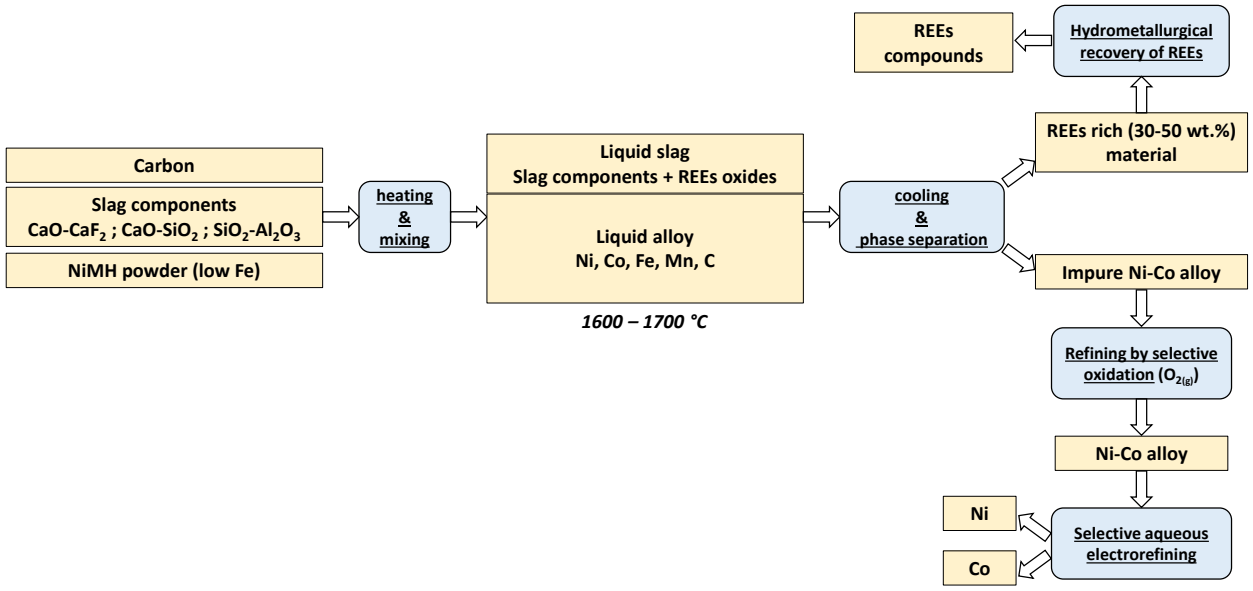


Figure 4 - Principle of pyrometallurgical processing of spent NiMH batteries

The thermodynamic principle of such separation is illustrated in Figure 5 using Ellingham's representation, calculated with the FactSage software. This diagram gathers the standard Gibbs energy $\Delta_r G°$ per mol of O_2, of reaction (Eq. 2) as a function of temperature.

$$\frac{2a}{b} M_{(s,liq)} + O_{2(g)} \xrightarrow{\Delta_r G°(T)} \frac{2}{b} M_a O_{b(s,liq)} \qquad \text{Eq. 2}$$

As evidenced in Figure 5, in presence of carbon excess, Ni, Co, Fe and Mn form a metal phase, while, in similar conditions, REEs form an oxide phase up to 2000 °C.

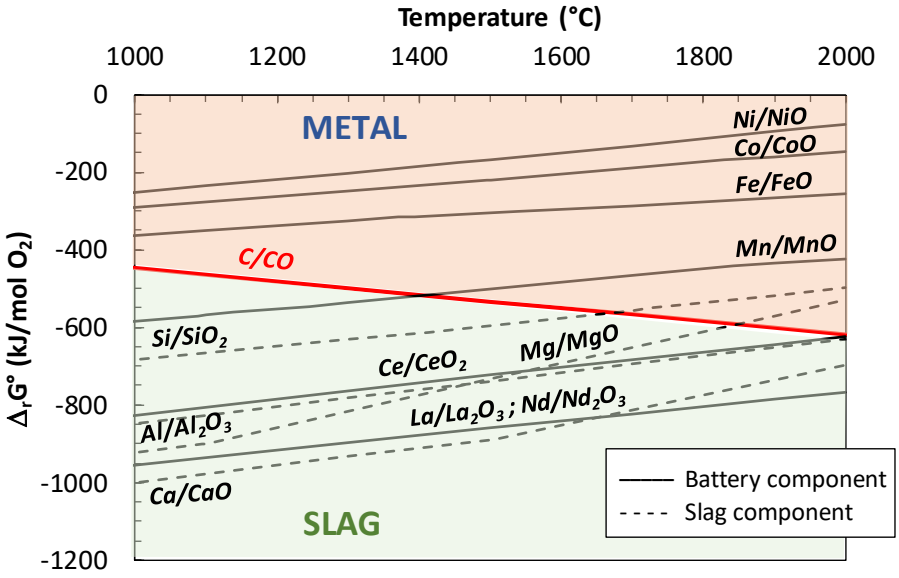


Figure 5 - Ellingham diagram for selected slags and NiMH battery components calculated using FactPS database of FactSage 8.1 [15] (systems above the C/CO equilibrium form a metal phase, system below the C/CO equilibrium form an oxide phase)

In order to facilitate mass transfer and achieve thermodynamic equilibrium, such processes require both metal and slag phases to be in the liquid state. As illustrated in Figure 6, Ni melts at 1455 °C, and alloying with Fe and Co only slighlty modifies the melting temperature, while Mn and Cu decrease the melting temperature. Moreover, La_2O_3, which is the main component of the oxide phase issued from NiMH, melts at a much higher temperature, i.e. 2309 °C. Consequently, the minimal operating temperature is driven by the use of additives allowing to decrease the melting temperature of the slag. The melting temperature of La_2O_3 mixed with SiO_2, CaO and Al_2O_3 is shown in Figure 6 [54]: none of these common additives does allow to decrease the melting temperature below 1766 °C (La_2O_3-SiO_2 eutectic). Consequently, to operate below 1700 °C, mixtures typically made of CaF_2, MgO, CaO, Al_2O_3 and/or SiO_2 need to be considered. As recently pointed out by Lan [55], the basic data on REEs in REE-bearing slags are scarce, and the development of an efficient process thus requires extensive experimental work.

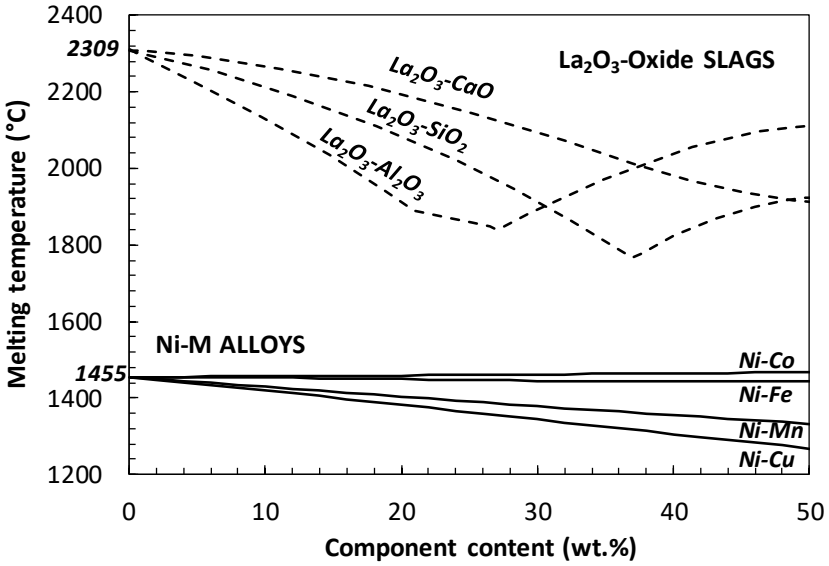


Figure 6 – Melting temperature of Ni-M (M=Co, Fe, Mn, Cu) and La_2O_3-Ox (Ox = CaO, SiO_2, Al_2O_3) binary mixtures. Melting temperature of liquid alloys (full lines) were calculated using

SGTE database of FactSage 8.1 [15]; melting temperature of slags (dotted lines) are reported from phase diagrams compiled in [54].

Müller and Friedrich [50] pointed out that the definition of an appropriate slag system is a key point for such operation. These authors performed successful pilot-scale tests (300-1000 kg) with CaO-CaF_2 and CaO-SiO_2 slags, but report incomplete refining of final Ni-Co alloys which contained 5-10 wt% of Fe and Mn. Further refining by selective oxidation of Mn and Fe thanks to O_2 bubbling in the liquid metal phase is then required. If satisfying purity is obtained, Ni-Co alloys can eventually be separated into pure Ni and pure Co through aqueous electro-refining (Figure 4).

Based on a slightly different concept, Jiang [56] proposed a pre-reduction step of BM by hydrogen at 800-900 °C, followed by high temperature (1550 °C) equilibration with a SiO_2-Al_2O_3 slag. Laboratory scale experiments led to high REEs contents in the slag (50 wt%). Deng [57] carried viscosity measurements of La_2O_3-SiO_2-Al_2O_3 mixtures, for improving the separation efficiency and reduce acid consumption in consecutive hydrometallurgical process.

The resulting REEs-rich slags need to be processed by aqueous leaching and further recovery of REEs compounds by selective precipitation (Figure 4). For instance, Deng [58] have recently reported excellent REEs leaching yield (95%) from SiO_2-Al_2O_3 slags in hydrochloric acid, while Kim [59] have characterized the leaching kinetics of La from silica based slags in sulfuric acid media.

It is also important to note that many authors (e.g. [10,14,60]) report the Umicore and Rhodia process, put into operation in the early 2010's. It is based on a smelting technology where resulting rare-earth concentrates were used as a feed in the separation plant of Rhodia/Solvay (France). However, no details of the process conditions or performances are available in open literature.

Apart from the conventional pyrometallurgical methods that could benefit from large-scale existing facilities, alternative processing routes based on high temperature thermal treatment of NiMH materials have been reported in the last years. For instance, Kuzuya [61] proposed a reactive thermal treatment based on carbochlorination reactions. Mir [62] investigated the effect of microwave oxidizing thermal treatment at 1000 °C, but the resulting NiO and La-Ni oxide phases are difficult to leach in HCl solutions. Maroufi [63] proposed a two-step oxidation – reduction approach, were the battery material was reduced at 1550 °C in order to produce a ferro-nickel alloy on the one side, and an oxide phase containing REEs on the other side. The small scale (gram scale) does not really allow to conclude on the potentiality of such routes. Some authors also focused on preparing metallic products from NiMH batteries using waste plastic sources (e-waste plastics [64], waste printed circuit printboard [41]) as reductant in replacement of carbon.

In conclusion, it makes no doubt that pyrometallurgical technologies are very attractive for metal recovery from secondary wastes such as NdFeB-magnets [60] or waste electrical and electronic equipment (WEEE) [65], owing to the possibilities of large scale and cost-effective processes and benefits from existing knowledge linked with primary metals production. However, the recycling of NiMH spent batteries by such methods has not been the topic of much research works in the last decade, and, to the best of the authors' knowledge, no process demonstration has been published.

4. Hydrometallurgical processes

Conversely to pyrometallurgy, the hydrometallurgical routes have been much more explored. The first step of hydrometallurgical treatments is the dissolution of the BM in an acid solution, followed by filtration of the solid residues (carbon particles, undissolved or precipitated phases). Then,

selective precipitation, solvent extraction and electrodeposition are the main separation options. The most recent routes are described in this section.

4.1 Leaching of BM

This section provides a description of the main features and specificities linked with NiMH BM leaching in sulfuric and hydrochloric acid, which are the dominant media reported for this operation. Alternatively, a few recent works implemented organic acids and a choline chloride-based deep eutectic solvent [66], which are potentially more environmentally friendly. Citric [67–69], formic [70,71] or nitric [72] acids have been reported, with subsequent metal recovery by adsorption [67], electrodeposition [66,69] or preparation of oxide compounds via sol-gel method [68,73]. Also, a first bioleaching attempt, aiming at reducing mineral acid consumption, has been recently reported [74], together with the evaluation of the leaching properties of gluconate organic acid and its bio-oxidation products [75].

4.1.1 Leaching reactions

BM particles contain metal, oxides and hydroxides phases leading to various kind of reactions during acid leaching, as exemplified in Eq. 3 to Eq. 5 for a given metal M.

$$M_{(s)} + 2\,H^{+}_{(aq)} = M^{2+}_{(aq)} + H_{2(g)} \qquad \textit{Eq. 3}$$

$$MO_{(s)} + 2\,H^{+}_{(aq)} = M^{2+}_{(aq)} + H_2O \qquad \textit{Eq. 4}$$

$$M(OH)_{2(s)} + 2\,H^{+}_{(aq)} = M^{2+}_{(aq)} + 2\,H_2O \qquad \textit{Eq. 5}$$

If the acid consumption per mol of M is equivalent for each reaction, the acid leaching of metals leads to the formation of hydrogen gas, which needs to be taken into account for large scale processing. Eh-pH analysis of the Ni-La-H_2O-HCl system shows that a pH below 6 is required in order to oxidize nickel metal (Eq. 3), and an acidic pH is also required to dissolve oxide and hydroxide phases [76].

The nature of the acid has large consequences on the chemistry of the leaching step, as well as on the further separation steps. First, the acid counter-ion (Cl^-, SO_4^{2-}) can lead to complexation with the metal cation, which can influence the solubility of the initial phases (Eq. 6).

$$M^{2+}_{(aq)} + n\,X^{-}_{(aq)} = MX^{2-n}_{n(aq)} \qquad \textit{Eq. 6}$$

More important, new solid phases can form during leaching by reaction between the acid counter-ion and metal cations, which affects the overall solubility. One of the most typical example is the formation of double sulfate salts due to the simultaneous presence of REEs, K, Na and sulfate ions, according to Eq. 7.

$$REE^{3+}_{(aq)} + 2\,A^{+}_{(aq)} + 2\,SO^{2-}_{4(aq)} = 2\,AREE(SO_4)_2.nH_2O_{(s)} \qquad \textit{Eq. 7}$$

where A = Na or K

4.1.2 Overview of operating parameters

Table 4 reports the effect of operating conditions on dissolution yields in HCl and H_2SO_4 media, based on recent work mostly carried out in small volume reactors (< 1 L except for two studies using > 5 L [76,77] and 500 L pilot data [32]). The yields are displayed only for REEs and Ni owing to their major concentration in BM. However, it has been shown (e.g. [76]) that Co and Fe exhibit similar dissolution behavior as Ni, while K dissolution is very fast.

Table 4 – Overview of operating parameters and leaching yields obtained for NiMH Black Mass leaching in acid media

Leaching solution	Temp. (°C)	S/L (%)	Volume (L)	Duration (h)	Leaching yields	Ref.
Sulfuric acid ***without pH regulation***						
H_2SO_4 3 M	95	13	0.75	4	99% Ni, 5% REEs	[78]
H_2SO_4 2 M	95	5	0.35	4	97% Ni, 96% REEs	[79]
H_2SO_4 2 M	90	5	1	4	83% Ni, 83% REEs	[80]
H_2SO_4 2 M	75	10	*ns*	2	90% Ni, 95% REEs	[44]
H_2SO_4 2 M	75	10	0.5	2	91.6% Ni, 90.2% REEs	[43]
H_2SO_4 3 M	70	10	*ns*	5	96% Ni, 96% REEs	[34]
H_2SO_4 2 M anode material	20	10	*ns*	2	77% Ni, 93.2% REEs	[81,82]
H_2SO_4 1-4 M anode material	1) 25 2) 90	5	*0.02*	4	1) 70% Ni, > 90% REEs 2) 98% Ni, >90% REEs	[27]
2-steps: 1) H_2SO_4 2 M 2) H_2SO_4 1 M	1) 83 2) 30	1) 15 2) 15	0.05	1) 3 2) 1	1) 90% Ni, 33% REEs 2) 89% Ni, 99% REEs	[39]
2-steps: H_2SO_4 1.5 M	30	10	1	2 x 1 h	80% Ni, 87% REEs	[46]
4-steps: H_2SO_4 0.75 M anode material	40	18	0.08	4 x 1 h	100% Ni, 100% REEs	[83]
2-steps: 1) H_2SO_4 2 M 2) H_2O	1) 30 2) 25	1) 10 2) 10	0.1	1) 3 1) 1.5	1) 90% Ni, 66% REEs 2) 90% Ni, 90% REEs	[47]
H_2SO_4 3 M	90	66	*ns*	3	93.5% Ni	[45]
H_2SO_4 3 M + 10 v.% H_2O_2	90	66	*ns*	1	99% Ni	
H_2SO_4 1 M + O_3(g)	25	8	0.5	3	100% Ni, 96% REEs	[84]
with pH regulation						
H_2SO_4 pHreg 3	1) 25 2) 40 3) 60	15	8	1) 22 2) 22 3) 6	1) 31% Ni, 62% REEs 2) 48% Ni, 45% REEs 3) 28% Ni, 54% REEs	[76]
H_2SO_4 pHreg 0-3	40-90	5-15	*ns*	8	34-90% Ni, 42-96% Co, 50-100% REEs	[32]
H_2SO_4 pHreg 1 + air	80	10	500	6	89% Ni, 94% Co, 99% REEs	
Hydrochloric acid ***without pH regulation***						
HCl 4 M	95	10	1	3	98% Ni, 99% REEs	[85]
HCl 3 M	95	11	0.1	3	96% Ni, 99% REEs	[86]
HCl 3.7 M Anode material	70	10	0.1	1.6	95% REEs	[87]
HCl 12 M	40	15	*ns*	1.6	100% Ni, 100% REEs	[40]
HCl 1-8 M Anode material	90	5	*0.02*	1	99% Ni, 99% REEs	[27]
HCl 8 M L	25	10	*ns*	5	100% Ni, 100% REEs	[88]
with pH regulation						
HCl pHreg 1	25	10	*ns*	5	83% Ni, 10% REEs	[88]
HCl pHreg 1 cathode material	30	51	5	0.5	22% Ni, 100% REEs	[77]
HCl pHreg 3	1) 25 2) 40 3) 60	15	8	1) 6 2) 22 3) 22	1) 16% Ni ; 90% REEs 2) 37.9% Ni ; 100% REEs 3) 57% Ni ; 100% REEs	[76]
HCl pHreg 5.5	40	15	8	22	11.9% Ni, 11.1% REEs	

ns : not specified

Based on the data compiled in Table 4, and the parametric study by Sobianowska-Turek [89], it comes that the main strategy implemented for efficient Ni and REEs leaching consists in using aggressive conditions combining high initial acid concentrations (> 3 M) and high temperature (70-95 °C) for maximum 4 h. The solid-liquid ratio is often limited to 10-15%, which corresponds to a compromise between the amount of BM that can be dissolved and the slurry density that could hinder mass transfer in the leaching reactor.

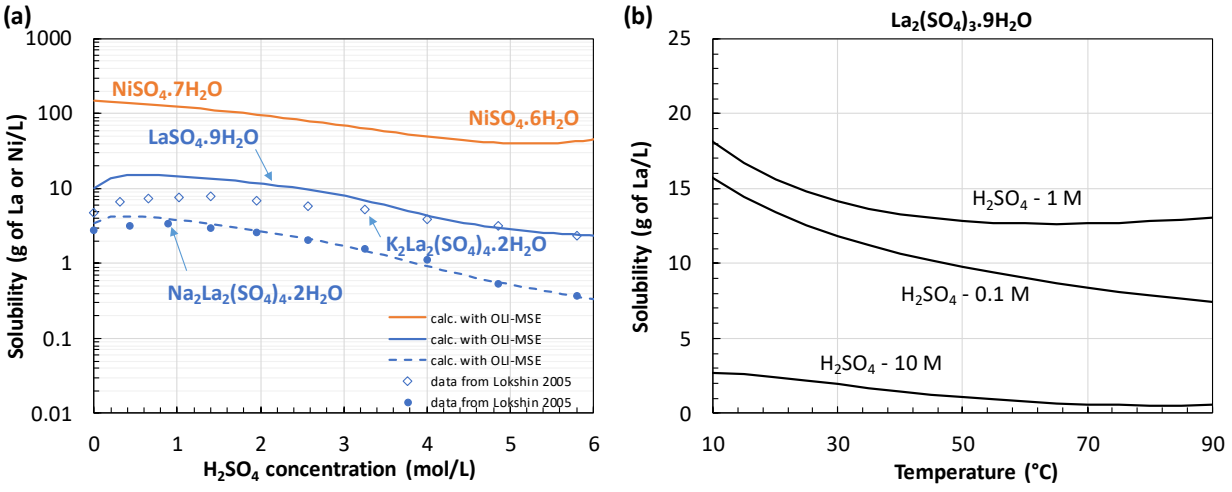
Whatever the type of acid, several authors report that Ni dissolution is slow at low temperature, possibly due to the presence of nickel oxide. For instance, Korkmaz [27] obtained a much better Ni yield (98% vs 70%) at 90 °C than 25 °C. Takano [32] implemented a primary roasting of the BM in order to reduce NiO and enhance nickel dissolution. A comparison between HCl and H_2SO_4 acid leaching kinetics, carried out in similar conditions (same BM, pH and temperature) showed that Ni leaching rate is mostly independent of the type of acid, and that REEs dissolve faster than Ni [76]. Furthermore, some works have shown that high temperature and low pH increase the rate of the anodic dissolution of metal nickel [90–93]. This could justify, at least in part, the aggressive conditions usually implemented to dissolve nickel more rapidly.

4.1.3 Solubility of Ni and REEs salts

Figure 7 reports the solubility of the most stable Ni and La salts in inorganic acid systems (H_2SO_4-H_2O, HCl-H_2O and H_3PO_4-H_2O). The data come from equilibrium calculations performed with the OLI software [16], based on the recent assessment of REEs systems by Das [17,94] as well as experimental data from Lokshin [95]. The solubilities, in g of element per L of solution, are plotted as a function of the acid concentration or temperature. Lanthanum was selected as model element for REEs (Ce and Nd behave similarly).

It first comes from Figure 7 that, due to the common ion effect, high acid content lowers the solubility of the sulfate and chloride salts. The reason for using contrated acid solutions thus rely more on kinetic aspects than on thermodynamics. Second, the overall solubility of Ni and La compounds is much higher in HCl than in H_2SO_4. Indeed, $NiCl_2.6H_2O$ and $LaCl_3.7H_2O$ compounds are highly soluble (170 g/L and 330 g/L, respectively, in 2 M HCl solutions), while the solubility of La salts is low (less than 20 g/L for $LaSO_4.9H_2O$), and even extremely low (less than 10 g/L) in presence of K^+ or Na^+ ions, due to the formation of double sulfate salts (Eq. 7). Third, the solubility of REEs sulfate salts (e.g. $LaSO_4.9H_2O$) decreases with temperature (Figure 7(b)).

According to the data compiled in Table 3, the mass ratio Ni/REEs is about 5 in the BM. Consequently, the overall solubility of BM in H_2SO_4 media is limited by the solubility of REEs sulfate compounds, while in HCl media it is limited (at a higher level) by Ni chloride compounds. Furthermore, REEs phosphates compounds exhibit a very low solubility in H_3PO_4 media, which led to recent investigation of selective leaching by Lie [96].



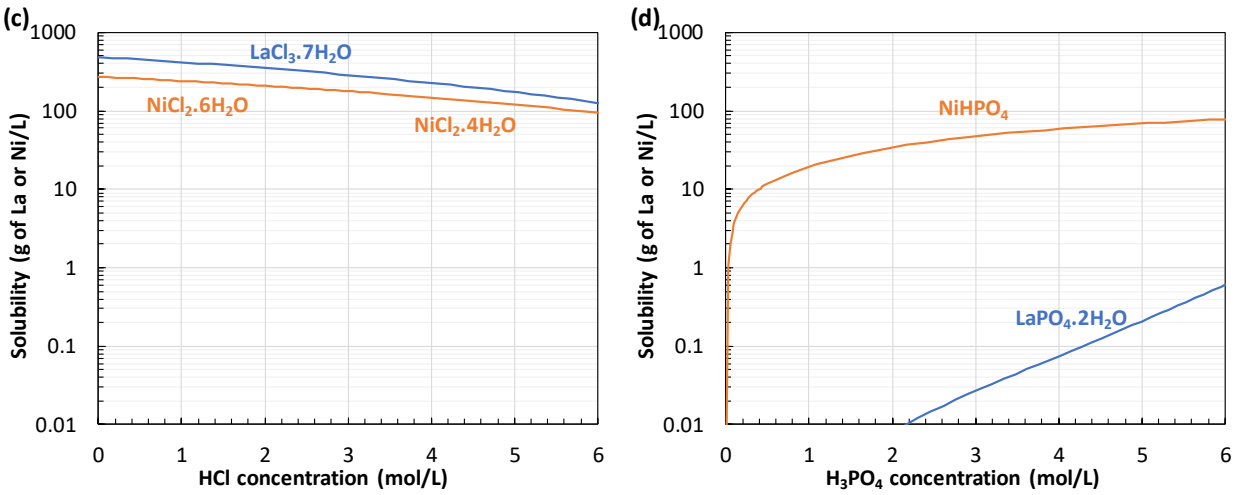


Figure 7 - Solubility of various Ni and La salts (in g of La or Ni/L of solution) in (a) H_2SO_4-H_2O media at 25 °C (b) HCl-H_2O media at 25 °C (c) H_2SO_4-H_2O media as a function of temperature (calculated with OLI-MSE [16,17,94]and experimental data from Lokshin [95])

4.1.4 Specificities of H_2SO_4 leaching

Enhancement of leaching kinetics with strong oxidants (ozone, hydrogen peroxide) in sulfuric acid has been considered in several works. Alonso [84] evidenced a significant effect of ozone on the dissolution yield of nickel at 25 °C. Rabah [45] reported an improvement of leaching kinetics with 10 vol% H_2O_2 additions. In contrast, most authors did not measure any impact of H_2O_2 (0-7 vol% [46,82,97]) and found it unnecessary for NiMH BM leaching.

As pointed out, a major specificity of H_2SO_4 media is the limited solubility of REEs elements, especially in the presence of K or Na. Meanwhile, the BM usually contains rather high levels of K (Table 3), with typical K/REEs molar ratio of 0.5 or even higher than 1. Therefore, REEs leached from the BM tend to re-precipitate as double REEs sulfates during H_2SO_4 leaching [47,76]. In accordance with the solubility values compiled in Figure 7, several options allow to maximize REEs leaching yield: decrease temperature, decrease H_2SO_4 content and minimize K content by initial washing of BM.

Pietrelli [81,82] showed that, at low temperature (25°C), 93% REEs could be dissolved, but the nickel dissolution was limited to 77%. To overcome this problem, some authors perform sequential dissolution at room temperature to extract most of the nickel while minimizing acid consumption [46,83]. For instance, Liu [83] achieved full Ni dissolution in 4 successive steps, in a weakly concentrated sulfuric acid (0.75 M) at 40 °C. However, this type of technique requires an intermediate filtration step after each dissolution, which increases the number of unit operations of the process and the associated mass losses.

Some authors studied the selective dissolution of nickel compared to the rare earths, in sulfuric acid, by increasing the temperature. For example, Li [78] achieved 95% REEs precipitation and 99% Ni dissolution thanks to leaching in 3 M H_2SO_4 at 95 °C for 4 h. Wu [98] reported similar results and obtained highly concentrated (over 100 g/L) nickel solutions. Innocenzi [39] dissolved only 33% REEs at 83 °C in 2 M H_2SO_4, while Ni dissolution was 90%. Another option envisaged by Porvali [47] consists in selective leaching of Ni thanks to REEs precipitation as double sulfates by Na_2SO_4 addition. As a result, less than 3.5% REEs were dissolved. However, this option requires a subsequent treatment of the solid phase to recover REEs, which are mixed with insoluble residues at the end of the leaching operation.

Preliminary washing of the BM in order to remove K and thus increase REEs solubility has also been considered. Some early works mentioned water washing prior leaching experiments [39,77,78], without providing much details on this operation. Innocenzi [39] indicated that K content in BM decreased from 5 to 0.5 wt% after washing in water, while Zielinski showed that K contained in BM dissolves within a few minutes in mild acid (pH=3) solutions [76]. The recent work of Porvali [38,47] provides additional quantitative data on BM washing, with evidence of quantitative dissolution of Na and K elements but minimal dissolution of other metal elements.

However, Figure 7(a) shows that even if the precipitation of (K, REEs) double sulfates can be limited by the washing of K, the solubility of the compound $La_2SO_4.9H_2O$ is not so much higher and thus BM leaching in H_2SO_4 media will always be limited by REEs sulfates precipitation.

4.1.5 Specificities of HCl leaching

Due to their high solubility, REEs contained in the BM do not form chlorides salts under standard dissolution conditions (S/L < 15% and T = 25-100 °C). However, in order to achieve complete dissolution (> 95%) of REEs and Ni in HCl media, most studies report (Table 4) that it is necessary to work either at 2-4 M HCl at high temperature (70-95 °C) [27,85–87], or at 25-40 °C with high HCl concentrations (8-12 M) [40,88]. These conditions lead to corrosion of industrial equipment, not only because HCl-H_2O solutions are corrosive, but also because HCl becomes volatile as temperature increases. Furthermore, using large initial amounts of acid increases the consumption of alkali solution needed to equilibrate pH for the selective precipitation in the following stages.

Ekberg [25,77] evaluated the selective dissolution of NiMH cathode and anode active materials at mild pH to overcome these industrial challenges. Ni metal dissolution from the cathode material was significantly slowed down when the pH increased from 1 to 3 at 30 °C [25]. On the other hand, $Ni(OH)_2$ from the cathode and the entire anode plates completely dissolved after about 5 h under the same conditions [25]. The authors suggest that the hydrogen adsorption properties on the surface of the metallic nickel are the origin of slow Ni dissolution [77].

With the similar objective of reducing acid concentration, Zielinski [76] studied the dissolution kinetics of BM at mild pH (3, 4, 5.5) for 25 < T < 60 °C. The results indicated a preferential dissolution of REEs towards Ni in any conditions, confirming the slow dissolution kinetics of Ni phases. As at 60 °C and pH = 3 the Ni yield was below 60 % after 22 h of leaching, it was concluded that a lower pH is required to fully leach Ni within reasonable duration.

4.1.6 Conclusions and typical leach liquors composition

Considering the data compiled in Table 4 and the solubility of Ni and REEs salts (Figure 7), the dissolution of the BM powder in HCl leads to the best yields in terms of REEs and Ni dissolution. However, aggressive operating conditions are required, increasing the economic costs (corrosion of the equipment, high amounts of alkali solution for the downstream precipitation step). The use of HCl at moderate pH has the advantage of reducing acid consumption but the rate of nickel dissolution is much reduced due to kinetics limitations. On the other hand, the use of H_2SO_4 at room temperature can bring good yields but requires to proceed by sequential dissolution steps. By increasing the leaching temperature, the dissolution of nickel by H_2SO_4 is favored but the REEs are less soluble and form double sulfate salts whose amount can be reduced by preliminary washing of BM. Both options increase the number of unit operations of the process. It is finally interesting to note that, in a recent work from Takano [32] implementing a 500 L scale leaching reactor, the authors discarded hydrochloric acid due to its corrosive properties and nitric acid due to the need of effluent denitrification, and thus selected H_2SO_4 as industrial leaching media.

Furthermore, the preliminary thermal treatment modifies the nature of the phases composing the BM, which has direct consequences on the leaching stage. The interest of this head-end step, apart from inerting the active materials, could be to convert the various Ni-Co phases either into metal (reductive conditions) or into oxides (oxidative conditions). However, it is not really clear at this point which way should be preferred, since some works indicate that the acid dissolution of BM is kinetically limited by nickel oxides phases [32], while others attribute it to adsorption phenomenon on metallic nickel [77].

The metal contents of several leach liquors is compiled in Table 5. As the composition of the various BM materials and the leaching processes are not homogeneous, the metal concentrations in leach solutions can also strongly vary. In relation to their overall solubility, the Ni and REEs concentrations in HCl leach liquors reported in Table 5 are generally higher than in H_2SO_4 ones.

The extraction of these metal from the PLS is developed in the following sections, according to each type of unit operation.

Table 5 – Examples of NiMH leach liquor composition ($g.L^{-1}$)

Type of powder	Metal concentration, g/L										Ref.
	Ni	Co	Fe	Zn	Al	Mn	La	Ce	Pr	Nd	
HCl leaching											
Mixed	23.4	1.7	3.4	0.7	0.4	1.2	4.2	0.3	0.8	2.6	[86]
	39.6	4.7	4.4	1.0	*ns*	1.9	18.0	*ns*	*ns*	*ns*	[40]
	ns	5.7	2.8	0.99	1.1	2.2	6.4	6.2	*na*	2.5	[85]
Cathode	89.0	19.0	0.4	1.0	0.3	0.2	0.2	0.03	0.2	0.2	
Anode	75.0	10.0	0.05	0.2	3.0	6.0	35.0	13.0	5.0	4	[77]
Mixed	69.0	12.0	0.3	0.5	1.9	6.0	21.0	8.2	3.0	3.0	
H_2SO_4 leaching											
Mixed	10.6	0.8	1.7	0.4	0.2	0.5	1.7	0.1	0.3	1.1	[79]
	103	10.7	0.8	2.7	*na*	4.9		2.8			
	22.3	2.4	0.05	0.8	*ns*	1.2	2.1	3	0.6	0.8	[80,99]
	41.5	5.9	1.1	1.4	1.0	2.8	8.0	*na*	*na*	*na*	[100]
	46.1	6.3	1.4	2.1	1.4	3.7	9.7	7.5	1.4	-	[38]
	25.2	5.0	0.1	1.1	0.4	0.7	5.5	3.0	0.2	0.9	[34]
	11.3	2.3	0.1	0.3	0.3	0.8	1.5	0.9	*na*	0.8	[101]
	53.0	4.4	1.6	1.8	*na*	2.5	1.7	2.2	2.1	4.3	[44]
	52.3	4.6	2.3	0.5	1.6	3.1	11.2	4.0	0.7	1.3	[102]
	50.0	4.9-5.5	*na*	*na*	*na*	*na*	10-14	5-7.3	*na*	*na*	[32]

ns: not specified
na: not analyzed

4.2 Selective precipitation

Selective precipitation operations consist in adding one or several reactants into the PLS in order to recover a solid product containing one of the valuable elements (Ni, Co, REEs) or to separate some impurities (Fe, Al). Figure 8 presents thermodynamic calculations based on a model PLS solution. It shows the effect of pH swing in H_2SO_4 and HCl media, by NaOH addition. The calculations evidence that most metals are expected to precipitate as solid hydroxides with a very high yield (> 99.9%). The overall order of precipitation with increasing pH is in accordance with former calculations at low concentrations (ideal solutions) [103].

The calculations evidence that the behavior of major elements is rather similar in both media, with the major exception of REEs double sulfates that form at low pH, as previously discussed. In relation, many works have focused on the recovery of REEs by selective precipitation. Furthermore, Fe(III) and Al(III) compounds precipitate at intermediate pH in both media (1<pH<6), which provides a way to eliminate these elements from the solution. The last elements

(Ni, Co, Fe(II), Mn, Zn, and REEs in HCl media) precipitate in the same range of pH, which prevents selective precipitation. Consequently, precipitation is often combined with solvent extraction (see section 4.3). Based on these preliminary considerations, this section is divided into four parts, devoted to (i) REEs selective recovery in sulfuric media, (ii) REEs selective recovery in hydrochloric media, (iii) Al-Fe elimination and (iv) Ni-Co recovery.

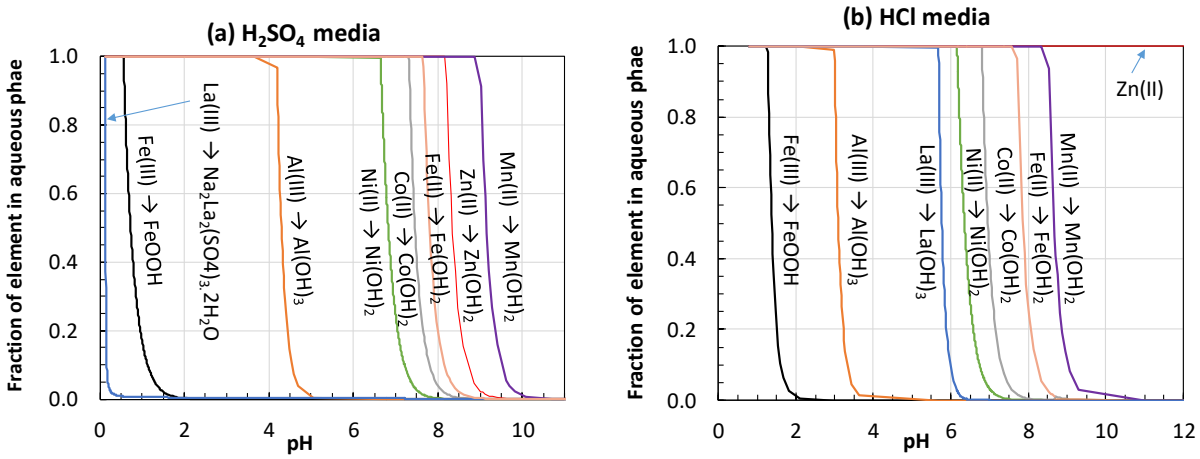


Figure 8 - Simulated precipitation of a model PLS (Ni(II) = 50 g/L ; La(III) = 15 g/L ; Co(II) = 5 g/L ; Al(III) = Fe(III) = Fe(II) = Mn(II) = Zn(II) = 2 g/L) during pH swing by addition of NaOH at 25 °C in (a) H_2SO_4 media (b) HCl media (calculated with OLI-MSE [16,17,94])

4.2.1 REEs precipitation from sulfuric media and further purification

Table 6 compiles the operating conditions and main results obtained for REEs precipitation from NiMH leach liquors. In early work from Bertuol [80], three different types of acid (sulfuric, hydrochloric and nitric) were evaluated to leach NiMH batteries, followed by REEs precipitation by addition of NaOH and KOH. The authors showed that only sulfuric acid was suitable, and that NaOH led to the best recovery yields. In nitric and hydrochloric media, no precipitation reaction occurred for pH < 7, and the resulting precipitate contained mostly Ni. These conclusions are in full accordance with calculations presented in Figure 8 and based on recent thermodynamic models. Many authors have then studied the selective precipitation of REEs. In most works, the pH of the PLS is set to 1.5-2.5 by adding a solution of NaOH [39,44,46,80,81,104] or NaOH-Na_2CO_3 [34,105], which makes possible the selective precipitation of $NaREE(SO_4)_2.H_2O$ salts according to Eq. 7. Several authors showed that the best selectivity is achieved at low pH [34,80,81,96,104]. However, the reported contamination by other metal elements (Ni, Co, Fe, Al) strongly differs between the studies, maybe due to different washing procedures.

Recently, Porvali [38,47] showed that such precipitation reaction does not depend so much on the pH but rather on the concentration of Na^+ and SO_4^{2-}. They achieved REEs precipitation by adding $Na_2SO_{4(aq)}$ to increase the Na/REE and SO_4/REE molar ratios without increasing the pH, which limits the co-precipitation of impurities as hydroxides. The REEs precipitate in a congruent way and form either a mixture of double sulfates monohydrate or a solid solution [47]. These results were confirmed by Zielinski [102], who showed that the composition of the REEs precipitate was almost constant for 25 < T < 60 °C and 0.8:1 < Na/REEs molar ratio < 3.2:1, while excellent REEs recovery yield were obtained at 60 °C. Takano [32] implemented this method at pilot scale (300 L) and report excellent La and Ce recovery yields at 80 °C. These authors also focused on Y recovery, which was otherwise barely studied due to its very low content in NiMH batteries (0.8 wt% in [32]), and showed that lower recovery yields (< 70%) were obtained due to a higher

solubility of the $Y_2La_2(SO_4)_4.2H_2O$ compound [17]. Korkmaz [27] also reported that Y does not precipitate in similar conditions.

It can also be noted from Table 6 that there is no study reporting the use of oxalic acid to recover REEs from sulfuric PLS, while it is commonly used in HCl media (see section 4.2.2). As shown by Zhang [106] based on thermodynamic calculations, this is likely caused by the co-precipitation of Fe and Al elements leading to poor selectivity.

Korkmaz [107] report an alternative technique to obtain REEs precipitates from sulfuric media, by application of antisolvent precipitation. The idea is to create supersaturation condition by adding a water-miscible organic solvent and thus decrease water activity. They showed that the addition of 2-propanol to a PLS allowed to recover about 80% of REEs with a purity of 99.99%. The solid product ($REEs_2(SO_4)_3.xH_2O$) has the noticeable advantage that it does not contain Na as in the other method, but the disadvantage of higher solubility (Figure 7(a)) which reduces the overall REEs recovery yield.

Another method for REEs separation by selective precipitation has been investigated by Zhi [108]) by the means of phosphate-based compounds, and especially dibenzyl phosphate (DBP). The method is close to solvent extraction in its principle, however, neither organic solvents nor saponification agents are required. The precipitation reaction is described by *Eq. 8*:

$$REE^{3+}_{(aq)} + 3\,HL_{(aq)} = REEL_{3(s)} + 3\,H^{+}_{(aq)} \qquad \textit{Eq. 8}$$

where HL is the acidic form of DBP

Table 6 – Overview of operating parameters and recovery yields obtained for REEs precipitation from NiMH leach liquors

Reactant/ Product	Conditions	Extraction yields and purity	Ref.
	H_2SO_4 media		
NaOH / $NaREE(SO_4)_2.H_2O$	NaOH addition until pH = 1.5 Room temperature	REEs yield ≈ 80% of REEs Impurities: Ni 1.7 wt%, Co 3.0 wt%, Mn 0.3 wt%, Zn 0.7 wt%, Fe 6.9 wt%	[81]
	Precipitation at pH 0.8-1.6 with 5 M NaOH Room temperature	REEs yield > 98% Impurities: Ni 3 wt%, K 2 wt%	[80]
	Precipitation at pH 1.2 with 5 M NaOH Room temperature	REEs yield > 98% Impurities recovery yield: Ni 1.8%, Fe 9.9%, Co 3.3%, Zn 5.9%	[99]
	Adjustment of pH to 2.0 with 5 M NaOH Room temperature	REEs yield ≈ 99% Purity ~ 90% Impurities: Al 3 wt%, Mn 3 wt%	[39]
	Adjustment of pH to 1.8 with 3 M NaOH	Not specified	[44]
	Adjustment of pH to 2.5 with NaOH Room temperature	REEs yield ≈ 50 %	[46]
	Adjustment of pH to 0 with NaOH Room temperature	REEs yield > 99 % No precipitation of Y	[27]
	Adjustment of pH to 1.8 with 10 M NaOH Room temperature	REEs yield = 97% Impurities: Co and Ni ~0.01%	[104,109]
$NaOH + Na_2CO_3$ / $NaREE(SO_4)_2.H_2O$	Adjustment of pH to 1.5-1.7 with 6.5 wt% NaOH + 3.5 wt% Na_2CO_3 (oxidation of Fe^{2+} to Fe^{3+} by H_2O_2) Room temperature	REEs yield 94% Impurities: Fe 9 wt%, Mn 11 wt%	[34,105]

$NaOH + H_2O_2$ / $REE_2(SO_4)_3$	Adjustment of pH to 1.5 with solid NaOH T = 80 °C	Not specified	[110]
	Addition of 18 M H_2SO_4 and 2 M Na_2SO_4 with SO_4/REEs up to 50 mol/mol and Na/REEs up to 10 mol/mol 30 °C < T < 60 °C	REEs yields: La > 98%, Ce > 99%, Pr > 99% purity > 98%	[38,47]
Na_2SO_4 / $NaREE(SO_4)_2.H_2O$	Precipitation at pH ~ 1.5 with 2.9 M Na_2SO_4 with Na/REEs = 0.8 to 3.2 mol/mol 25 °C < T < 60 °C	REEs yield: 99.2% at 60 °C Impurities: ~ 5 wt% Ni, 5 wt% Na, 1.5 wt% Al	[102]
	Addition of 40-180 g/L Na_2SO_4 40 °C < T < 80 °C	REEs yields: La 99.9%, Ce 99.9%, Y 98.7% Impurities: Ni and Co < 0.05%	[32]
	Pilot scale tests (300 L) with 90 g/L Na_2SO_4 T = 80 °C	REEs yields: La 99.7%, Ce 99.7%, Y 41-72% Impurities: Ni and Co < 0.04%	
KOH / ns	Precipitation at pH 1.2 with 5 M KOH Room temperature	REEs yield > 98% Impurities: 3.2 wt% Ni, 0.7 wt% K	[80]
Alcohols (antisolvent) / $REE_2(SO_4)_3.xH_2O$	Addition of 7.55 M ethanol with organic/aqueous volumetric ratio of 0.56 T = -10 or +25 °C	REEs yield 86.5% Purity 99.9%	[107]
	Addition of 5.64 M 2-propanol with organic/aqueous volumetric ratio of 0.7 T = -10 or +25 °C	REEs yield 82% Purity 99.9%	
Dibenzyl phosphate (DPB) / $REEL_3$	Addition of solid DBP with DBP/REEs molar ratio of 6, at pH 4.5 Room temperature	REEs yield > 97.8% Purity (after redissolution in HCl) 99.85%	[108]
HCl media			
$NaOH + Na_2SO_4$ / $REE_2(SO_4)_3.xH_2O$	Adjustment of pH to 3 with NaOH Addition of Na_2SO_4 150 g/L Room temperature	Impurities: 0.15 wt% Ni, <0.1 wt% Co, 0.46 wt% Fe	[111]
$H_2C_2O_4$ / $REE_2(C_2O_4)_3.xH_2O$	Adjustment of pH to 0.4–0.6 with NaOH Addition of $H_2C_2O_4$ Room temperature	REEs yield 95.2% Purity 99%	[87]
	Addition of $H_2C_2O_4$ solution into a leach liquor prepared with 4M HCl Room temperature	REEs yield 95% for 3:1 oxalate:REEs ratio Purity 90%	[27]
$(NH_4)_2C_2O_4$ / $REE_2(C_2O_4)_3.xH_2O$	Adjustment of pH to 0.5 with 6M NaOH; Addition of 0.3M $(NH_4)_2C_2O_4$ T = 60 °C	REEs yield 98.5%	[40]
$H_2C_2O_4$ to HCl strip liquor / $REE_2(C_2O_4)_3.xH_2O$	Adjustment of pH to 0.7; T = 25 °C	REEs yield 99% Impurities: 0.07 wt% Co, 0.02 wt% Mn, 0.61 wt% Al	[83]
	Adjustment of pH to 1.5; T = 70 °C	REEs yield > 99.9% Impurities: 0.01 wt.% Fe and Mg	[112]
	Adjustment of pH to 2-3 with NH_3 solution; Addition of $H_2C_2O_4$ saturated solution with $H_2C_2O_4$/REEs = 2 mol/mol	REEs yield 99% Impurities: Co, Mn, Zn, < 0.01%, 0.05% Fe, 0.6% Al	[79,86]

Up to now, the precipitation of REEs double sulfate salts has been the most used (Table 6) thanks to the extreme efficiency and selectivity of this technique. However, the obtained products need to be further processed to remove Na and S elements and produce a mixture of pure REEs compounds. In this objective, a few works report the conversion of the REEs double sulfates into mixed hydroxide or carbonate compounds. Wu *[98]* prepared hydroxides by alkalinization (Eq. 9), followed by redissolution into a HCl solution and crystallization of $REEsCl_3$ compounds. Ahn

[104] report the conversion of the salts into carbonates according to (Eq. 10). They finally obtained a mixture of pure REEs oxides by subsequent thermal decomposition at 800 °C *[109]*.

$$NaREE(SO_4)_2.H_2O_{(s)} + 3\,NaOH_{(aq)} = REE(OH)_{3(s)} + 2\,Na_2SO_{4(aq)} + H_2O \qquad Eq.\ 9$$

$$2\,NaREE(SO_4)_2.H_2O_{(s)} + 3\,Na_2CO_{3(aq)} + (x-1)\,H_2O = REE_2(CO_3)_3.xH_2O_{(s)} + 4\,Na_2SO_{4(aq)} \qquad Eq.\ 10$$

Even if treatments based on solvent extraction methods and aiming at producing separate fluxes of individual REE have been developed for the recycling of permanent magnets or lamp phosphors [10], not much has been reported in relation with NiMH batteries. An alternative to solvent extraction is to separate Ce at tetravalent state from other trivalent REEs such as investigated by Porvali [100], who adapted separation routes established for primary Ce production from minerals such as monazite [113,114]. The three steps process consists of (i) a conversion of the double sulfates salts into REEs hydroxides in NaOH media according to (Eq. 9), (ii) a subsequent conversion of $Ce(OH)_3$ into $Ce(OH)_4$ by air oxidation and (iii) a selective dissolution of trivalent REEs by HNO_3 additions which leaves a pure $Ce(OH)_4$ product. The method relies on the fact that solid $Ce(OH)_4$ hydroxide is insoluble at pH>2 conversely to trivalent REE hydroxides that dissolve at pH<6. However, the authors report that the high sulfur level contained in $Ce(OH)_4$ is problematic for the subsequent recovery of the precipitate [100].

4.2.2 REEs precipitation from hydrochloric solutions

Less studies were dedicated to REEs recovery from HCl media (Table 6). Several works are based on REEs oxalate precipitation according to (Eq. 11):

$$2\,REE^{3+}_{(aq)} + 3\,C_2O^{2-}_{4(aq)} + x\,H_2O = REE_2(C_2O_4)_3.xH_2O_{(s)} \qquad Eq.\ 11$$

Yang [115] studied REEs precipitation from PLS obtained by HCl leaching by adding an oxalic acid solution at pH ~ 0.5. A subsequent purification method based on ammonia complexation of divalent metals was required, which brought a final product containing 99% pure rare earth oxides. Korkmaz [27] confirmed that a good recovery yield of REEs could be achieved by direct addition of oxalic acid into the PLS, but they reported Ni co-precipitation. Fernandes [40] evaluated the selectivity of REEs oxalate precipitation from a hydrochloric PLS and showed that the pH needs to be carefully monitored in order to maximize REE recovery while avoiding Ni and Mn co-precipitation, with a best compromise at pH = 0.5.

Several authors performed solvent extraction of REEs from leach liquor (see section 4.3.2), and subsequent precipitation of oxalate REEs compounds from an HCl strip liquor. Zhang [86] report that REEs were selectively precipitated by pH adjustment at 2-3 with a concentrated ammonia solution followed by the addition of $H_2C_2O_4$ solution, while the strip solution still contained Zn, Mn, Al, and Fe. The final product contained 99.9% of REOs after calcination. These results may seem rather contradictory compared to Fernandes' study [40], who obtained quantitative Mn co-precipitation at pH = 2 and recommended a lower pH to achieve acceptable selectivity. This could be linked to a concentration effect, since Mn concentration was about 2 g/L in [40] while it was only 0.3 g/L in [86]. Based on a similar route, Liu [83] obtained 99% pure REEs oxides at pH=0.5, and Xia [112] reports a good selectivity versus Fe at pH=1.5.

4.2.3 Precipitation of metals impurities (Fe, Al, Zn)

As illustrated in Figure 8, the pH of precipitation of Fe(III) and Al(III) (pH<5) is quite distinct from that of divalent hydroxides (pH>7). After REEs removal, a selective precipitation of these

trivalent impurities is thus expected by a pH increase. Although iron purification has been mentioned in a few works [44,80,81,105], not many studies have effectively quantified its selectivity. Nan [34] report the removal of 99% of Fe from a PLS containing 0.13 g/L of Fe. They performed oxidation of Fe(II) to Fe(III) by addition of H_2O_2 at pH<2 followed by pH increase to 5.8 by NaOH additions. Bertuol [80,99] also implemented a purification step by NaOH additions that resulted in precipitation of 100% Fe at pH=6 (with initial Fe concentration of 0.05 g/L), while the co-precipitation of Ni and Co was only about 2% and 6% respectively. The authors also mentioned that, during this operation, Zn partly precipitated (24%), while Mn did not.

As for Al elimination, which has similar concentration than Fe in the PLS (typically 0.1-1.5 g/L, see Table 5), no specific data have been published. However grouped Al-Fe precipitation is commonly performed in LiBs leachates (e.g. [116]). Regarding Zn, Innocenzi [117] demonstrated that selective precipitation could not be achieved by pH swing in solutions containing high amounts of Zn (10 g/L versus 36 g/L of Ni). Consistently with the calculations (Figure 8), precipitations implemented at pH values of 5 and 7 led to large co-precipitation of Ni.

In summary, Fe and Al elements can be removed by selective precipitation (if Fe is in the trivalent state), while Zn cannot.

4.2.4 Precipitation of nickel, cobalt and manganese

Table 7 summarizes the main reactions reported to recover nickel and cobalt products by precipitation. In comparison with the studies devoted to REEs (Table 6), it is interesting to note that less academic works concern Ni, while it is the most concentrated and valuable elements in NiMH batteries. Several reasons may account for this, among which the existing knowledge related to $Ni(OH)_2$ particles synthesis for NiMH battery manufacturing, but also the reduced difficulty in term of selectivity since REEs and Al-Fe impurities can be removed in prior steps.

In chloride media, several works report the precipitation of Ni or Co oxalates from strip solutions after solvent extraction by addition of ammonium oxalate at pH=2 [40,86], according to (*Eq. 12*).

$$Ni^{2+}_{(aq)} + C_2O^{2-}_{4(aq)} = NiC_2O_{4(s)} \qquad \textit{Eq. 12}$$

The method is reported to be efficient without specific difficulty, mostly because no selectivity is required.

Conversely, in sulfuric PLS, one of the main difficulty related to Ni hydroxide precipitation is that the precipitates obtained by NaOH addition (*Eq. 13*) are amorphous and porous due to the preferential precipitation of the amorphous polymorph α-$Ni(OH)_2$, which raises difficulties for filtration and lead to poor product quality [118]. As reviewed by Hall [119], the loose lamellar structure of this compound leads to large hydration and inclusion of ions such as SO_4^{2-}. An option consists in adding aqueous ammonia in the solution, which leads to precipitation of spherical and dense $Ni(OH)_2$ particles. This is attributed to the formation of nickel ammine complexes that lower the activity of Ni ions and slow down the precipitation reaction with hydroxide ions (*Eq. 14*).

$$Ni^{2+}_{(aq)} + 2\,OH^{-}_{(aq)} = Ni(OH)_{2(s,\alpha)} \qquad \textit{Eq. 13}$$

$$Ni(NH_3)^{2+}_{6(aq)} + 2\,OH^{-}_{(aq)} = Ni(OH)_{2(s,\beta)} + 6\,NH_{3(aq)} \qquad \textit{Eq. 14}$$

Consequently, in the late 2000s, several authors [34,78,120] used stoichiometric ammonia addition in sulfuric PLS to prepare $Ni(OH)_2$ precursors for battery manufacturing. Nan [34] precipitated $Ni(OH)_2$ particles at 50 °C and pH 10.7 by adding a ($NaOH + NH_{3(aq)}$) solution to a sulfuric PLS. Similarly Li [78] synthesized spherical $Ni(OH)_2$ at pH 11 and 60 °C and report low level of

impurities. Kanamori [121] also used the complexation properties of ammonium in order to selectively extract Ni from a mixture of La, Co and Ni hydroxydes and further recovered Ni hydroxide after filtration.

Table 7 – Overview of operating parameters and recovery yields obtained for nickel and cobalt precipitation from NiMH leach liquor

Reactant / Product	Conditions	Extraction yields and purity	Ref.
Sulfate media			
NH_3 + NaOH / $Ni(OH)_2$	Addition of NaOH, $NH_3 \cdot H_2O$ (up to Ni:NH_3 = 0.9 mol/mol) and $Ni(OH)_2$ precursors at pH 10.7-11.0 ; Ni:NH_3 = 0.8-0.9 T = 50 °C	Not mentioned	[34]
	Adjustment of pH to 11 with NaOH into $NiSO_4$ solution NH_3 :Ni ≈ 1 mol/mol T = 60 °C	Yield not mentioned Impurities: 0.9% Co, 1.4% Zn, 0.005% Mn, 0.008% Fe	[78]
Diacetyldioxime / NiO	Not specified Thermal decomposition at 400 °C to obtain NiO	Not mentioned	[45]
Na_2S / NiS, CoS	Addition of Na_2S 200 g/L 2 < pH regulated < 4 T = 25 °C	Yields at pH = 3: Ni 99.8%, Co 99.9%	[32]
NaSH / NiS, CoS	Pilot scale tests (400 L) with NaHS 300 g/L pH = 3.0 Room Temperature	Yields : Ni 98.1% and Co 96.1% Impurities: Y 0.049%, La 0.007%, Ce 0.003%	
Chloride media			
NH_3 + NaOH / $Ni(OH)_2$	5 M NH_3 solution + air bubbling T = 80 °C	Not mentionned	[120]
$(NH_4)_2C_2O_4$ / CoC_2O_4 and NiC_2O_4	Addition of oxalate into Co HCl strip solution at pH = 2 ; Addition of oxalate to the raffinate to recover Ni	Co yield : 98.5% Ni yield : 99.9%	[79,86]
	Adjustment of pH to 2 with 6 M NaOH to a solution free of REEs and Co ; Addition of 0.3M $(NH_4)_2C_2O_4$ T = 60 °C	Ni yield 99.5% Impurities : Co < 1%, Mn < 4%	[40]

Very recently, Takano [32] proposed an alternative way consisting in preparing mixed nickel and cobalt sulfide compounds by precipitation with Na_2S or NaHS according to *Eq. 15* and *Eq. 16*. The authors recommend to increase pH to 3 after selective REEs removal with Na_2SO_4. They performed pilot scale tests with 400 L of PLS containing 14 g/L of Ni and 1.5 g/L of Co and report high recovery yields (>96%). The obtained mixed sulfide can then be use as secondary raw materials in existing nickel refineries.

$$NiSO_{4(aq)} + Na_2S_{(aq)} = NiS_{(s)} + Na_2SO_{4(aq)} \qquad Eq.\ 15$$

$$2\,NiSO_{4(aq)} + 2\,NaHS_{(aq)} = 2\,NiS_{(s)} + Na_2SO_{4(aq)} + H_2SO_{4(aq)} \qquad Eq.\ 16$$

It is interesting to note that, to our knowledge, no trial to separate Ni, Co and Mn by selective precipitation has been reported. The separation of Co, Mn and Ni from mixed hydroxides has for instance been explored by Vaughan and coll. [122,123] by sulfuric acid leaching and selective oxidative precipitation (with $Na_2S_2O_8$ or O_3) in the frame of nickel laterite ores processing. Furthermore, several works related to LiBs processing focused on Ni, Co and Mn separation using strong oxidants (e.g. NaClO [124], $Na_2S_2O_8$ [125], $Ni(OH)_3$ [126]) and careful pH control. These routes, based on the use of an oxidizing agent capable to oxidize Mn^{2+} to Mn^{4+} and Co^{2+} to Co^{3+},

have been barely considered in the case of NiMH batteries. First attempts by Ricknell [127] led to high losses of Ni.

The difficulty for the separation is related to the very close chemical properties of these elements, for which co-precipitation is hardly avoidable. Furthermore, contrarily to LiBs, the PLS have low Co and Mn contents related to Ni (Table 5). Thus, when a precipitation process is selected for Ni recovery from sulfuric PLS, it implies that the product will also contain most of the Co and Mn. Full separation of these elements can be carried out by solvent extraction methods, as detailed in the following section.

4.3 Solvent extraction

Similar to selective precipitation, solvent extraction has been widely studied in order to separate the valuable elements contained in the BM prepared from spent NiMH batteries. A compilation of the various processes is provided in *Table 8*. It shows that the whole panel of available extractants (for which general reactions involved in the separations are described in Eq. 17 to Eq. 19) has been evaluated:

- Acidic extractants (*Eq. 17*): Cyanex 272 (phosphinic acid), D2EHPA (phosphoric acid), PC88A (phosphonic acid), Cyanex 301 (dithiophosphinic acid)
- Alkaline extractants (*Eq. 18*): N1923 (primary amine), Tri-octyl amine and Alamine 336 (tertiary amines), Aliquat 336 (quaternary ammonium salt)
- Solvating agents (*Eq. 19*): Cyanex 923 and TBP
- Ionic liquids: Cyphos 104 and Cyphos 101 (phosphonium salts)

$$M_{(aq)}^{n+} + n\,HA_{(org)} = MA_{n(org)} + n\,H_{(aq)}^{+} \qquad Eq.\ 17$$

$$M_{(aq)}^{n+} + n\,R_3NHCl_{(org)} = M(R_3NH)_{n(org)} + n\,Cl_{(aq)}^{-} \qquad Eq.\ 18$$

$$M_{(aq)}^{n+} + n\,Cl_{(aq)}^{-} + S_{(org)} = SMCl_{n(org)} \qquad Eq.\ 19$$

Table 8 – Overview of solvent extraction methods implemented for NiMH processing

Reagent	Initial solution	Separation	Extraction yields	Ref.
Impurities (Fe, Zn, Al, Mn, Cd) removal				
D2EHPA /P204	NiMH leachate in H_2SO_4 with REEs precipitation during leaching 61 g/L Ni, 5 g/L Co, 0.8 g/L REEs, 1.7 g/L Mn, 2.2 g/L Zn, 0.3 g/L Fe	O: REEs, Fe, Zn, Mn A: Co, Ni	5 stages at pH=1 REE, Mn, Zn, Fe > 99.9% Co 3.5%, Ni 0.1%	[78]
	NiMH leachate in H_2SO_4 with prior precipitation of REEs	O: Cd A: Ni, Co	1 stage at pH = 3.0 Cd 80% Co, Ni < 5% Ni 0%	[46]
	NiMH leachate in H_2SO_4 with prior REEs precipitation	O: Al, Fe, Mn, Zn A: Co, Ni	1 stage at pH = 2.5 Al, Fe, Mn, Zn 75-99% Ni 0%, Co 0.8-4%	[104]
	NiMH leachate in H_2SO_4 with prior REEs precipitation 43 g/L Ni, 6 g/L Co, 3 g/L Mn, 1.2 g/L Fe, 1.4 g/L Zn, 1.0 g/L Al, 0.08 g/L Cd	O: Zn, Fe, Al, Mn, Cd A: Ni, Co	3 stages at pH = 1.5 Zn, Fe, Al > 99% 5 stages at pH = 2.3 Mn, Cd > 99%	[128]
	Synthetic solution in H_2SO_4 15 g/L Ni, 12 g/L Co, 31 g/L Mn	O: Mn A: Ni, Co	1 stage at pH = 4 Mn 98% Co 60% Ni 40%	[48]
	Synthetic solution in H_2SO_4 40 g/L Ni, 20 g/L Mn, 10 g/L Zn	O: Mn, Zn A: Ni	2 stages at pH=2.5 Zn 100% Mn 95%	[117]

	NiMH leachate in H_2SO_4 3.4 g/L Ni, 0.9 g/L REEs, 0.4 g/L Co, 1.6 g/L Fe, 0.1 g/L Mn, 0.1 g/L Zn	O: Fe, Zn, Mn A: REEs, Ni, Co	Ni 20% (high Mn nd Zn load) 1 stage at pH = 0.1 Fe, Zn > 99%, Mn > 97% Ni, Co, REEs < 5%	[129]
TBP	NiMH leachate in HCl (see Table 5)	O: Fe, Zn A: Ni, Co, REEs, Mn	1 stage at pH <0 Fe, Zn 99.9%	[40]
Cyanex 923	NiMH leachate in HCl (see Table 5)	O: Fe, Zn A: Ni, Co, REEs, Mn, Al, K	4 stages at pH = 1 Fe, Zn 99.9% Co 8%	[77,130,131]
		REEs extraction		
Cyanex 272 + Cyphos IL 104	NiMH leachate in H_2SO_4 with prior removal of Fe, Mn, Zn by SX 3.4 g/L Ni, 0.9 g/L REEs, 0.4 g/L Co	O: REEs A: Ni, Co	1 stage at pH = 3.8 REEs>95%, Ni, Co <5%	[129]
	NiMH anode leachate in H_2SO_4 Composition not provided	O: REEs, Al, Mn A: Ni, Co	4 stages REEs > 96%	[83]
	Raffinate in HCl with previous SX step	O: REEs, Mn A: Ni	2 stages at pH = 1 REEs 99.9%	[40]
PC88A /P507	NiMH leachate in H_2SO_4 (see Table 5)	O: REEs, Zn, Mn A: Co, Ni	8 stages at pH = 3.5 REEs, Zn, Mn>99.9% Co 13% Ni < 1%	[98]
	NiMH leachate in H_2SO_4 29 g/L Ni, 5.1 g/L Co, 4 g/L Nd, 12 g/L Ce, 8 g/L La	O: Nd, Ce A: La, Co, Ni	1 stage at pH = 1.5 Nd, Ce 80% La ~ 10% Ni, Co < 5%	[132]
	NiMH leachate in HCl (see Table 5)	O: REEs, Fe, Al, Zn A: Ni, Co, Mn	1 stage at pH = 2.5 REEs 99% Fe 85% Zn: 35% Mn 20% Co, Ni 5%	[85]
D2EHPA	NiMH leachate in HCl (see Table 5)	O: REEs, Al, Fe, Zn, Mn A: Ni, Co	6 stages at pH = 2 REEs, Zn, Al, Fe, Mn > 99.9% Co 13% Ni 0%	[86]
	NiMH leachate in H_2SO_4 (see Table 5)	O: REEs, Al, Fe, Zn, Mn A: Ni, Co	6 stages at pH = 2.6 REEs, Zn, Al, Fe > 99.9% Mn > 98% Co 4.7% Ni 0.8%	[79]
N1923	NiMH leachate in H_2SO_4 26 g/L Ni, 5 g/L REEs, 1.4 g/L Co, 13.7 g/L Fe	O: REEs A: Ni, Co, Fe	5 stages at pH=1.5 REEs 99.8% Ni, Co < 0.1% Fe~5%	[112]
Cyanex 923 + Cyphos IL 101	Raffinate in HCl with previous SX step	O: REEs A: Ni	3 stages REEs > 99.9% Ni < 0.1%	[133]
		Ni-Co separation		
	LiB+ NiMH leach solution in H_2SO_4 with prior precipitation of REEs, Al, Fe		2 stages at pH= 5.1-5.3 97% Co	[105]
	NiMH leachate in H_2SO_4 with prior precipitation of REEs		1 stage at pH = 5.7 Co >95% Ni <5%	[46]
Cyanex 272	Raffinate in H_2SO_4 with previous SX step with 15 g/L Ni, 12 g/L Co	O: Co A: Ni	2 stages at pH = 5.5 Co 100% Ni 10%	[48]
	Raffinate in H_2SO_4 with previous SX step		6 stages at pH = 4.8 Co > 98% Ni < 1%	[79]
	Raffinate in H_2SO_4 with previous SX step		1 stage at pH = 4.7 Co 97% Ni 5%	[104]
	Raffinate in H_2SO_4		2 stages:	[78]

	with previous SX step		Co > 99.9%	
Cyanex 301	NiMH secondary stream in HCl 2.8 g/L Ni, 11.8 g/L Co, 9.3 g/L Mn, 4.4 g/L REEs	O: Co A: Ni, REEs, Mn	3 stages Co: 98%, Ni 26%	[134]
Cyanex 923 + TBP	Raffinate in HCl with previous SX step	O: Co, REEs, Al, Mn A: Ni, K	3 stages at pH = 1 Al, Co, REES, Mn > 99.9% Ni 2%	[77,130,131]
Tri-Octyl Amine	Raffinate in HCl with previous SX step	O: Co A: Ni	2 stages at pH = 0.6 Co 99.7%	[86]
Alamine 336	Raffinate in HCl with previous SX step	O: Co A: Ni, REEs, Mn	2 stages at pH = -2 Co 94%, Ni 3%	[40]
Aliquat 336	NiMH leachate in H_2SO_4	O: Co A: Ni, REEs	Co 90% Ni < 1%	[135]
Cyphos IL 101	Synthetic solution in 8 M HCl 174 g/L Ni, 27 g/L Co, 55 g/L REEs, 7 g/L Mn, 2.2 g/L Fe, 1.3 g/L Zn	O: Co, Fe, Zn, Mn A: Ni, REEs	Distribution ratio > 100 for Co, Fe, Mn, Zn Distribution ratio < 0.1 for Ni and REEs	[133]
Cyphos IL 104	Raffinate in H_2SO_4 with previous SX step	O: Co A: Ni	1 stage at pH 5.4 Co > 95%, Ni < 20%	[129]

A: aqueous phase
O: organic phase

Solvent extraction offers more options than precipitation in terms of selectivity, and, depending on the nature of the extractant, the number of stages and the order in which the elements are separated, many separation routes have been proposed. This section is structured in three parts dedicated to the extraction of impurities, the extraction of REEs and the separation between Co and Ni.

4.3.1 Extraction of metal impurities (Fe, Al, Zn, Mn, Cd)

As evidenced in Table 8, several studies report the use of the acidic extractant D2EHPA to remove the typical metal impurities (Fe, Al, Zn, Mn) according to *Eq. 17*, at 1 < pH < 3 [46,78,104,128]. This extraction method requires the prior removal of REEs by precipitation methods, because they are co-extracted with impurities in these conditions [79,85,86]. Mn extraction requires more extraction stages than Fe, Al, Zn because the selectivity with Co is lower [104,128]. Specifically, Granata [48] and Innocenzi [117] showed the feasibility of Mn extraction with D2EHPA from synthetic solutions with high Mn loads. As for Cd, which has very low content in PLS but exhibits hazardous issues, specific studies have shown that efficient extraction can be achieved with D2EHPA [128,136]. The most detailed study dedicated to this route (i.e. extraction of metal impurities after REEs removal by precipitation) is provided by Agarwal [128]. The authors recommend a 2-steps extraction process using D2EHPA, consisting of 3 stages at pH = 1.5 in order to remove Zn, Fe and Al, followed by 5 stages at pH = 2.3 to remove Mn and Cd. The extraction efficiency is above 99% for all elements, which allows to produce a feed for primary nickel process plants.

Based on different separation routes, several works also report the selective removal (>99.9%) of Fe and Zn from NiMH leachate in HCl as a first step of the process, using solvating agents (TBP, Cyanex 923) [40,77,130,131].

4.3.2 Extraction of REEs

Similar to the extraction of impurities, many works (Table 8) investigated the extraction of REEs from the PLS by using an acidic extractant (Cyanex 272, PC88A, D2EHPA), in the view of leaving purified Ni and Co in the raffinate for further recovery. The typical route is to perform REEs extraction as the first step of PLS treatment. Several authors showed that many stages (6 to 8) are required to achieve a REEs extraction yield above 99.9% [79,83,86,98]. As mentioned in the previous section, in such conditions most metal impurities (Al, Mn, Zn, Fe) are co-extracted with REEs, which calls for further separation steps for recovery of pure REEs. Jha [132] reports the

selective extraction of Ce and Nd with PC88A while La is in the raffinate, which could provide a way to achieve partial separation of REEs.

Due to the poor selectivity of acidic extractants which produce impure REEs fluxes, some authors investigated alkaline extractants [112] and ionic liquids extractants [129,133,137] to enhance REE selective recovery. Specifically, Larson [133] reported, after extraction of Co, Mn, Fe and Zn in a first step, a very selective extraction of REEs by using Cyanex 923 dissolved in the nitrated forms of Cyphos IL101.

4.3.3 Extraction and separation of Ni and Co

Separation of Ni from Co aqueous compounds is a challenge due to their close chemical properties. However, Co(II) has a higher tendency to form stable complexes with ligands, and solvent extraction is thus one of the only method that allows to perform an efficient separation. Accordingly, several works devoted to Ni and Co separation in sulfuric PLS have been carried out by extracting Co with Cyanex 272 (Table 8), at pH around 4.7-5.7. In these studies, the leachates were purified from other metal impurities and REEs in preliminary steps, either by precipitation [46,105] or by solvent extraction [48,78,79,104], in order to obtain pure Co in the organic phase. Especially, it has been shown that Co extraction with Cyanex 272 was not selective over Mn [48,97]. Petranikova [134] recently managed to produce a pure Co solution from a Ni depleted strip solution using Cyanex 301 as an alternative to Cyanex 272.

An alternative way for performing Co extraction is to use amine extractants, which can be effective at much lower pH than organo-phosphorous extractants [40,79,135]. For instance, Fernandes [40] reports efficient extraction of Co with Alamine 336, in a 2 M HCl leachate containing Ni and REEs.

Larsson, Petranikova and coll. [77,130,131] established three detailed flow-charts for metal extraction from cathode-based, anode-based and mixed-material-based leach liquors using mixture of neutral extractants (Cyanex 923 and TBP). In this route, Co was co-extracted in early steps together with REEs and Mn in order to obtain a pure Ni leachate.

Finally, some attempts using ionic liquids (Cyphos IL 101 and 104) have been reported, which offer the opportunity to extract Co, Mn, Fe and Zn directly from the 8 M HCl leachate, while leaving REEs and Ni in the aqueous phase [133].

4.3.4 Alternative extraction systems

Although solvent extraction offers many options in the view of element separation, this technique has not been scaled up for battery recycling yet, notably because of the high amount of chemicals (mineral and organic solvents, extractants), the number of stages and operations required for this process. It can be mentioned that several groups have very recently investigated alternative extraction methods, based on aqueous two-phase systems, to process NiMH leachates without large use of organic solvents. Polypropylene glycol-425 [138] and pluronic triblock copolymers [139,140] were investigated for Fe/Ni, Co/Ni and even full Co/Ni/La/Ce separations. Furthermore, adsorption and ion exchange methods, which are commonly used for Ni and REEs extraction or pre-concentrations from primary and secondary sources [141,142], have been considered as an alternative to solvent extraction for both Ni and REEs recovery from NiMH batteries leachates. The main potential advantage put forward by the authors is to avoid the consumption of large quantities of solvents. As summarized in Table 9, four types of systems have been considered so far: two commercial resins (Purolite and Diphonix) [67,72,143], an activated charcoal [55] and a

layered double hydroxide [144]. These studies mainly consist in preliminary evaluations, with low concentrated solutions (e.g. 0.4-2.7 g/L of Ni).

Table 9 – Summary of metal separation studies based on ion exchangers for NiMH leach liquors treatment

System / Functional groups	Media	Metal elements concentration	Main results	Ref.
Layered double hydroxydes / hydroxides	HCl leachate of REEs hydroxides prepared by NaOH precipitation of PLS pH = 1	1.35 g/L La, 0.9 g/L Nd	Efficient separation (98:1) of La and Nd (products: $LaCl_3$ and Nd_2O_3)	[144]
Purolite S957 resin / phosphonic and sulfonic Diphonix resin / diphosphonic, sulfonic and carboxylic Diphonix / diphosphonic, sulfonic and carboxylic Purolite S957 / phosphonic and sulfonic	Synthetic solution in citric acid, pH = 5	0.6 g/L of Ni and La	Efficient adsorption (almost 100%) of Ni and La	[67]
	Synthetic solution in nitric acid 0.2 and 2.0 M	Ni 2.7 g/L, Co 0.3 g/L, La 0.7 g/L, Ce 0.1 g/L, Fe 1.1 g/L, Zn 0.09 g/L	Efficient adsorption (almost 100%) of REEs and Fe Lower adsorption (50-60%) for divalent metals Ni, Co, Zn	[72] [143]
LIX-841 activated charcoal / oxime	Cathode leachate in nitric acid, pH = 5	Ni 0.4 g/L, Co 0.04 g/L, Zn 0.002 g/L	Efficient adsorption (almost 100%) of Ni Lower adsorption (4-10%) of Co, Zn, Cd	[145]

4.4 Electrowinning of Ni and Co

4.4.1 Principles of industrial electrowinning

Nickel electrowinning from pure sulfuric or hydrochloric leach liquors is implemented at industrial scale in primary nickel metal production and accounts for about half of the total world production [126]. The metal formation at the cathode occurs according to *Eq. 20*, with concurrent H^+ reduction according to *Eq. 21*.

$$Ni^{2+}_{(aq)} + 2\,e^- = Ni_{(s)} \qquad \textit{Eq. 20}$$

$$H^+_{(aq)} + 2\,e^- = H_{2(g)} \qquad \textit{Eq. 21}$$

In sulfuric media, the anode reaction is the decomposition of water (*Eq. 22*), which implies the production of large amount of acid that is re-used for leaching processes. In hydrochloric media, the anodic reaction generates chlorine gas (*Eq. 23*) that is captured and also used for leaching operations [126]. Similar reactions and processes exist for Co electrowinning [146].

$$2\,H_2O = O_{2(g)} + 4\,H^+_{(aq)} + 2\,e^- \qquad \textit{Eq. 22}$$

$$2\,Cl^-_{(aq)} = Cl_{2(g)} + 2\,e^- \qquad \textit{Eq. 23}$$

The addition of boric acid (H_3BO_3) avoids pH increase near the cathode (preventing the formation of nickel hydroxide) and reduces the overpotential of the Ni deposition [147]. Electrochemical cells require a separating membrane in order to avoid a strong acidification near to the cathode, which would promote H^+ reduction (*Eq. 21*) over Ni^{2+} (*Eq. 20*) and thus decrease the current efficiency.

Figure 9 indicates the reduction potentials of the most concentrated metal elements in PLS. Due to their extremely low reduction potentials, deposition of metallic REEs or Al is not achievable in aqueous media and requires alternative solvents such as molten salts [148,149]. However, some transition metals contained in the PLS (Co, Fe and Zn) have reduction potentials close to Ni and may lead to co-deposition with Ni. This is why primary Ni electrowinning is carried out in purified electrolytes in which other metal elements (and specifically Co) have been previously removed by solvent extraction methods [126].

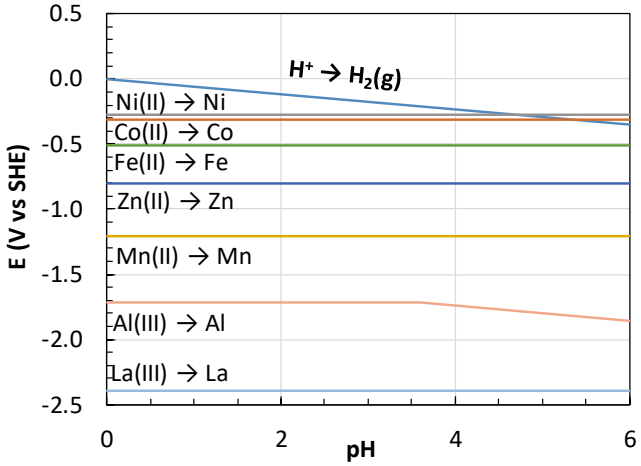


Figure 9 - Reduction potential of the main elements contained in NiMH leach liquor (calculated with OLI-MSE [16,17,94])

4.4.2 Electrowinning of NiMH leachates

Table 10 gathers an overview of electrochemical studies focused on Ni-Co electrowinning involving NiMH leachates as starting solutions. Based on the existing industrial processes, most works implemented boric acid additions (20-30 g/L), a pH around 4, and used a membrane in order to separate the cell compartments [99,150–154]. Most authors prepared synthetic Ni-Co solutions to determine optimal conditions, and obtained dense deposits with high current efficiencies (> 85%). Due to the close reduction potentials of Ni and Co (Figure 9), the co-deposition of Ni and Co is reported in all studies. Lupi [154] showed that, for a large range of Ni/Co concentration ratio in the electrolyte, good quality Ni-Co alloys can be obtained by electrowinning.

Table 10 – Overview of electrochemical studies and operating parameters for nickel and cobalt electrodeposition from NiMH leach liquors

Electrolyte composition	Electrochemical cell	Conditions	Deposit composition	Ref.
Sulfuric acid				
1 g/L Ni, 3-5 g/L Co	Anode: Ti Cathode: stainless steel Membrane: Ionac 7500	Room temp. pH = 7 Potentiostatic	Not specified	[84]
40 g/L Ni, 0.1-16 g/L Co + 20 g/L H_3BO_4	Anode: Pb-Sb Cathode: Al Membrane: Polypropylene or Anionic	T = 60 °C pH = 4 CD 250 A/m^2	Various compositions depending on the initial electrolyte composition	[154]
22 g/L Ni, 2.4 g/L Co, 1.2 g/L Mn, 0.5 g/L Zn + 30 g/L H_3BO_4	Anode: Ti coated by Pt/Ir Cathode: stainless steel Membrane: Anionic PCAcid 60	T = 50 °C pH = 4 CD 250 A/m^2	74 wt% Ni, 18 wt% Co, 6 wt% Zn, 2 wt% Mn	[99]
0.3 g/L Ni, 0.1 g/L Co, 0.02 g/L Mn, 0.1 g/L Zn + 25 g/L H_3BO_4 + 34 g/L $SO_3N_2H_6$	Anode : Pt Cathode : Al	Room temp. pH = 1.5 Potentiostatic	Ni, Co, Mn	[151]

70 g/L Ni, 7 g/L Co, 1 g/L Mn + 20 g/L H_3BO_4	Anode: Pb-Sb Cathode: stainless steel Membrane: Polypropylene	T = 50 °C pH = 4.3 CD 250 A/m^2	60 wt% Ni, 40 wt% Co	[150]
14 g/L Ni, 0.8 g/L Co, 0.2 g/L Mn, 0.8 g/L Zn + 6 g/L H_3BO_4 + 23 g/L $SO_3N_2H_6$	Anode : Au Cathode: Au-coated	Room temp. pH = 3 Potentiostatic	90-95 wt% Ni, 2-4 wt% Co, 2-5 wt% Zn, 0-3 wt% Mn	[152]
Hydrochloric acid				
Synthetic solutions and solution issued from HCl leaching and REEs solvent extraction: 5.5 g/L Ni, 0.6 g/L Co, 0.2 g/L Mn, 0.4 g/L Fe, 0.7 g/L Zn + 0.15 g/L H_3BO_4 + 142 g/L $NaSO_4$	Anode: Ti coated by Pt Cathode: stainless steel Membrane: Nafion 117	Room temp. pH = 3 CD 10-100 A/m^2	10 A/m^2 : 83 wt% Ni, 14 wt% Co, 1 wt% Al, 1 wt% Fe 100 A/m^2 : 82 wt% Ni, 11 wt% Co, 1 wt% Al, 1 wt% Fe, 3 wt% Mn	[153]
Citric acid				
6.9 g/L Ni, 0.3 g/L Co, 0.2 g/L Mn, 0.3 g/L Zn	Anode: graphite Cathode: Cu	T = 50 °C pH = 1.85 Potentiostatic	82 wt% Ni, 11 wt% Zn, 6 wt% Co	[69]

CD: Current Density

However, several authors report that the presence of additional elements in the electrolyte, coming from the NiMH batteries, was highly detrimental to the electrowinning process[99,153]. For instance, Bertuol [99] obtained powdery deposits attributed to the presence of Zn in the electrolyte. Tzanetakis [153] showed that low current densities (10 A/cm^2) were required to obtain well crystallized metallic phases, due to the inclusion of oxide or hydroxide impurities at higher current densities. Several electrochemical studies confirmed that the presence of Zn^{2+} [152,155] or Na^+ [155] in the electrolyte decreased current efficiencies. Tzanetakis [153] reports low Fe contents (about 1 wt%) in the deposits, while the initial proportion is about 5 wt% in the electrolyte. Conversely, it was shown that the presence of Mn in the electrolyte does not interfere with Ni and Co electrodeposition [99,150], which is consistent with its low reduction potential (Figure 9).

To conclude, direct transfer of the industrial Ni electrowinning processes to NiMH leachates is not straightforward, mostly because metal impurities (especially Zn) modify the cathodic reactions. No work has yet reported satisfying quality of Ni alloys obtained by electrowinning.

5. Conclusion

In the present paper, it was first shown that NiMH batteries have high REEs and nickel contents, and much less cobalt, graphite and lithium than LiBs. This induces specificities in the reprocessing operations, and in particular, the recovery of REEs needs to be considered, while the separation between Ni and Co, which is complex due to close chemical properties and low cobalt content, is not compulsory. The in-depth review of unit operations allows to draw a comparative summary of the main operations and to propose potential research directions for NiMH recycling processes, compiled in Table 11.

Table 11 – Comparative summary of main operations and potential research directions for NiMH recycling processes

Type of operation	Advantages	Drawbacks	Potential research directions
Pyrometallurgical methods			
Carbothermic reduction at high temperature	• Simplicity of operation • Large volumes	• Carbon consumption & CO_2 release • Low purities of products	• Alternative carbon sources or hydrogen usage

			• Improvement of slag composition
Leaching in acidic media			
Leaching in HCl	• High solubility of BM phases • Adapted for further solvent extraction methods	• Corrosive properties of HCl • Low dissolution kinetics of Ni compounds • Not compatible with selective precipitation	• Improvement of Ni leaching kinetics: initial thermal treatment, use of oxidant
Leaching in H_2SO_4	• High chemical stability and low cost of the acid • Adpated for further selective precipitation methods	• Limited solubility of REEs compounds • Low dissolution kinetics of Ni compounds	
Leaching in organic acids	• Lower environmental footprint	• Limited knowledge on solution and solid chemistry	• Development of knowledge on solution and solid chemistry
Selective precipitation from H_2SO_4 PLS			
REEs selective precipitation	• Efficient and robust	• Requires further treatment of REEs double sulfate salts	• Improvement of methods for conversion of salts into pure REEs products
Removal of impurities (Fe, Al, Zn, Cd, Mn)	• Efficient removal of Fe (and probably Al) by pH swing	• No removal of Zn and Mn	• Evaluation of Cd behavior • Selective removal of Mn by oxidative treatment
$Ni(OH)_2$ precipitation using ammonia	• Efficient • Good control of product properties	• Constraint with ammonia use • No Co-Ni separation	• Evaluation of selectivity on industrial PLS
NiS precipitation with Na_2S/NaHS	• Efficient	• Product needs to be included in primary Ni refineries • No Co-Ni separation	• Assessment of impurities behaviour
Solvent extraction from H_2SO_4 or HCl PLS			
Removal of impurities (Fe, Al, Zn, Cd, Mn) with DEHPA after REEs selective precipitation	• Removal of all impurities • Efficient to produce clean Ni-Co solution	• Many stages required	• Combination of solvent extraction and selective precipitation
Extraction of REEs and impurities by acidic extractant	• Efficient to produce clean Ni-Co solution	• Many stages required • Low selectivity REEs vs impurities: not adapted for selective REEs recovery	
Selective recovery of REEs by alkaline or ionic liquid extractants	• Efficient	• Requires very acidic media (HCl 8M) • Complex flowsheet	• Evaluation of solvent cost and losses
Co-Ni separation	• Efficient production of Co and Ni solutions	• Requires very acidic media (HCl 8M) • Complex flowsheet	• XX • Assess economical interest in relation with low Co content
Electrodeposition of Ni & Co			
Ni-Co co-deposition from HCl or H_2SO_4 media	• Already implemented for primary Ni and Co production	• Require a pure solution (especially free of Zn) • No Co-Ni separation	• Demonstration that good quality Co-Ni deposits can be obtained from a Zn-free PLS

Among the key learnings based on scientific literature, it comes that pyrochemical methods allow to prepare low purity Ni-Co alloys while rare earth elements are dissolved in the slags. The recovery of the rare earths from the slags requires more investigation in order to design chemical systems allowing high rare earths load and an easier extraction by hydrochemical methods. As for hydrometallurgical methods, one of the most promising routes may consist in battery leaching in sulfuric acid, followed by selective precipitation of rare earths compounds. Then, extraction of impurities by a combination of precipitation methods and solvent extraction should allow to obtain pure Ni-Co sulfate solutions that can be further used in electrowinning cells to prepare valuable Ni-Co alloys. The final form of REEs products still requires to be determined.

On top of the specific research directions proposed in Table 11, several challenges based on current process schemes need to be addressed in the years to come, including processes integration and scale-up, life cycle analyses based on similar starting waste materials, treatment and recycling of effluents (e.g. some exploratory works [27,156]). Emerging strategies, such as hydrogen-based pyrometallurgy [56], preparation of functional materials [71,157,158] or process coupling with LiBs recycling [42] also provide interesting options that need to be explored.

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