



HAL
open science

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

Laurent Cassayre, Boris Guzhov, Margot Zielinski, Béatrice Biscans

► To cite this version:

Laurent Cassayre, Boris Guzhov, Margot Zielinski, Béatrice Biscans. Chemical processes for the recovery of valuable metals from spent nickel metal hydride batteries: A review. *Renewable and Sustainable Energy Reviews*, 2022, 170 (112983), 10.1016/j.rser.2022.112983 . hal-03863165

HAL Id: hal-03863165

<https://cnrs.hal.science/hal-03863165>

Submitted on 10 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

L. Cassayre^{1,*}, B. Guzhov¹, M. Zielinski¹, B. Biscans¹

¹ : Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INP, UPS, Toulouse, France

* Corresponding author : laurent.cassayre@ensiacet.fr

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, electrowinning

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 abbreviations

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].

1 The NiMH batteries were introduced in 1991 as a replacement of hazardous Ni-Cd batteries, and
2 constituted the majority of the batteries used in HEV at the beginning of the 21st century [2]. NiMH
3 market peaked at about 1.5 million HEV packs in 2012-2013 and is now slowly dropping due to
4 replacing by higher performance LiBs [1]. In 2013, more than half of HEVs used NiMH batteries
5 and the quantity of NiMH batteries on the market is still large [3–5]. Accordingly, important
6 amounts of spent NiMH batteries are discarded and represent hazardous wastes that need to be
7 correctly disposed. Besides, spent NiMH batteries contain specific metal elements that represent
8 valuable secondary resources: for example, each Toyota Prius HEV contains 10-15 kg of REEs
9 [6] whose large scale recovery could account for significant resources for new battery
10 manufacturing [7]. REEs are also among the most critical raw material groups in several regions
11 (especially Europe [8]), while the recovery of nickel is made attractive due to its high sales price.

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

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

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

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

4 **2. From spent NiMH batteries to Black Mass**

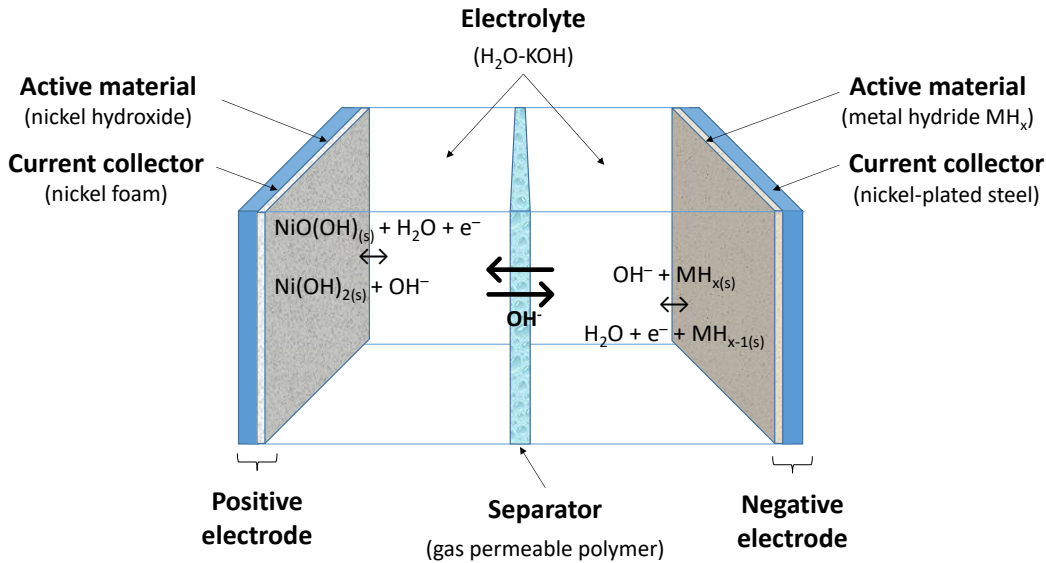
5 **2.1 Major battery components and electrode composition**

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



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

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



16
 17 *Figure 1: Operating principle of a NiMH battery*

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

Component (wt.%)	[12]	[23] without casing and electrolyte	[24]	[25]
	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 AB₅ and A₂B₇ 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 LaNi₅, which allows hydrogen storage as LaNi₅H₆ 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, with 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.

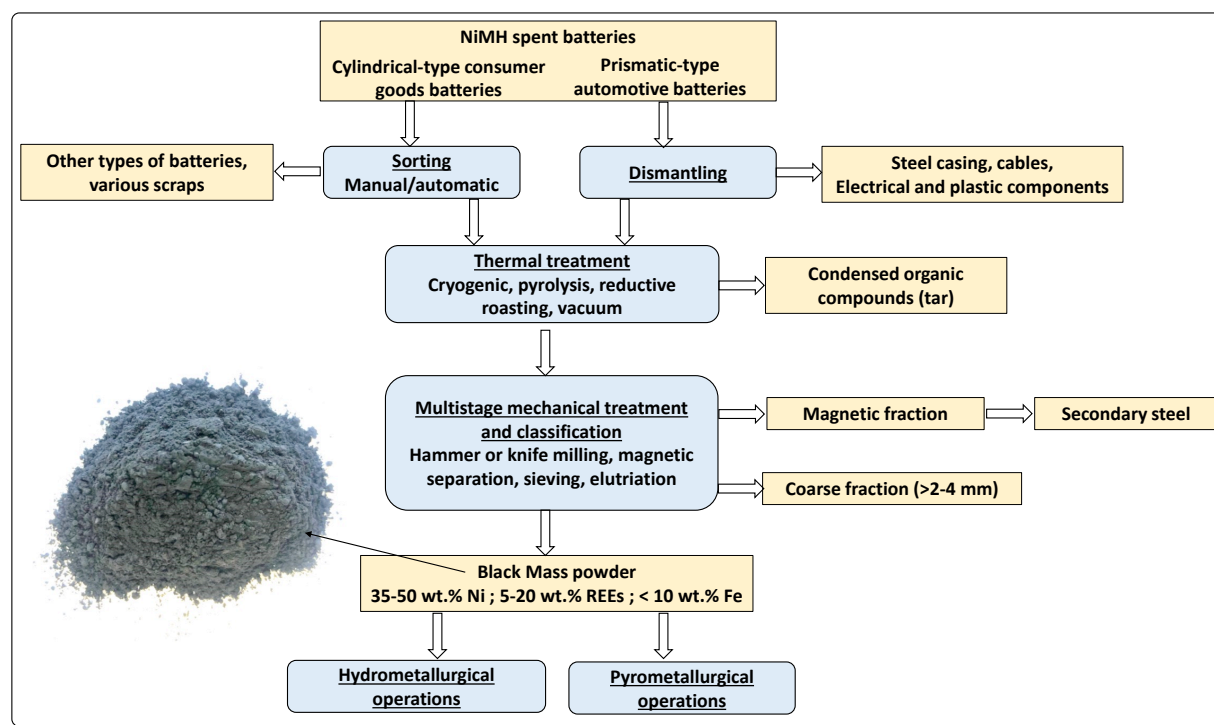
2.2 Pretreatment processes: physical based technologies

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

1 during subsequent comminution operations [32–34]. Cryogenic freezing has been implemented at
 2 Retrieval Technologies/Toxco to make the batteries fragile [31]. Tang [35] reported that liquid
 3 nitrogen (-196 °C) was to be preferred over liquid CO₂ (-78.5 °C) to separate the steel case.
 4 Moreover, heat treatment can be carried out at 250-550 °C with controlled atmospheric conditions
 5 (vacuum or low oxygen content). Various operation conditions are reported: at SNAM company
 6 the heat treatment is performed with low oxygen content [33], while Sumitomo Metal Mining uses
 7 a roasting operation with carbon in order to reduce nickel oxide and facilitate further Ni leaching
 8 [32]. Korkmaz [36] also investigated selective roasting of NiMH anode material after reaction into
 9 concentrated sulfuric acid.

10 Next, the material is crushed by hammer or knife mill, followed by separation operations. Tanabe
 11 [24] report that spouted bed elutriation after hammer milling and sieving allows to separate the
 12 NiMH materials into three different fluxes (plastics, iron-based metals and electrodes powder).
 13 Magnetic separation may also be implemented. The highly magnetic part (from the protective steel
 14 case) is recovered for the production of secondary steel. The weak magnetic fraction is sieved, and
 15 the resulting fine fraction, in the form of a black powder (the BM, see Figure 2), is finally recovered
 16 [12,26].



17
 18 *Figure 2 – Flow chart of typical physical based pretreatments of spent NiMH batteries,*
 19 *including a picture of a black mass sample (prepared at the SNAM facilities)*

20 21 **2.3 Black Mass elemental composition**

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

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

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

9 *Table 3 – Composition (wt%) of different BM powders prepared from mixed (anode+cathode)*
 10 *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	[33]	
		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		
Unknown	no	< 500	100 - 250	44.9	4.8	1.9	1.2	7.4	2.9	1.1	0.3	11.7	4.4	0.4	5.1	[39]
			< 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	105 °C; 24 h	< 500	100 - 250	11.7	2.6	14.3	1.1	3.6	1.7	na	na	5.3	2.5	na	na	[39]
			< 100	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]

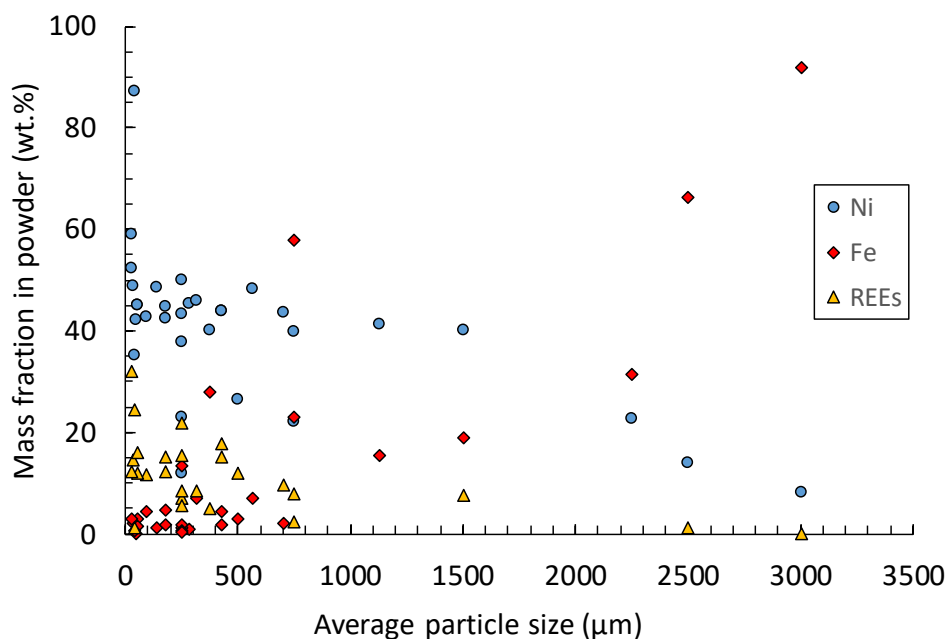
Mixed: all components of the battery are included in the Black Mass

na – element not analyzed

ns – element analyzed but data not specified (only the total concentration of REEs is provided)

bd – concentration below detection limit

1



2

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

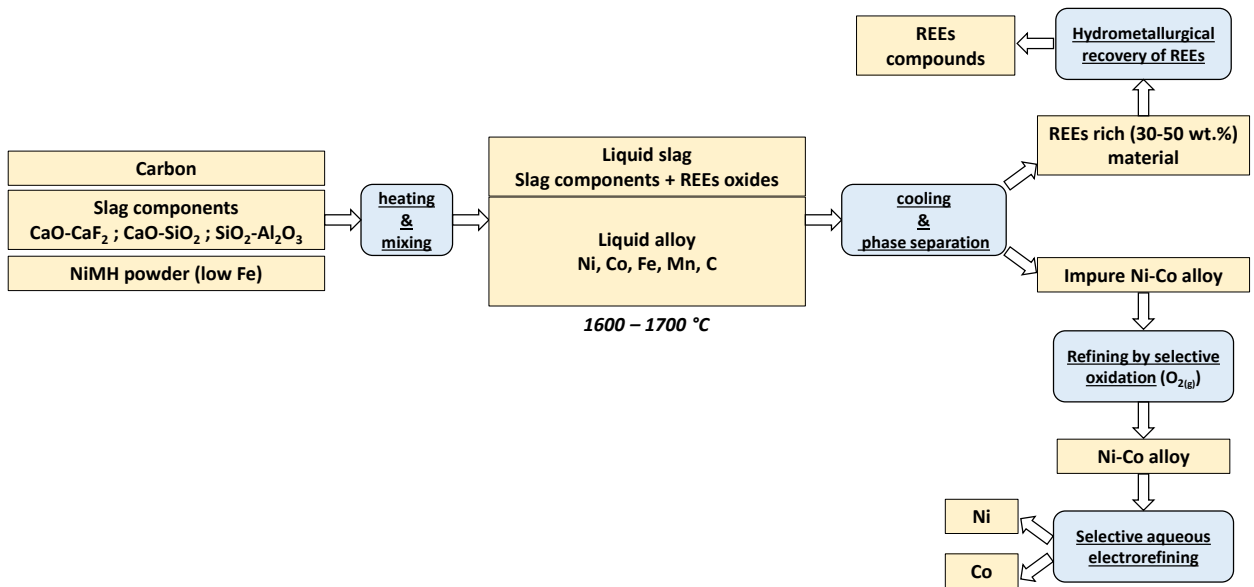
5 Grinding and sieving operations have a strong impact on the overall material balance, since a large
6 amount of the initial material is likely to be discarded in the coarse fraction depending on the
7 grinding technology. Ebin [37] showed that lab-scale sieving with a sieve size above 4 mm leads
8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

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

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

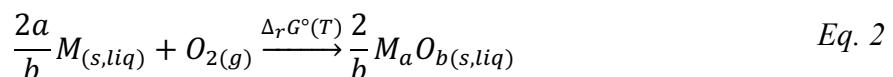
3 3. Pyrometallurgical processes

4 As reported by Müller and Friedrich [50], in the early 2000's the "discarded NiMH batteries were
 5 used as a cheap nickel source in the steel industry, while cobalt was not considered and REEs were
 6 lost in the slags". More recently, Tirronen [51] have investigated the element distributions (Ni, Co,
 7 Mn, Nd) in copper converting process facilities. They concluded that the secondary copper
 8 smelting circuits are not effective for NiMH metals recovery, since a large fraction of the valuable
 9 elements is lost and diluted in the slag phases. Wang [52] studied in 2002 the direct smelting and
 10 re-use of dismantled bulk cathode materials but, even if good performances of the secondary alloys
 11 were obtained, this route has not been further mentioned nor put into application. With the
 12 exception of these publications, only a few works have been devoted to the valorization of Ni and
 13 Co on one side and REEs on the other side in the frame of a dedicated pyrometallurgical process
 14 [53]. The general principle of such operations, as established for instance by [35,50], is
 15 schematized in Figure 4. It consists in melting the battery material, either after pretreatments
 16 (Figure 2) in order to decrease the Fe content, or sometimes as a full piece including plastic
 17 elements. In contact with a slag (i.e. an oxide liquid phase), the process leads to the reduction of
 18 Ni and Co elements into a liquid Ni-Co alloy, while REEs oxidize and dissolve into the slag.
 19
 20

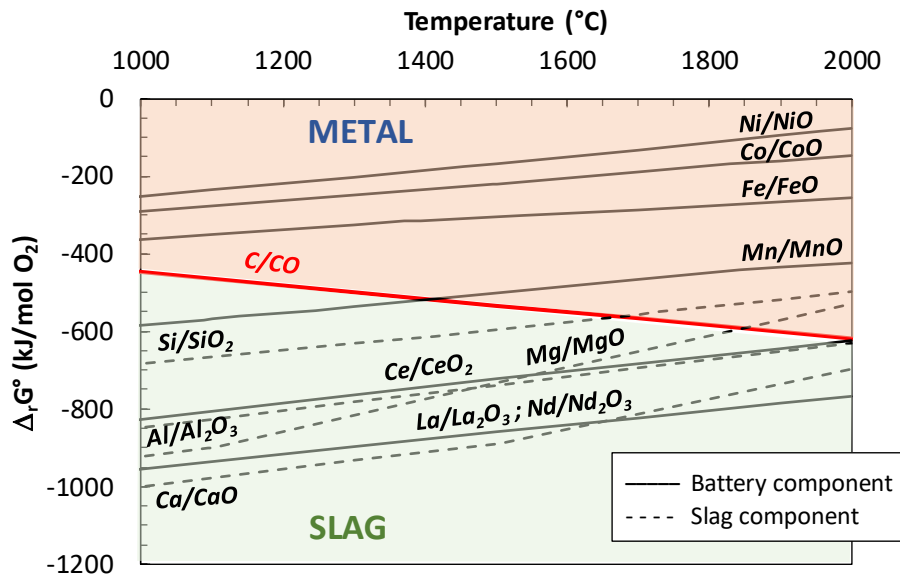


21
 22 *Figure 4 - Principle of pyrometallurgical processing of spent NiMH batteries*

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



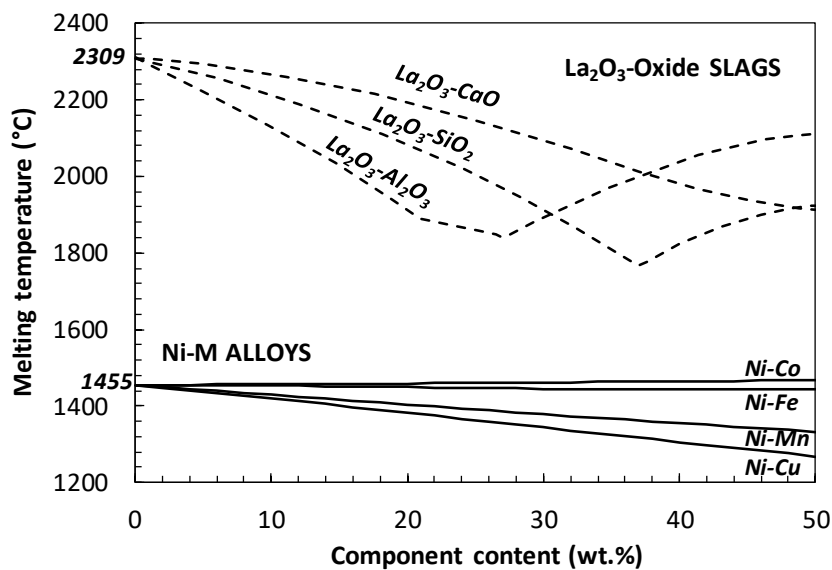
26 As evidenced in Figure 5, in presence of carbon excess, Ni, Co, Fe and Mn form a metal phase,
 27 while, in similar conditions, REEs form an oxide phase up to 2000 °C.



1

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

5 In order to facilitate mass transfer and achieve thermodynamic equilibrium, such processes require
 6 both metal and slag phases to be in the liquid state. As illustrated in Figure 6, Ni melts at 1455 °C,
 7 and alloying with Fe and Co only slightly modifies the melting temperature, while Mn and Cu
 8 decrease the melting temperature. Moreover, La₂O₃, which is the main component of the oxide
 9 phase issued from NiMH, melts at a much higher temperature, i.e. 2309 °C. Consequently, the
 10 minimal operating temperature is driven by the use of additives allowing to decrease the melting
 11 temperature of the slag. The melting temperature of La₂O₃ mixed with SiO₂, CaO and Al₂O₃ is
 12 shown in Figure 6 [54]: none of these common additives does allow to decrease the melting
 13 temperature below 1766 °C (La₂O₃-SiO₂ eutectic). Consequently, to operate below 1700 °C,
 14 mixtures typically made of CaF₂, MgO, CaO, Al₂O₃ and/or SiO₂ need to be considered. As recently
 15 pointed out by Lan [55], the basic data on REEs in REE-bearing slags are scarce, and the
 16 development of an efficient process thus requires extensive experimental work.



17

18 *Figure 6 – Melting temperature of Ni-M (M=Co, Fe, Mn, Cu) and La₂O₃-Ox (Ox = CaO, SiO₂,*
 19 *Al₂O₃) binary mixtures. Melting temperature of liquid alloys (full lines) were calculated using*

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

3 Müller and Friedrich [50] pointed out that the definition of an appropriate slag system is a key
4 point for such operation. These authors performed successful pilot-scale tests (300-1000 kg) with
5 CaO-CaF₂ and CaO-SiO₂ slags, but report incomplete refining of final Ni-Co alloys which
6 contained 5-10 wt% of Fe and Mn. Further refining by selective oxidation of Mn and Fe thanks to
7 O₂ bubbling in the liquid metal phase is then required. If satisfying purity is obtained, Ni-Co alloys
8 can eventually be separated into pure Ni and pure Co through aqueous electro-refining (Figure 4).

9 Based on a slightly different concept, Jiang [56] proposed a pre-reduction step of BM by hydrogen
10 at 800-900 °C, followed by high temperature (1550 °C) equilibration with a SiO₂-Al₂O₃ slag.
11 Laboratory scale experiments led to high REEs contents in the slag (50 wt%). Deng [57] carried
12 viscosity measurements of La₂O₃-SiO₂-Al₂O₃ mixtures, for improving the separation efficiency
13 and reduce acid consumption in consecutive hydrometallurgical process.

14 The resulting REEs-rich slags need to be processed by aqueous leaching and further recovery of
15 REEs compounds by selective precipitation (Figure 4). For instance, Deng [58] have recently
16 reported excellent REEs leaching yield (95%) from SiO₂-Al₂O₃ slags in hydrochloric acid, while
17 Kim [59] have characterized the leaching kinetics of La from silica based slags in sulfuric acid
18 media.

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

23
24 Apart from the conventional pyrometallurgical methods that could benefit from large-scale
25 existing facilities, alternative processing routes based on high temperature thermal treatment of
26 NiMH materials have been reported in the last years. For instance, Kuzuya [61] proposed a reactive
27 thermal treatment based on carbochlorination reactions. Mir [62] investigated the effect of
28 microwave oxidizing thermal treatment at 1000 °C, but the resulting NiO and La-Ni oxide phases
29 are difficult to leach in HCl solutions. Maroufi [63] proposed a two-step oxidation – reduction
30 approach, where the battery material was reduced at 1550 °C in order to produce a ferro-nickel alloy
31 on the one side, and an oxide phase containing REEs on the other side. The small scale (gram
32 scale) does not really allow to conclude on the potentiality of such routes. Some authors also
33 focused on preparing metallic products from NiMH batteries using waste plastic sources (e-waste
34 plastics [64], waste printed circuit printboard [41]) as reductant in replacement of carbon.

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

42 **4. Hydrometallurgical processes**

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

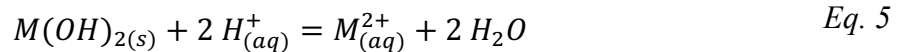
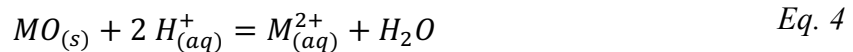
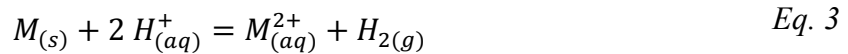
1 selective precipitation, solvent extraction and electrodeposition are the main separation options.
 2 The most recent routes are described in this section.

3 **4.1 Leaching of BM**

4 This section provides a description of the main features and specificities linked with NiMH BM
 5 leaching in sulfuric and hydrochloric acid, which are the dominant media reported for this
 6 operation. Alternatively, a few recent works implemented organic acids and a choline chloride-
 7 based deep eutectic solvent [66], which are potentially more environmentally friendly. Citric [67–
 8 69], formic [70,71] or nitric [72] acids have been reported, with subsequent metal recovery by
 9 adsorption [67], electrodeposition [66,69] or preparation of oxide compounds via sol-gel method
 10 [68,73]. Also, a first bioleaching attempt, aiming at reducing mineral acid consumption, has been
 11 recently reported [74], together with the evaluation of the leaching properties of gluconate organic
 12 acid and its bio-oxidation products [75].

13 **4.1.1 Leaching reactions**

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



16 If the acid consumption per mol of M is equivalent for each reaction, the acid leaching of metals
 17 leads to the formation of hydrogen gas, which needs to be taken into account for large scale
 18 processing. Eh-pH analysis of the Ni-La-H₂O-HCl system shows that a pH below 6 is required in
 19 order to oxidize nickel metal (Eq. 3), and an acidic pH is also required to dissolve oxide and
 20 hydroxide phases [76].

21 The nature of the acid has large consequences on the chemistry of the leaching step, as well as on
 22 the further separation steps. First, the acid counter-ion (Cl⁻, SO₄²⁻) can lead to complexation with
 23 the metal cation, which can influence the solubility of the initial phases (Eq. 6).



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



where A = Na or K

28 **4.1.2 Overview of operating parameters**

29 Table 4 reports the effect of operating conditions on dissolution yields in HCl and H₂SO₄ media,
 30 based on recent work mostly carried out in small volume reactors (< 1 L except for two studies
 31 using > 5 L [76,77] and 500 L pilot data [32]). The yields are displayed only for REEs and Ni
 32 owing to their major concentration in BM. However, it has been shown (e.g. [76]) that Co and Fe
 33 exhibit similar dissolution behavior as Ni, while K dissolution is very fast.

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

Leaching solution	Temp. (°C)	S/L (%)	Volume (L)	Duration (h)	Leaching yields	Ref.
Sulfuric acid						
<i>without pH regulation</i>						
H ₂ SO ₄ 3 M	95	13	0.75	4	99% Ni, 5% REEs	[78]
H ₂ SO ₄ 2 M	95	5	0.35	4	97% Ni, 96% REEs	[79]
H ₂ SO ₄ 2 M	90	5	1	4	83% Ni, 83% REEs	[80]
H ₂ SO ₄ 2 M	75	10	<i>ns</i>	2	90% Ni, 95% REEs	[44]
H ₂ SO ₄ 2 M	75	10	0.5	2	91.6% Ni, 90.2% REEs	[43]
H ₂ SO ₄ 3 M	70	10	<i>ns</i>	5	96% Ni, 96% REEs	[34]
H ₂ SO ₄ 2 M anode material	20	10	<i>ns</i>	2	77% Ni, 93.2% REEs	[81,82]
H ₂ SO 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 ₂ SO ₄ 2 M 2) H ₂ SO 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 ₂ SO ₄ 1.5 M	30	10	1	2 x 1 h	80% Ni, 87% REEs	[46]
4-steps: H ₂ SO ₄ 0.75 M anode material	40	18	0.08	4 x 1 h	100% Ni, 100% REEs	[83]
2-steps: 1) H ₂ SO ₄ 2 M 2) H ₂ O	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 ₂ SO ₄ 3 M	90	66	<i>ns</i>	3	93.5% Ni	[45]
H ₂ SO ₄ 3 M + 10 v.% H ₂ O ₂	90	66	<i>ns</i>	1	99% Ni	[45]
H ₂ SO ₄ 1 M + O ₃ (g)	25	8	0.5	3	100% Ni, 96% REEs	[84]
<i>with pH regulation</i>						
H ₂ SO 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 ₂ SO ₄ pHreg 0-3	40-90	5-15	<i>ns</i>	8	34-90% Ni, 42-96% Co, 50-100% REEs	[32]
H ₂ SO ₄ pHreg 1 + air	80	10	500	6	89% Ni, 94% Co, 99% REEs	
Hydrochloric acid						
<i>without pH regulation</i>						
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	<i>ns</i>	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	<i>ns</i>	5	100% Ni, 100% REEs	[88]
<i>with pH regulation</i>						
HCl pHreg 1	25	10	<i>ns</i>	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

3 Based on the data compiled in Table 4, and the parametric study by Sobianowska-Turek [89], it
 4 comes that the main strategy implemented for efficient Ni and REEs leaching consists in using
 5 aggressive conditions combining high initial acid concentrations (> 3 M) and high temperature
 6 (70-95 °C) for maximum 4 h. The solid-liquid ratio is often limited to 10-15%, which corresponds
 7 to a compromise between the amount of BM that can be dissolved and the slurry density that could
 8 hinder mass transfer in the leaching reactor.

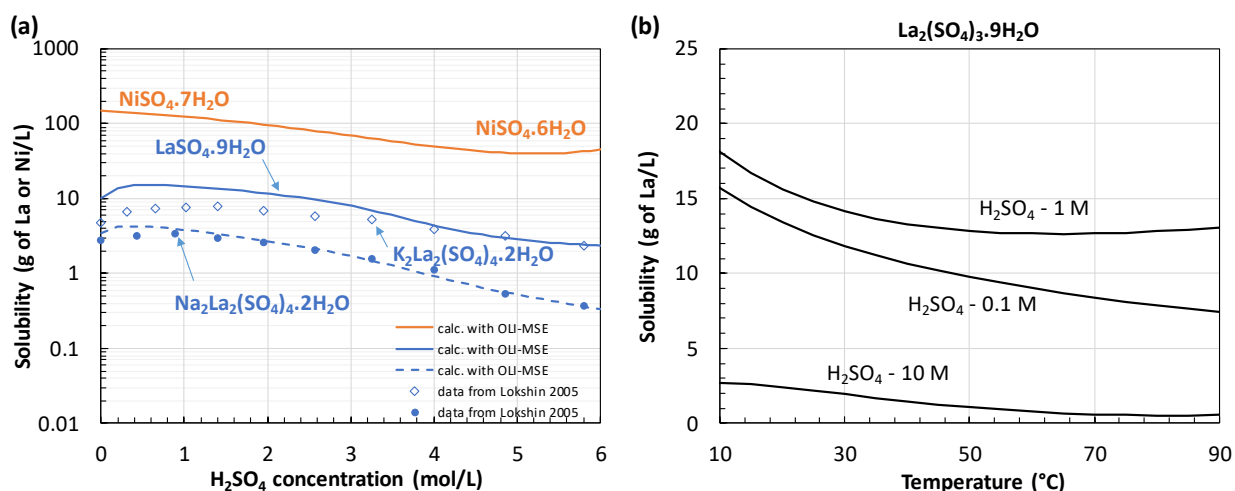
1 Whatever the type of acid, several authors report that Ni dissolution is slow at low temperature,
 2 possibly due to the presence of nickel oxide. For instance, Korkmaz [27] obtained a much better
 3 Ni yield (98% vs 70%) at 90 °C than 25 °C. Takano [32] implemented a primary roasting of the
 4 BM in order to reduce NiO and enhance nickel dissolution. A comparison between HCl and H₂SO₄
 5 acid leaching kinetics, carried out in similar conditions (same BM, pH and temperature) showed
 6 that Ni leaching rate is mostly independent of the type of acid, and that REEs dissolve faster than
 7 Ni [76]. Furthermore, some works have shown that high temperature and low pH increase the rate
 8 of the anodic dissolution of metal nickel [90–93]. This could justify, at least in part, the aggressive
 9 conditions usually implemented to dissolve nickel more rapidly.

10 4.1.3 Solubility of Ni and REEs salts

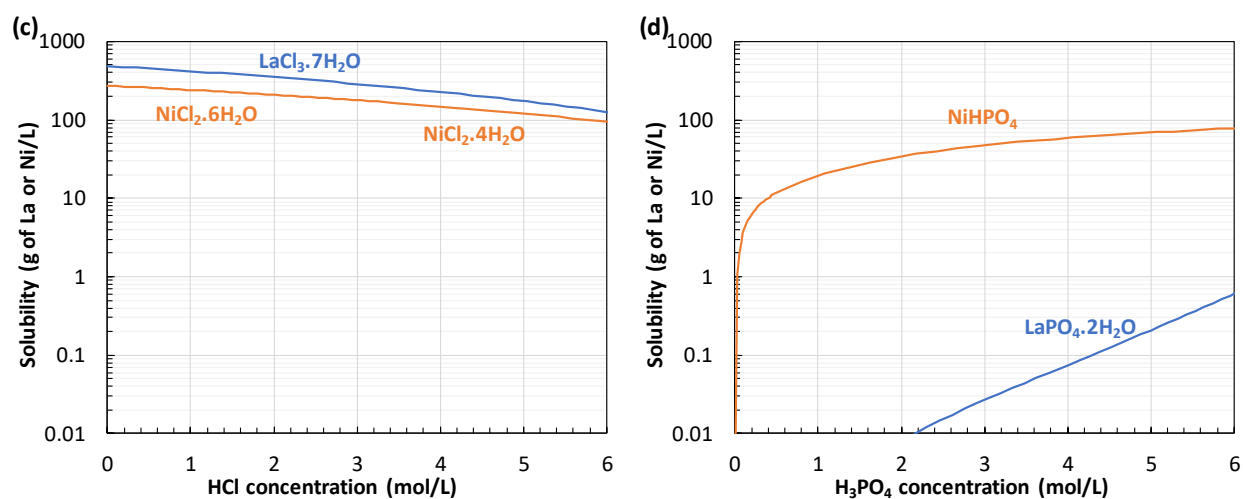
11 Figure 7 reports the solubility of the most stable Ni and La salts in inorganic acid systems (H₂SO₄-
 12 H₂O, HCl-H₂O and H₃PO₄-H₂O). The data come from equilibrium calculations performed with
 13 the OLI software [16], based on the recent assessment of REEs systems by Das [17,94] as well as
 14 experimental data from Lokshin [95]. The solubilities, in g of element per L of solution, are plotted
 15 as a function of the acid concentration or temperature. Lanthanum was selected as model element
 16 for REEs (Ce and Nd behave similarly).

17 It first comes from Figure 7 that, due to the common ion effect, high acid content lowers the
 18 solubility of the sulfate and chloride salts. The reason for using contrated acid solutions thus rely
 19 more on kinetic aspects than on thermodynamics. Second, the overall solubility of Ni and La
 20 compounds is much higher in HCl than in H₂SO₄. Indeed, NiCl₂.6H₂O and LaCl₃.7H₂O
 21 compounds are highly soluble (170 g/L and 330 g/L, respectively, in 2 M HCl solutions), while
 22 the solubility of La salts is low (less than 20 g/L for LaSO₄.9H₂O), and even extremely low (less
 23 than 10 g/L) in presence of K⁺ or Na⁺ ions, due to the formation of double sulfate salts (Eq. 7).
 24 Third, the solubility of REEs sulfate salts (e.g. LaSO₄.9H₂O) decreases with temperature (Figure
 25 7(b)).

26 According to the data compiled in Table 3, the mass ratio Ni/REEs is about 5 in the BM.
 27 Consequently, the overall solubility of BM in H₂SO₄ media is limited by the solubility of REEs
 28 sulfate compounds, while in HCl media it is limited (at a higher level) by Ni chloride compounds.
 29 Furthermore, REEs phosphates compounds exhibit a very low solubility in H₃PO₄ media, which
 30 led to recent investigation of selective leaching by Lie [96].



31



1
2 *Figure 7 - Solubility of various Ni and La salts (in g of La or Ni/L of solution) in (a) H₂SO₄-H₂O*
3 *media at 25 °C (b) HCl-H₂O media at 25 °C (c) H₂SO₄-H₂O media as a function of temperature*
4 *(calculated with OLI-MSE [16,17,94] and experimental data from Lokshin [95])*

5 **4.1.4 Specificities of H₂SO₄ leaching**

6 Enhancement of leaching kinetics with strong oxidants (ozone, hydrogen peroxide) in sulfuric acid
7 has been considered in several works. Alonso [84] evidenced a significant effect of ozone on the
8 dissolution yield of nickel at 25 °C. Rabah [45] reported an improvement of leaching kinetics with
9 10 vol% H₂O₂ additions. In contrast, most authors did not measure any impact of H₂O₂ (0-7 vol%
10 [46,82,97]) and found it unnecessary for NiMH BM leaching.

11 As pointed out, a major specificity of H₂SO₄ media is the limited solubility of REEs elements,
12 especially in the presence of K or Na. Meanwhile, the BM usually contains rather high levels of K
13 (Table 3), with typical K/REEs molar ratio of 0.5 or even higher than 1. Therefore, REEs leached
14 from the BM tend to re-precipitate as double REEs sulfates during H₂SO₄ leaching [47,76]. In
15 accordance with the solubility values compiled in Figure 7, several options allow to maximize
16 REEs leaching yield: decrease temperature, decrease H₂SO₄ content and minimize K content by
17 initial washing of BM.

18 Pietrelli [81,82] showed that, at low temperature (25°C), 93% REEs could be dissolved, but the
19 nickel dissolution was limited to 77%. To overcome this problem, some authors perform sequential
20 dissolution at room temperature to extract most of the nickel while minimizing acid consumption
21 [46,83]. For instance, Liu [83] achieved full Ni dissolution in 4 successive steps, in a weakly
22 concentrated sulfuric acid (0.75 M) at 40 °C. However, this type of technique requires an
23 intermediate filtration step after each dissolution, which increases the number of unit operations
24 of the process and the associated mass losses.

25 Some authors studied the selective dissolution of nickel compared to the rare earths, in sulfuric
26 acid, by increasing the temperature. For example, Li [78] achieved 95% REEs precipitation and
27 99% Ni dissolution thanks to leaching in 3 M H₂SO₄ at 95 °C for 4 h. Wu [98] reported similar
28 results and obtained highly concentrated (over 100 g/L) nickel solutions. Innocenzi [39] dissolved
29 only 33% REEs at 83 °C in 2 M H₂SO₄, while Ni dissolution was 90%. Another option envisaged
30 by Porvali [47] consists in selective leaching of Ni thanks to REEs precipitation as double sulfates
31 by Na₂SO₄ addition. As a result, less than 3.5% REEs were dissolved. However, this option
32 requires a subsequent treatment of the solid phase to recover REEs, which are mixed with insoluble
33 residues at the end of the leaching operation.

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

8 However, Figure 7(a) shows that even if the precipitation of (K, REEs) double sulfates can be
9 limited by the washing of K, the solubility of the compound $\text{La}_2\text{SO}_4 \cdot 9\text{H}_2\text{O}$ is not so much higher
10 and thus BM leaching in H_2SO_4 media will always be limited by REEs sulfates precipitation.

11 **4.1.5 Specificities of HCl leaching**

12 Due to their high solubility, REEs contained in the BM do not form chlorides salts under standard
13 dissolution conditions (S/L < 15% and T = 25-100 °C). However, in order to achieve complete
14 dissolution (> 95%) of REEs and Ni in HCl media, most studies report (Table 4) that it is necessary
15 to work either at 2-4 M HCl at high temperature (70-95 °C) [27,85–87], or at 25-40 °C with high
16 HCl concentrations (8-12 M) [40,88]. These conditions lead to corrosion of industrial equipment,
17 not only because HCl-H₂O solutions are corrosive, but also because HCl becomes volatile as
18 temperature increases. Furthermore, using large initial amounts of acid increases the consumption
19 of alkali solution needed to equilibrate pH for the selective precipitation in the following stages.

20 Ekberg [25,77] evaluated the selective dissolution of NiMH cathode and anode active materials at
21 mild pH to overcome these industrial challenges. Ni metal dissolution from the cathode material
22 was significantly slowed down when the pH increased from 1 to 3 at 30 °C [25]. On the other
23 hand, Ni(OH)₂ from the cathode and the entire anode plates completely dissolved after about 5 h
24 under the same conditions [25]. The authors suggest that the hydrogen adsorption properties on
25 the surface of the metallic nickel are the origin of slow Ni dissolution [77].

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

31 **4.1.6 Conclusions and typical leach liquors composition**

32 Considering the data compiled in Table 4 and the solubility of Ni and REEs salts (Figure 7), the
33 dissolution of the BM powder in HCl leads to the best yields in terms of REEs and Ni dissolution.
34 However, aggressive operating conditions are required, increasing the economic costs (corrosion
35 of the equipment, high amounts of alkali solution for the downstream precipitation step). The use
36 of HCl at moderate pH has the advantage of reducing acid consumption but the rate of nickel
37 dissolution is much reduced due to kinetics limitations. On the other hand, the use of H_2SO_4 at
38 room temperature can bring good yields but requires to proceed by sequential dissolution steps.
39 By increasing the leaching temperature, the dissolution of nickel by H_2SO_4 is favored but the REEs
40 are less soluble and form double sulfate salts whose amount can be reduced by preliminary
41 washing of BM. Both options increase the number of unit operations of the process. It is finally
42 interesting to note that, in a recent work from Takano [32] implementing a 500 L scale leaching
43 reactor, the authors discarded hydrochloric acid due to its corrosive properties and nitric acid due
44 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 H₂SO₄ 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	<i>ns</i>	1.9	18.0	<i>ns</i>	<i>ns</i>	<i>ns</i>	[40]
	<i>ns</i>	5.7	2.8	0.99	1.1	2.2	6.4	6.2	<i>na</i>	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	
H₂SO₄ 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	<i>na</i>	4.9		2.8			
	22.3	2.4	0.05	0.8	<i>ns</i>	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	<i>na</i>	<i>na</i>	<i>na</i>	[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	<i>na</i>	0.8	[101]
	53.0	4.4	1.6	1.8	<i>na</i>	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	<i>na</i>	<i>na</i>	<i>na</i>	<i>na</i>	10-14	5-7.3	<i>na</i>	<i>na</i>	[32]

ns: not specified

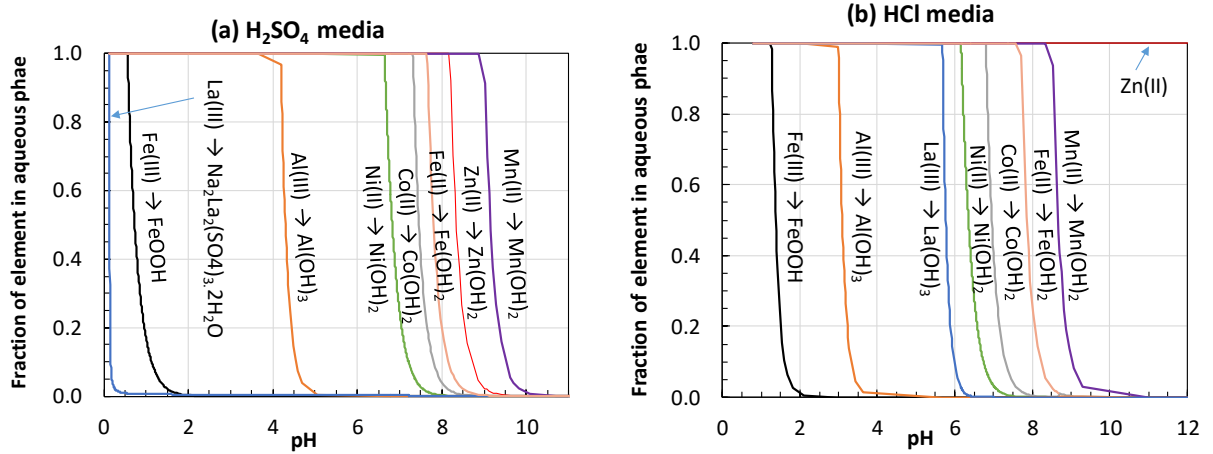
na: not analyzed

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 H₂SO₄ 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

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



6

7 *Figure 8 - Simulated precipitation of a model PLS (Ni(II) = 50 g/L ; La(III) = 15 g/L ; Co(II) =*
 8 *5 g/L ; Al(III) = Fe(III) = Fe(II) = Mn(II) = Zn(II) = 2 g/L) during pH swing by addition of*
 9 *NaOH at 25 °C in (a) H₂SO₄ media (b) HCl media (calculated with OLI-MSE [16,17,94])*

10 4.2.1 REEs precipitation from sulfuric media and further purification

11 Table 6 compiles the operating conditions and main results obtained for REEs precipitation from
 12 NiMH leach liquors. In early work from Bertuol [80], three different types of acid (sulfuric,
 13 hydrochloric and nitric) were evaluated to leach NiMH batteries, followed by REEs precipitation
 14 by addition of NaOH and KOH. The authors showed that only sulfuric acid was suitable, and that
 15 NaOH led to the best recovery yields. In nitric and hydrochloric media, no precipitation reaction
 16 occurred for pH < 7, and the resulting precipitate contained mostly Ni. These conclusions are in
 17 full accordance with calculations presented in Figure 8 and based on recent thermodynamic
 18 models. Many authors have then studied the selective precipitation of REEs. In most works, the
 19 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-
 20 Na₂CO₃ [34,105], which makes possible the selective precipitation of NaREE(SO₄)₂·H₂O salts
 21 according to Eq. 7. Several authors showed that the best selectivity is achieved at low pH
 22 [34,80,81,96,104]. However, the reported contamination by other metal elements (Ni, Co, Fe, Al)
 23 strongly differs between the studies, maybe due to different washing procedures.

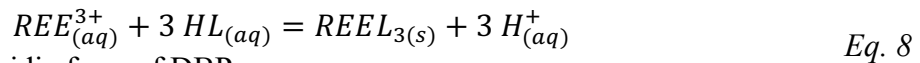
24 Recently, Porvali [38,47] showed that such precipitation reaction does not depend so much on the
 25 pH but rather on the concentration of Na⁺ and SO₄²⁻. They achieved REEs precipitation by adding
 26 Na₂SO_{4(aq)} to increase the Na/REE and SO₄/REE molar ratios without increasing the pH, which
 27 limits the co-precipitation of impurities as hydroxides. The REEs precipitate in a congruent way
 28 and form either a mixture of double sulfates monohydrate or a solid solution [47]. These results
 29 were confirmed by Zielinski [102], who showed that the composition of the REEs precipitate was
 30 almost constant for 25 < T < 60 °C and 0.8:1 < Na/REEs molar ratio < 3.2:1, while excellent REEs
 31 recovery yield were obtained at 60 °C. Takano [32] implemented this method at pilot scale (300
 32 L) and report excellent La and Ce recovery yields at 80 °C. These authors also focused on Y
 33 recovery, which was otherwise barely studied due to its very low content in NiMH batteries (0.8
 34 wt% in [32]), and showed that lower recovery yields (< 70%) were obtained due to a higher

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

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

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

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



where HL is the acidic form of DBP

18

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

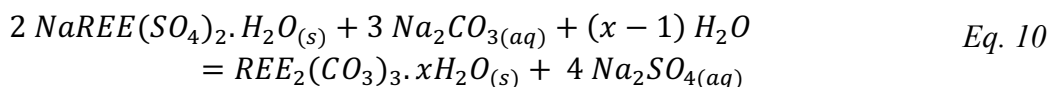
Reactant/ Product	Conditions	Extraction yields and purity	Ref.
H₂SO₄ media			
	NaOH addition until pH = 1.5 Room temperature	REEs yield ≈ 80% of REEs Impurities: Ni 1.7 wt%, Co 3.0 wt%, Mn 0.3 wt%, Zn 0.7 wt%, Fe 6.9 wt%	[81]
	Precipitation at pH 0.8-1.6 with 5 M NaOH Room temperature	REEs yield > 98% 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]
NaOH / NaREE(SO ₄) ₂ ·H ₂ O	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%	[104,10 9]
NaOH + Na ₂ CO ₃ / NaREE(SO ₄) ₂ ·H ₂ O	Adjustment of pH to 1.5-1.7 with 6.5 wt% NaOH + 3.5 wt% Na ₂ CO ₃ (oxidation of Fe ²⁺ to Fe ³⁺ by H ₂ O ₂) Room temperature	REEs yield 94% Impurities: Fe 9 wt%, Mn 11 wt%	[34,105]

NaOH + H ₂ O 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 ₂ SO ₄ and 2 M Na ₂ SO 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 ₂ SO ₄ / NaREE(SO ₄) ₂ .H ₂ O	Precipitation at pH ~ 1.5 with 2.9 M Na ₂ SO 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 ₂ SO 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 ₂ SO ₄ T = 80 °C	REEs yields: La 99.7%, Ce 99.7%, Y 41- 72% Impurities: Ni and Co < 0.04%	[80]
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 ₂ O	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%	[107]
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 ₂ SO ₄ / REE ₂ (SO ₄) ₃ .xH ₂ O	Adjustment of pH to 3 with NaOH Addition of Na ₂ SO ₄ 150 g/L Room temperature	Impurities: 0.15 wt% Ni, <0.1 wt% Co, 0.46 wt% Fe	[111]
H ₂ C ₂ O ₄ / REE ₂ (C ₂ O ₄) ₃ .xH ₂ O	Adjustment of pH to 0.4–0.6 with NaOH Addition of H ₂ C ₂ O ₄ Room temperature	REEs yield 95.2% Purity 99%	[87]
	Addition of H ₂ C ₂ O 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) ₂ C ₂ O ₄ / REE ₂ (C ₂ O ₄) ₃ .xH ₂ O	Adjustment of pH to 0.5 with 6M NaOH; Addition of 0.3M (NH ₄) ₂ C ₂ O ₄ T = 60 °C	REEs yield 98.5%	[40]
	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]
H ₂ C ₂ O ₄ to HCl strip liquor / REE ₂ (C ₂ O ₄) ₃ .xH ₂ O	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 ₂ C ₂ O ₄ saturated solution with H ₂ C ₂ O ₄ /REEs = 2 mol/mol	REEs yield 99% Impurities: Co, Mn, Zn, < 0.01%, 0.05% Fe, 0.6% Al	[79,86]

1

2 Up to now, the precipitation of REEs double sulfate salts has been the most used (Table 6) thanks
3 to the extreme efficiency and selectivity of this technique. However, the obtained products need
4 to be further processed to remove Na and S elements and produce a mixture of pure REEs
5 compounds. In this objective, a few works report the conversion of the REEs double sulfates into
6 mixed hydroxide or carbonate compounds. Wu [98] prepared hydroxides by alkalization (Eq.
7 9), followed by redissolution into a HCl solution and crystallization of REEsCl₃ compounds. Ahn

1 [104] report the conversion of the salts into carbonates according to (Eq. 10). They finally obtained
2 a mixture of pure REEs oxides by subsequent thermal decomposition at 800 °C [109].



3 Even if treatments based on solvent extraction methods and aiming at producing separate fluxes
4 of individual REE have been developed for the recycling of permanent magnets or lamp phosphors
5 [10], not much has been reported in relation with NiMH batteries. An alternative to solvent
6 extraction is to separate Ce at tetravalent state from other trivalent REEs such as investigated by
7 Porvali [100], who adapted separation routes established for primary Ce production from minerals
8 such as monazite [113,114]. The three steps process consists of (i) a conversion of the double
9 sulfates salts into REEs hydroxides in NaOH media according to (Eq. 9), (ii) a subsequent
10 conversion of Ce(OH)₃ into Ce(OH)₄ by air oxidation and (iii) a selective dissolution of trivalent
11 REEs by HNO₃ additions which leaves a pure Ce(OH)₄ product. The method relies on the fact that
12 solid Ce(OH)₄ hydroxide is insoluble at pH>2 conversely to trivalent REE hydroxides that dissolve
13 at pH<6. However, the authors report that the high sulfur level contained in Ce(OH)₄ is
14 problematic for the subsequent recovery of the precipitate [100].

15 4.2.2 REEs precipitation from hydrochloric solutions

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



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

26 Several authors performed solvent extraction of REEs from leach liquor (see section 4.3.2), and
27 subsequent precipitation of oxalate REEs compounds from an HCl strip liquor. Zhang [86] report
28 that REEs were selectively precipitated by pH adjustment at 2-3 with a concentrated ammonia
29 solution followed by the addition of H₂C₂O₄ solution, while the strip solution still contained Zn,
30 Mn, Al, and Fe. The final product contained 99.9% of REOs after calcination. These results may
31 seem rather contradictory compared to Fernandes' study [40], who obtained quantitative Mn co-
32 precipitation at pH = 2 and recommended a lower pH to achieve acceptable selectivity. This could
33 be linked to a concentration effect, since Mn concentration was about 2 g/L in [40] while it was
34 only 0.3 g/L in [86]. Based on a similar route, Liu [83] obtained 99% pure REEs oxides at pH=0.5,
35 and Xia [112] reports a good selectivity versus Fe at pH=1.5.

36 4.2.3 Precipitation of metals impurities (Fe, Al, Zn)

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

1 trivalent impurities is thus expected by a pH increase. Although iron purification has been
 2 mentioned in a few works [44,80,81,105], not many studies have effectively quantified its
 3 selectivity. Nan [34] report the removal of 99% of Fe from a PLS containing 0.13 g/L of Fe. They
 4 performed oxidation of Fe(II) to Fe(III) by addition of H₂O₂ at pH<2 followed by pH increase to
 5 5.8 by NaOH additions. Bertuol [80,99] also implemented a purification step by NaOH additions
 6 that resulted in precipitation of 100% Fe at pH=6 (with initial Fe concentration of 0.05 g/L), while
 7 the co-precipitation of Ni and Co was only about 2% and 6% respectively. The authors also
 8 mentioned that, during this operation, Zn partly precipitated (24%), while Mn did not.

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

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

17 4.2.4 Precipitation of nickel, cobalt and manganese

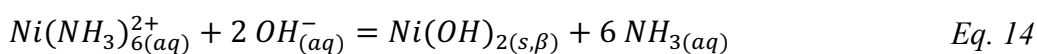
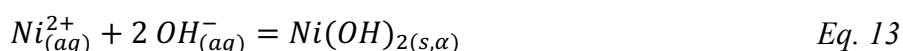
18 Table 7 summarizes the main reactions reported to recover nickel and cobalt products by
 19 precipitation. In comparison with the studies devoted to REEs (Table 6), it is interesting to note
 20 that less academic works concern Ni, while it is the most concentrated and valuable elements in
 21 NiMH batteries. Several reasons may account for this, among which the existing knowledge
 22 related to Ni(OH)₂ particles synthesis for NiMH battery manufacturing, but also the reduced
 23 difficulty in term of selectivity since REEs and Al-Fe impurities can be removed in prior steps.

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



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

28 Conversely, in sulfuric PLS, one of the main difficulty related to Ni hydroxide precipitation is that
 29 the precipitates obtained by NaOH addition (Eq. 13) are amorphous and porous due to the
 30 preferential precipitation of the amorphous polymorph α -Ni(OH)₂, which raises difficulties for
 31 filtration and lead to poor product quality [118]. As reviewed by Hall [119], the loose lamellar
 32 structure of this compound leads to large hydration and inclusion of ions such as SO₄²⁻. An option
 33 consists in adding aqueous ammonia in the solution, which leads to precipitation of spherical and
 34 dense Ni(OH)₂ particles. This is attributed to the formation of nickel ammine complexes that lower
 35 the activity of Ni ions and slow down the precipitation reaction with hydroxide ions (Eq. 14).



36 Consequently, in the late 2000s, several authors [34,78,120] used stoichiometric ammonia addition
 37 in sulfuric PLS to prepare Ni(OH)₂ precursors for battery manufacturing. Nan [34] precipitated
 38 Ni(OH)₂ particles at 50 °C and pH 10.7 by adding a (NaOH + NH_{3(aq)}) solution to a sulfuric PLS.
 39 Similarly Li [78] synthesized spherical Ni(OH)₂ at pH 11 and 60 °C and report low level of

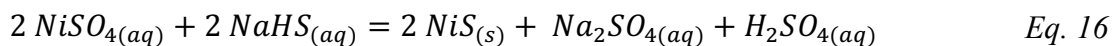
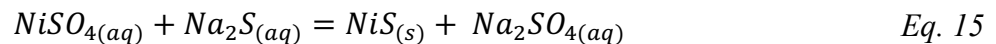
1 impurities. Kanamori [121] also used the complexation properties of ammonium in order to
 2 selectively extract Ni from a mixture of La, Co and Ni hydroxydes and further recovered Ni
 3 hydroxide after filtration.

4 *Table 7 – Overview of operating parameters and recovery yields obtained for nickel and cobalt*
 5 *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 ·H ₂ O (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]
Diacetyldioxime / NiO Na ₂ S / NiS, CoS	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]
NiO Na ₂ S / NiS, CoS	Not specified Thermal decomposition at 400 °C to obtain NiO	Not mentioned	[45]
NaSH / NiS, CoS	Addition of Na ₂ S 200 g/L 2 < pH regulated < 4 T = 25 °C Pilot scale tests (400 L) with NaHS 300 g/L pH = 3.0 Room Temperature	Yields at pH = 3: Ni 99.8%, Co 99.9%	[32]
		Yields : Ni 98.1% and Co 96.1% Impurities: Y 0.049%, La 0.007%, Ce 0.003%	[32]
Chloride media			
NH ₃ + NaOH / Ni(OH) ₂	5 M NH ₃ solution + air bubbling T = 80 °C	Not mentioned	[120]
(NH ₄) ₂ C ₂ O ₄ / CoC ₂ O ₄ and NiC ₂ O ₄	Addition of oxalate into Co HCl strip solution at pH = 2 ; Addition of oxalate to the raffinate to recover Ni Adjustment of pH to 2 with 6 M NaOH to a solution free of REEs and Co ; Addition of 0.3M (NH ₄) ₂ C ₂ O ₄ T = 60 °C	Co yield : 98.5% Ni yield : 99.9%	[79,86]
		Ni yield 99.5% Impurities : Co < 1%, Mn < 4%	[40]

6

7 Very recently, Takano [32] proposed an alternative way consisting in preparing mixed nickel and
 8 cobalt sulfide compounds by precipitation with Na₂S or NaHS according to *Eq. 15* and *Eq. 16*.
 9 The authors recommend to increase pH to 3 after selective REEs removal with Na₂SO₄. They
 10 performed pilot scale tests with 400 L of PLS containing 14 g/L of Ni and 1.5 g/L of Co and report
 11 high recovery yields (>96%). The obtained mixed sulfide can then be use as secondary raw
 12 materials in existing nickel refineries.



13 It is interesting to note that, to our knowledge, no trial to separate Ni, Co and Mn by selective
 14 precipitation has been reported. The separation of Co, Mn and Ni from mixed hydroxides has for
 15 instance been explored by Vaughan and coll. [122,123] by sulfuric acid leaching and selective
 16 oxidative precipitation (with Na₂S₂O₈ or O₃) in the frame of nickel laterite ores processing.
 17 Furthermore, several works related to LiBs processing focused on Ni, Co and Mn separation using
 18 strong oxidants (e.g. NaClO [124], Na₂S₂O₈ [125], Ni(OH)₃ [126]) and careful pH control. These
 19 routes, based on the use of an oxidizing agent capable to oxidize Mn²⁺ to Mn⁴⁺ and Co²⁺ to Co³⁺,

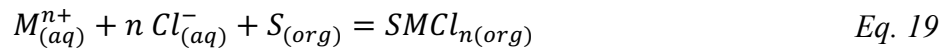
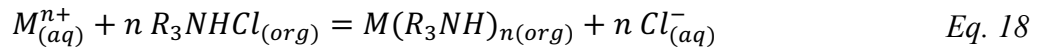
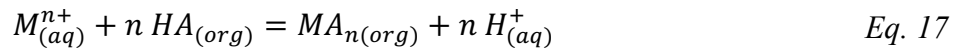
1 have been barely considered in the case of NiMH batteries. First attempts by Ricknell [127] led to
2 high losses of Ni.

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

9 4.3 Solvent extraction

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

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



21

22 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				
	NiMH leachate in H ₂ SO 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 ₂ SO 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 ₂ SO 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]
D2EHPA /P204	NiMH leachate in H ₂ SO 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 ₂ SO 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 ₂ SO 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 ₂ SO 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 and 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 ₂ SO 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 ₂ SO 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 ₂ SO 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 ₂ SO 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 ₂ SO 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 ₂ SO 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 ₂ SO ₄ with prior precipitation of REEs, Al, Fe		2 stages at pH = 5.1-5.3 97% Co	[105]
	NiMH leachate in H ₂ SO ₄ with prior precipitation of REEs		1 stage at pH = 5.7 Co > 95% Ni < 5%	[46]
Cyanex 272	Raffinate in H ₂ SO 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 ₂ SO ₄ with previous SX step		6 stages at pH = 4.8 Co > 98% Ni < 1%	[79]
	Raffinate in H ₂ SO ₄ with previous SX step		1 stage at pH = 4.7 Co 97% Ni 5%	[104]
	Raffinate in H ₂ SO 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 ₂ SO 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 ₂ SO 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

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

6 4.3.1 Extraction of metal impurities (Fe, Al, Zn, Mn, Cd)

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

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

24 4.3.2 Extraction of REEs

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

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

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

8 **4.3.3 Extraction and separation of Ni and Co**

9 Separation of Ni from Co aqueous compounds is a challenge due to their close chemical properties.
10 However, Co(II) has a higher tendency to form stable complexes with ligands, and solvent
11 extraction is thus one of the only method that allows to perform an efficient separation.
12 Accordingly, several works devoted to Ni and Co separation in sulfuric PLS have been carried out
13 by extracting Co with Cyanex 272 (Table 8), at pH around 4.7-5.7. In these studies, the leachates
14 were purified from other metal impurities and REEs in preliminary steps, either by precipitation
15 [46,105] or by solvent extraction [48,78,79,104], in order to obtain pure Co in the organic phase.
16 Especially, it has been shown that Co extraction with Cyanex 272 was not selective over Mn
17 [48,97]. Petranikova [134] recently managed to produce a pure Co solution from a Ni depleted
18 strip solution using Cyanex 301 as an alternative to Cyanex 272.

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

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

27 Finally, some attempts using ionic liquids (Cyphos IL 101 and 104) have been reported, which
28 offer the opportunity to extract Co, Mn, Fe and Zn directly from the 8 M HCl leachate, while
29 leaving REEs and Ni in the aqueous phase [133].
30

31 **4.3.4 Alternative extraction systems**

32 Although solvent extraction offers many options in the view of element separation, this technique
33 has not been scaled up for battery recycling yet, notably because of the high amount of chemicals
34 (mineral and organic solvents, extractants), the number of stages and operations required for this
35 process. It can be mentioned that several groups have very recently investigated alternative
36 extraction methods, based on aqueous two-phase systems, to process NiMH leachates without
37 large use of organic solvents. Polypropylene glycol-425 [138] and pluronic triblock copolymers
38 [139,140] were investigated for Fe/Ni, Co/Ni and even full Co/Ni/La/Ce separations. Furthermore,
39 adsorption and ion exchange methods, which are commonly used for Ni and REEs extraction or
40 pre-concentrations from primary and secondary sources [141,142], have been considered as an
41 alternative to solvent extraction for both Ni and REEs recovery from NiMH batteries leachates.
42 The main potential advantage put forward by the authors is to avoid the consumption of large
43 quantities of solvents. As summarized in Table 9, four types of systems have been considered so
44 far: two commercial resins (Purolite and Diphonix) [67,72,143], an activated charcoal [55] and a

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

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

System / Functional groups	Media	Metal elements concentration	Main results	Ref.
Layered double hydroxydes / hydroxydes Purolite S957 resin / phosphonic and sulfonic Diphonix resin	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 ₂ O ₃)	[144]
diphosphonic, sulfonic and carboxylic Diphonix / diphosphonic, sulfonic and carboxylic Purolite S957	Synthetic solution in citric acid, pH = 5	0.6 g/L of Ni and La	Efficient adsorption (almost 100%) of Ni and La	[67]
phosphonic and sulfonic LIX-841 activated charcoal / oxime	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]
	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]

5

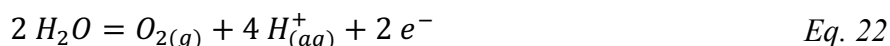
6 **4.4 Electrowinning of Ni and Co**

7 **4.4.1 Principles of industrial electrowinning**

8 Nickel electrowinning from pure sulfuric or hydrochloric leach liquors is implemented at industrial
 9 scale in primary nickel metal production and accounts for about half of the total world production
 10 [126]. The metal formation at the cathode occurs according to *Eq. 20*, with concurrent H⁺ reduction
 11 according to *Eq. 21*.

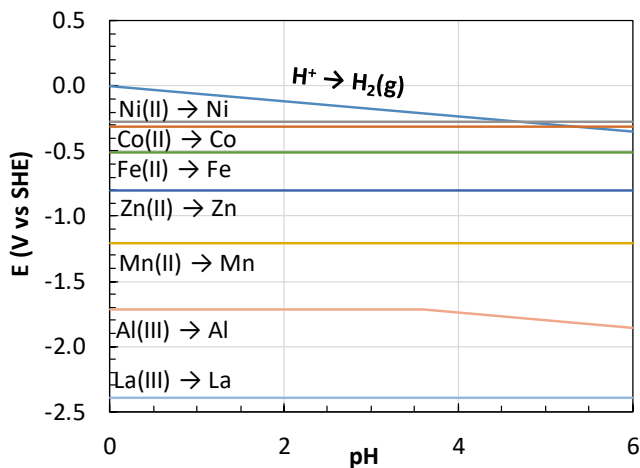


12 In sulfuric media, the anode reaction is the decomposition of water (*Eq. 22*), which implies the
 13 production of large amount of acid that is re-used for leaching processes. In hydrochloric media,
 14 the anodic reaction generates chlorine gas (*Eq. 23*) that is captured and also used for leaching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



16 The addition of boric acid (H₃BO₃) avoids pH increase near the cathode (preventing the formation
 17 of nickel hydroxide) and reduces the overpotential of the Ni deposition [147]. Electrochemical
 18 cells require a separating membrane in order to avoid a strong acidification near to the cathode,
 19 which would promote H⁺ reduction (*Eq. 21*) over Ni²⁺ (*Eq. 20*) and thus decrease the current
 20 efficiency.

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



8

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

11 4.4.2 Electrowinning of NiMH leachates

12 Table 10 gathers an overview of electrochemical studies focused on Ni-Co electrowinning
 13 involving NiMH leachates as starting solutions. Based on the existing industrial processes, most
 14 works implemented boric acid additions (20-30 g/L), a pH around 4, and used a membrane in order
 15 to separate the cell compartments [99,150–154]. Most authors prepared synthetic Ni-Co solutions
 16 to determine optimal conditions, and obtained dense deposits with high current efficiencies (>
 17 85%). Due to the close reduction potentials of Ni and Co (Figure 9), the co-deposition of Ni and
 18 Co is reported in all studies. Lupi [154] showed that, for a large range of Ni/Co concentration ratio
 19 in the electrolyte, good quality Ni-Co alloys can be obtained by electrowinning.

20 *Table 10 – Overview of electrochemical studies and operating parameters for nickel and cobalt*
 21 *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 ₃ BO 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 ₃ BO 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 ₃ BO ₄ + 34 g/L SO ₃ N ₂ H 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 ₃ BO 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 ₃ BO ₄ + 23 g/L SO ₃ N ₂ H 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 ₃ BO 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

1 However, several authors report that the presence of additional elements in the electrolyte, coming
2 from the NiMH batteries, was highly detrimental to the electrowinning process[99,153]. For
3 instance, Bertuol [99] obtained powdery deposits attributed to the presence of Zn in the electrolyte.
4 Tzanetakis [153] showed that low current densities (10 A/cm²) were required to obtain well
5 crystallized metallic phases, due to the inclusion of oxide or hydroxide impurities at higher current
6 densities. Several electrochemical studies confirmed that the presence of Zn²⁺ [152,155] or Na⁺
7 [155] in the electrolyte decreased current efficiencies. Tzanetakis [153] reports low Fe contents
8 (about 1 wt%) in the deposits, while the initial proportion is about 5 wt% in the electrolyte.
9 Conversely, it was shown that the presence of Mn in the electrolyte does not interfere with Ni and
10 Co electrodeposition [99,150], which is consistent with its low reduction potential (Figure 9).

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

14 5. Conclusion

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

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

Type of operation	Advantages	Drawbacks	Potential research directions
Pyrometallurgical methods			
Carbothermic reduction at high temperature	<ul style="list-style-type: none"> •Simplicity of operation •Large volumes 	<ul style="list-style-type: none"> •Carbon consumption & CO₂ release •Low purities of products 	<ul style="list-style-type: none"> •Alternative carbon sources or hydrogen usage

			<ul style="list-style-type: none"> •Improvement of slag composition
Leaching in acidic media			
Leaching in HCl	<ul style="list-style-type: none"> •High solubility of BM phases •Adapted for further solvent extraction methods 	<ul style="list-style-type: none"> •Corrosive properties of HCl •Low dissolution kinetics of Ni compounds •Not compatible with selective precipitation 	<ul style="list-style-type: none"> •Improvement of Ni leaching kinetics: initial thermal treatment, use of oxidant
Leaching in H ₂ SO ₄	<ul style="list-style-type: none"> •High chemical stability and low cost of the acid •Adapted for further selective precipitation methods 	<ul style="list-style-type: none"> •Limited solubility of REEs compounds •Low dissolution kinetics of Ni compounds 	
Leaching in organic acids	<ul style="list-style-type: none"> •Lower environmental footprint 	<ul style="list-style-type: none"> • Limited knowledge on solution and solid chemistry 	<ul style="list-style-type: none"> • Development of knowledge on solution and solid chemistry
Selective precipitation from H₂SO₄ PLS			
REEs selective precipitation	<ul style="list-style-type: none"> •Efficient and robust 	<ul style="list-style-type: none"> •Requires further treatment of REEs double sulfate salts 	<ul style="list-style-type: none"> •Improvement of methods for conversion of salts into pure REEs products •Evaluation of Cd behavior •Selective removal of Mn by oxidative treatment
Removal of impurities (Fe, Al, Zn, Cd, Mn)	<ul style="list-style-type: none"> •Efficient removal of Fe (and probably Al) by pH swing 	<ul style="list-style-type: none"> •No removal of Zn and Mn 	
Ni(OH) ₂ precipitation using ammonia	<ul style="list-style-type: none"> •Efficient •Good control of product properties 	<ul style="list-style-type: none"> •Constraint with ammonia use •No Co-Ni separation 	<ul style="list-style-type: none"> •Evaluation of selectivity on industrial PLS
NiS precipitation with Na ₂ S/NaHS	<ul style="list-style-type: none"> •Efficient 	<ul style="list-style-type: none"> •Product needs to be included in primary Ni refineries •No Co-Ni separation 	<ul style="list-style-type: none"> •Assessment of impurities behaviour
Solvent extraction from H₂SO₄ or HCl PLS			
Removal of impurities (Fe, Al, Zn, Cd, Mn) with DEHPA after REEs selective precipitation	<ul style="list-style-type: none"> •Removal of all impurities •Efficient to produce clean Ni-Co solution 	<ul style="list-style-type: none"> •Many stages required 	<ul style="list-style-type: none"> •Combination of solvent extraction and selective precipitation
Extraction of REEs and impurities by acidic extractant	<ul style="list-style-type: none"> •Efficient to produce clean Ni-Co solution 	<ul style="list-style-type: none"> •Many stages required •Low selectivity REEs vs impurities: not adapted for selective REEs recovery 	
Selective recovery of REEs by alkaline or ionic liquid extractants	<ul style="list-style-type: none"> •Efficient 	<ul style="list-style-type: none"> •Requires very acidic media (HCl 8M) •Complex flowsheet 	<ul style="list-style-type: none"> •Evaluation of solvent cost and losses
Co-Ni separation	<ul style="list-style-type: none"> •Efficient production of Co and Ni solutions 	<ul style="list-style-type: none"> •Requires very acidic media (HCl 8M) •Complex flowsheet 	<ul style="list-style-type: none"> • XX •Assess economical interest in relation with low Co content
Electrodeposition of Ni & Co			
Ni-Co co-deposition from HCl or H ₂ SO ₄ media	<ul style="list-style-type: none"> •Already implemented for primary Ni and Co production 	<ul style="list-style-type: none"> •Require a pure solution (especially free of Zn) •No Co-Ni separation 	<ul style="list-style-type: none"> •Demonstration that good quality Co-Ni deposits can be obtained from a Zn-free PLS

1
2
3
4
5
6
7
8
9
10

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.

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

7 Acknowledgments

8 The careful reading and comments of Nicolas Coppey (SNAM company) was greatly appreciated.

9 References

- 10 [1] W. Liu, T. Placke, K.T. Chau, Overview of batteries and battery management for electric
11 vehicles, *Energy Reports*. 8 (2022) 4058–4084. <https://doi.org/10.1016/j.egyr.2022.03.016>.
- 12 [2] S. Arya, S. Verma, Nickel-Metal Hydride (Ni-MH) Batteries, in: *Rechargeable Batteries:*
13 *History, Progress, and Applications*, Wiley Online Library, 2020: pp. 131–175.
14 <https://doi.org/10.1002/9781119714774.ch8>.
- 15 [3] L. Silvestri, A. Forcina, G. Arcese, G. Bella, Recycling technologies of nickel–metal
16 hydride batteries: An LCA based analysis, *Journal of Cleaner Production*. 273 (2020)
17 123083. <https://doi.org/10.1016/j.jclepro.2020.123083>.
- 18 [4] M.A.P. Mahmud, N. Huda, S.H. Farjana, C. Lang, Comparative Life Cycle Environmental
19 Impact Analysis of Lithium-Ion (LiIo) and Nickel-Metal Hydride (NiMH) Batteries,
20 *Batteries*. 5 (2019) 22. <https://doi.org/10.3390/batteries5010022>.
- 21 [5] Y. Zhao, O. Pohl, A.I. Bhatt, G.E. Collis, P.J. Mahon, T. Rütther, A.F. Hollenkamp, A
22 Review on Battery Market Trends, Second-Life Reuse, and Recycling, *Sustainable*
23 *Chemistry*. 2 (2021) 167–205. <https://doi.org/10.3390/suschem2010011>.
- 24 [6] K. Binnemans, P.T. Jones, T. Müller, L. Yurramendi, Rare Earths and the Balance Problem:
25 How to Deal with Changing Markets?, *Journal of Sustainable Metallurgy*. 4 (2018) 126–
26 146. <https://doi.org/10.1007/s40831-018-0162-8>.
- 27 [7] G. Xu, J. Yano, S. Sakai, Scenario analysis for recovery of rare earth elements from end-of-
28 life vehicles, *J Mater Cycles Waste Manag.* 18 (2016) 469–482.
29 <https://doi.org/10.1007/s10163-016-0487-y>.
- 30 [8] European Commission, Study on the EU’s list of Critical Raw Materials – Final Report,
31 (2020). <https://doi.org/10.2873/904613>.
- 32 [9] J. Wang, Y. Zhang, L. Yu, K. Cui, T. Fu, H. Mao, Effective separation and recovery of
33 valuable metals from waste Ni-based batteries: A comprehensive review, *Chemical*
34 *Engineering Journal*. 439 (2022) 135767. <https://doi.org/10.1016/j.cej.2022.135767>.
- 35 [10] K. Binnemans, P.T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton, M. Buchert,
36 Recycling of rare earths: a critical review, *Journal of Cleaner Production*. 51 (2013) 1–22.
37 <https://doi.org/10.1016/j.jclepro.2012.12.037>.
- 38 [11] C. Tunsu, M. Petranikova, M. Gergorić, C. Ekberg, T. Retegan, Reclaiming rare earth
39 elements from end-of-life products: A review of the perspectives for urban mining using
40 hydrometallurgical unit operations, *Hydrometallurgy*. 156 (2015) 239–258.
41 <https://doi.org/10.1016/j.hydromet.2015.06.007>.
- 42 [12] S. Al-Thyabat, T. Nakamura, E. Shibata, A. Iizuka, Adaptation of minerals processing
43 operations for lithium-ion (LiBs) and nickel metal hydride (NiMH) batteries recycling:
44 Critical review, *Minerals Engineering*. 45 (2013) 4–17.
45 <https://doi.org/10.1016/j.mineng.2012.12.005>.
- 46 [13] S. Pradhan, R. Nayak, S. Mishra, A review on the recovery of metal values from spent nickel
47 metal hydride and lithium-ion batteries, *Int. J. Environ. Sci. Technol.* (2021).
48 <https://doi.org/10.1007/s13762-021-03356-5>.

- 1 [14] V. Innocenzi, N.M. Ippolito, I. De Michelis, M. Prisciandaro, F. Medici, F. Vegliò, A review
2 of the processes and lab-scale techniques for the treatment of spent rechargeable NiMH
3 batteries, *Journal of Power Sources*. 362 (2017) 202–218.
4 <https://doi.org/10.1016/j.jpowsour.2017.07.034>.
- 5 [15] C.W. Bale, E. Bélisle, P. Chartrand, S.A. Deckerov, G. Eriksson, A.E. Gheribi, K. Hack, I.-
6 H. Jung, Y.-B. Kang, J. Melançon, A.D. Pelton, S. Petersen, C. Robelin, J. Sangster, P.
7 Spencer, M.-A. Van Ende, FactSage thermochemical software and databases, 2010–2016,
8 *Calphad*. 54 (2016) 35–53. <https://doi.org/10.1016/j.calphad.2016.05.002>.
- 9 [16] P. Wang, A. Anderko, R.D. Young, A speciation-based model for mixed-solvent electrolyte
10 systems, *Fluid Phase Equilibria*. 203 (2002) 141–176. [https://doi.org/10.1016/S0378-3812\(02\)00178-4](https://doi.org/10.1016/S0378-3812(02)00178-4).
- 11 [17] G. Das, M.M. Lencka, A. Eslamimanesh, P. Wang, A. Anderko, R.E. Riman, A. Navrotsky,
12 Rare earth sulfates in aqueous systems: Thermodynamic modeling of binary and
13 multicomponent systems over wide concentration and temperature ranges, *The Journal of*
14 *Chemical Thermodynamics*. 131 (2019) 49–79. <https://doi.org/10.1016/j.jct.2018.10.020>.
- 15 [18] P. Bernard, M. Lippert, Chapter 14 - Nickel–Cadmium and Nickel–Metal Hydride Battery
16 Energy Storage, in: P.T. Moseley, J. Garche (Eds.), *Electrochemical Energy Storage for*
17 *Renewable Sources and Grid Balancing*, Elsevier, Amsterdam, 2015: pp. 223–251.
18 <https://doi.org/10.1016/B978-0-444-62616-5.00014-0>.
- 19 [19] C. Glaize, S. Genies, Nickel–Metal Hydride Batteries, in: *Lead and Nickel Electrochemical*
20 *Batteries*, John Wiley & Sons, Ltd, 2012: pp. 251–271.
21 <https://doi.org/10.1002/9781118562659.ch7>.
- 22 [20] B. Dunn, H. Kamath, J.M. Tarascon, Electrical energy storage for the grid: A battery of
23 choices, *Science*. 334 (2011) 928–935. <https://doi.org/10.1126/science.1212741>.
- 24 [21] M. Buchert, Life Cycle Assessment (LCA) of Nickel Metal Hydride Batteries for HEV
25 Application, *International Journal of Life Cycle Assessment*. 21 (2010).
- 26 [22] R. Laucournet, E. Billy, Method for recovering metals contained in an Ni-MH battery,
27 WO2015071848A1, 2015.
- 28 [23] S.-L. Lin, K.-L. Huang, I.-C. Wang, I.-C. Chou, Y.-M. Kuo, C.-H. Hung, C. Lin,
29 Characterization of spent nickel–metal hydride batteries and a preliminary economic
30 evaluation of the recovery processes, *Journal of the Air & Waste Management Association*.
31 66 (2016) 296–306. <https://doi.org/10.1080/10962247.2015.1131206>.
- 32 [24] E.H. Tanabe, D.F. Schlemmer, M.L. Aguiar, G.L. Dotto, D.A. Bertuol, Recovery of
33 valuable materials from spent NIMH batteries using spouted bed elutriation, *Journal of*
34 *Environmental Management*. 171 (2016) 177–183.
35 <https://doi.org/10.1016/j.jenvman.2016.02.011>.
- 36 [25] K. Larsson, C. Ekberg, A. Ødegaard-Jensen, Dissolution and characterization of HEV
37 NiMH batteries, *Waste Management*. 33 (2013) 689–698.
38 <https://doi.org/10.1016/j.wasman.2012.06.001>.
- 39 [26] D.A. Bertuol, A.M. Bernardes, J.A.S. Tenório, Spent NiMH batteries: Characterization and
40 metal recovery through mechanical processing, *Journal of Power Sources*. 160 (2006)
41 1465–1470. <https://doi.org/10.1016/j.jpowsour.2006.02.091>.
- 42 [27] K. Korkmaz, M. Alemrajabi, Å.C. Rasmuson, K.M. Forsberg, Sustainable
43 Hydrometallurgical Recovery of Valuable Elements from Spent Nickel–Metal Hydride
44 HEV Batteries, *Metals*. 8 (2018) 1062. <https://doi.org/10.3390/met8121062>.
- 45 [28] M.R. Palacín, A. de Guibert, Why do batteries fail?, *Science*. 351 (2016) 1253292.
46 <https://doi.org/10.1126/science.1253292>.
- 47 [29] K. Huang, J. Li, Z. Xu, Enhancement of the recycling of waste Ni–Cd and Ni–MH batteries
48 by mechanical treatment, *Waste Management*. 31 (2011) 1292–1299.
49 <https://doi.org/10.1016/j.wasman.2011.01.006>.
- 50

- 1 [30] J.A.S. Tenório, D.C.R. Espinosa, Recovery of Ni-based alloys from spent NiMH batteries,
2 Journal of Power Sources. 108 (2002) 70–73. [https://doi.org/10.1016/S0378-7753\(02\)00007-1](https://doi.org/10.1016/S0378-7753(02)00007-1).
- 3
- 4 [31] H. Wang, B. Friedrich, Development of a Highly Efficient Hydrometallurgical Recycling
5 Process for Automotive Li–Ion Batteries, Journal of Sustainable Metallurgy. 1 (2015) 168–
6 178. <https://doi.org/10.1007/s40831-015-0016-6>.
- 7 [32] M. Takano, S. Asano, M. Goto, Recovery of nickel, cobalt and rare-earth elements from
8 spent nickel–metal-hydride battery: Laboratory tests and pilot trials, Hydrometallurgy. 209
9 (2022) 105826. <https://doi.org/10.1016/j.hydromet.2022.105826>.
- 10 [33] M. Zielinski, L. Cassayre, P. Floquet, M. Macouin, P. Destrac, N. Coppey, C. Foulet, B.
11 Biscans, A multi-analytical methodology for the characterization of industrial samples of
12 spent Ni-MH battery powders, Waste Management. 118 (2020) 677–687.
13 <https://doi.org/10.1016/j.wasman.2020.09.017>.
- 14 [34] J. Nan, D. Han, M. Yang, M. Cui, Dismantling, Recovery, and Reuse of Spent Nickel–Metal
15 Hydride Batteries, J. Electrochem. Soc. 153 (2006) A101.
16 <https://doi.org/10.1149/1.2133721>.
- 17 [35] K. Tang, A. Ciftja, der E.C. Van, S. Wilson, G. Tranell, Recycling of the rare earth oxides
18 from spent rechargeable batteries using waste metallurgical slags, Journal of Mining and
19 Metallurgy, Section B: Metallurgy. 49 (2013) 233–236.
- 20 [36] K. Korkmaz, M. Alemrajabi, Å. Rasmuson, K. Forsberg, Recoveries of Valuable Metals
21 from Spent Nickel Metal Hydride Vehicle Batteries via Sulfation, Selective Roasting, and
22 Water Leaching, J. Sustain. Metall. 4 (2018) 313–325. <https://doi.org/10.1007/s40831-018-0169-1>.
- 23
- 24 [37] B. Ebin, M. Petranikova, C. Ekberg, Physical separation, mechanical enrichment and
25 recycling-oriented characterization of spent NiMH batteries, J Mater Cycles Waste Manag.
26 20 (2018) 2018–2027. <https://doi.org/10.1007/s10163-018-0751-4>.
- 27 [38] A. Porvali, S. Ojanen, B.P. Wilson, R. Serna-Guerrero, M. Lundström, Nickel Metal
28 Hydride Battery Waste: Mechano-hydrometallurgical Experimental Study on Recycling
29 Aspects, J. Sustain. Metall. 6 (2020) 78–90. <https://doi.org/10.1007/s40831-019-00258-2>.
- 30 [39] V. Innocenzi, F. Vegliò, Recovery of rare earths and base metals from spent nickel-metal
31 hydride batteries by sequential sulphuric acid leaching and selective precipitations, Journal
32 of Power Sources. 211 (2012) 184–191. <https://doi.org/10.1016/j.jpowsour.2012.03.064>.
- 33 [40] A. Fernandes, J.C. Afonso, A.J.B. Dutra, Separation of nickel(II), cobalt(II) and lanthanides
34 from spent Ni-MH batteries by hydrochloric acid leaching, solvent extraction and
35 precipitation, Hydrometallurgy. 133 (2013) 37–43.
36 <https://doi.org/10.1016/j.hydromet.2012.11.017>.
- 37 [41] R. Farzana, K. Hassan, W. Wang, V. Sahajwalla, Selective synthesis of CuNi alloys using
38 waste PCB and NiMH battery, Journal of Environmental Management. 234 (2019) 145–
39 153. <https://doi.org/10.1016/j.jenvman.2018.11.099>.
- 40 [42] F. Liu, C. Peng, A. Porvali, Z. Wang, B.P. Wilson, M. Lundström, Synergistic Recovery of
41 Valuable Metals from Spent Nickel–Metal Hydride Batteries and Lithium-Ion Batteries,
42 ACS Sustainable Chem. Eng. 7 (2019) 16103–16111.
43 <https://doi.org/10.1021/acssuschemeng.9b02863>.
- 44 [43] P. Meshram, B.D. Pandey, T.R. Mankhand, Leaching of base metals from spent Ni–metal
45 hydride batteries with emphasis on kinetics and characterization, Hydrometallurgy. 158
46 (2015) 172–179. <https://doi.org/10.1016/j.hydromet.2015.10.028>.
- 47 [44] P. Meshram, B.D. Pandey, T.R. Mankhand, Process optimization and kinetics for leaching
48 of rare earth metals from the spent Ni–metal hydride batteries, Waste Management. 51
49 (2016) 196–203. <https://doi.org/10.1016/j.wasman.2015.12.018>.
- 50 [45] M.A. Rabah, F.E. Farghaly, M.A. Abd-El Motaleb, Recovery of nickel, cobalt and some
51 salts from spent Ni-MH batteries, Waste Management. 28 (2008) 1159–1167.
52 <https://doi.org/10.1016/j.wasman.2007.06.007>.

- 1 [46] L.E.O.C. Rodrigues, M.B. Mansur, Hydrometallurgical separation of rare earth elements,
2 cobalt and nickel from spent nickel–metal–hydride batteries, *Journal of Power Sources*. 195
3 (2010) 3735–3741. <https://doi.org/10.1016/j.jpowsour.2009.12.071>.
- 4 [47] A. Porvali, B.P. Wilson, M. Lundström, Lanthanide-alkali double sulfate precipitation from
5 strong sulfuric acid NiMH battery waste leachate, *Waste Management*. 71 (2018) 381–389.
6 <https://doi.org/10.1016/j.wasman.2017.10.031>.
- 7 [48] G. Granata, F. Pagnanelli, E. Moscardini, Z. Takacova, T. Havlik, L. Toro, Simultaneous
8 recycling of nickel metal hydride, lithium ion and primary lithium batteries:
9 Accomplishment of European Guidelines by optimizing mechanical pre-treatment and
10 solvent extraction operations, *Journal of Power Sources*. 212 (2012) 205–211.
11 <https://doi.org/10.1016/j.jpowsour.2012.04.016>.
- 12 [49] S. Srivastava, O.N. Srivastava, Synthesis, characterization and hydrogenation behaviour of
13 composite hydrogen storage alloys, LaNi₅/La₂Ni₇, LaNi₃, *Journal of Alloys and
14 Compounds*. 282 (1999) 197–205. [https://doi.org/10.1016/S0925-8388\(98\)00741-5](https://doi.org/10.1016/S0925-8388(98)00741-5).
- 15 [50] T. Müller, B. Friedrich, Development of a recycling process for nickel-metal hydride
16 batteries, *Journal of Power Sources*. 158 (2006) 1498–1509.
17 <https://doi.org/10.1016/j.jpowsour.2005.10.046>.
- 18 [51] T. Tirronen, D. Sukhomlinov, H. O'Brien, P. Taskinen, M. Lundström, Distributions of
19 lithium-ion and nickel-metal hydride battery elements in copper converting, *Journal of
20 Cleaner Production*. 168 (2017) 399–409. <https://doi.org/10.1016/j.jclepro.2017.09.051>.
- 21 [52] R. Wang, J. Yan, Z. Zhou, X. Gao, D. Song, Z. Zhou, Regeneration of hydrogen storage
22 alloy in spent nickel–metal hydride batteries, *Journal of Alloys and Compounds*. 336 (2002)
23 237–241. [https://doi.org/10.1016/S0925-8388\(01\)01862-X](https://doi.org/10.1016/S0925-8388(01)01862-X).
- 24 [53] M. Assefi, S. Maroufi, Y. Yamauchi, V. Sahajwalla, Pyrometallurgical recycling of Li-ion,
25 Ni–Cd and Ni–MH batteries: A minireview, *Current Opinion in Green and Sustainable
26 Chemistry*. 24 (2020) 26–31. <https://doi.org/10.1016/j.cogsc.2020.01.005>.
- 27 [54] ACerS – NIST, Phase Equilibria Diagrams, NIST Standard Reference Database 31, version
28 4.1, (2016).
- 29 [55] X. Lan, J. Gao, Y. Li, Z. Guo, Thermodynamics and kinetics of REEs in CaO–SiO₂–CaF₂–
30 Ce₂O₃ system: A theoretical basis toward sustainable utilization of REEs in REE-Bearing
31 slag, *Ceramics International*. 47 (2021) 6130–6138.
32 <https://doi.org/10.1016/j.ceramint.2020.10.192>.
- 33 [56] Y. Jiang, Y. Deng, W. Bu, Pyrometallurgical Extraction of Valuable Elements in Ni-Metal
34 Hydride Battery Electrode Materials, *Metall Mater Trans B*. 46 (2015) 2153–2157.
35 <https://doi.org/10.1007/s11663-015-0362-6>.
- 36 [57] Y. Deng, S. Wu, Y. Jiang, S. Jia, Study on Viscosity of the La₂O₃-SiO₂-Al₂O₃ Slag
37 System, *Metall Mater Trans B*. 47 (2016) 2433–2439. [https://doi.org/10.1007/s11663-016-
0711-0](https://doi.org/10.1007/s11663-016-
38 0711-0).
- 39 [58] Y. Deng, W. Xin, Y. Jiang, P. Wang, Y. Yuan, Experimental Study on Recovering Rare
40 Earths from Separation Slag of Ni–Metal Hydride Battery Wastes by Hydrochloric Acid
41 Leaching, *Trans Indian Inst Met*. 73 (2020) 2529–2538. [https://doi.org/10.1007/s12666-
020-02057-w](https://doi.org/10.1007/s12666-
42 020-02057-w).
- 43 [59] C.-J. Kim, H.-S. Yoon, K.W. Chung, J.-Y. Lee, S.-D. Kim, S.M. Shin, S.-J. Lee, A.-R. Joe,
44 S.-I. Lee, S.-J. Yoo, S.-H. Kim, Leaching kinetics of lanthanum in sulfuric acid from rare
45 earth element (REE) slag, *Hydrometallurgy*. 146 (2014) 133–137.
46 <https://doi.org/10.1016/j.hydromet.2014.04.003>.
- 47 [60] E.G. Polyakov, A.S. Sibilev, Recycling Rare-Earth-Metal Wastes by Pyrometallurgical
48 Methods, *Metallurgist*. 59 (2015) 368–373. <https://doi.org/10.1007/s11015-015-0111-8>.
- 49 [61] T. Kuzuya, S. Hirai, V.V. Sokolov, Recovery of valuable metals from a spent nickel–metal
50 hydride battery: Selective chlorination roasting of an anodic active material with CCl₄ gas,
51 *Separation and Purification Technology*. 118 (2013) 823–827.
52 <https://doi.org/10.1016/j.seppur.2013.08.008>.

- 1 [62] S. Mir, N. Shukla, N. Dhawan, Investigation of Microwave and Thermal Processing of
2 Electrode Material of End-of-Life Ni-MH Battery, *JOM.* (2021).
3 <https://doi.org/10.1007/s11837-020-04530-9>.
- 4 [63] S. Maroufi, R.K. Nekouei, R. Hossain, M. Assefi, V. Sahajwalla, Recovery of Rare Earth
5 (i.e., La, Ce, Nd, and Pr) Oxides from End-of-Life Ni-MH Battery via Thermal Isolation,
6 *ACS Sustainable Chem. Eng.* 6 (2018) 11811–11818.
7 <https://doi.org/10.1021/acssuschemeng.8b02097>.
- 8 [64] P.R. Behera, R. Farzana, V. Sahajwalla, Reduction of oxides obtained from waste Ni-MH
9 battery's positive electrode using waste plastics to produce nickel based alloy, *Journal of*
10 *Cleaner Production.* 249 (2020) 119407. <https://doi.org/10.1016/j.jclepro.2019.119407>.
- 11 [65] B. Ebin, M.I. Isik, Chapter 5 - Pyrometallurgical Processes for the Recovery of Metals from
12 WEEE, in: A. Chagnes, G. Cote, C. Ekberg, M. Nilsson, T. Retegan (Eds.), *WEEE*
13 *Recycling*, Elsevier, 2016: pp. 107–137. [https://doi.org/10.1016/B978-0-12-803363-](https://doi.org/10.1016/B978-0-12-803363-0.00005-5)
14 [0.00005-5](https://doi.org/10.1016/B978-0-12-803363-0.00005-5).
- 15 [66] M. Landa-Castro, J. Aldana-González, M.G. Montes de Oca-Yemha, M. Romero-Romo,
16 E.M. Arce-Estrada, M. Palomar-Pardavé, Ni–Co alloy electrodeposition from the cathode
17 powder of Ni-MH spent batteries leached with a deep eutectic solvent (reline), *Journal of*
18 *Alloys and Compounds.* 830 (2020) 154650.
19 <https://doi.org/10.1016/j.jallcom.2020.154650>.
- 20 [67] K. Araucz, A. Aurich, D. Kołodyńska, Novel multifunctional ion exchangers for metal ions
21 removal in the presence of citric acid, *Chemosphere.* 251 (2020) 126331.
22 <https://doi.org/10.1016/j.chemosphere.2020.126331>.
- 23 [68] A.A.L. Marins, L.M. Boasquevisque, E.J.B. Muri, M.B.J.G. Freitas, Environmentally
24 friendly recycling of spent Ni–MH battery anodes and electrochemical characterization of
25 nickel and rare earth oxides obtained by sol–gel synthesis, *Materials Chemistry and Physics.*
26 280 (2022) 125821. <https://doi.org/10.1016/j.matchemphys.2022.125821>.
- 27 [69] H. Rueda, M. Arenas, R. Vargas-Balda, S. Blanco, P. Delvasto, Production of a nickel-based
28 catalyst for urea electrooxidation using spent batteries as raw material: Electrochemical
29 synthesis and implications from a circular economy stand-point, *Sustainable Materials and*
30 *Technologies.* 29 (2021) e00296. <https://doi.org/10.1016/j.susmat.2021.e00296>.
- 31 [70] P.R. Gismonti, J.F. Paulino, J. Afonso, Recovery of metals from electroactive components
32 of spent ni-mh batteries after leaching with formic acid, *Detritus.* (2021) 68.
33 <https://doi.org/10.31025/2611-4135/2021.14063>.
- 34 [71] A.A.L. Marins, S.G. Banhos, P.C.M. Cruz, R.V. Rodrigues, L. Marciniak, E.J.B. Muri, W.
35 Stręk, M.B.J.G. de Freitas, Synthesis of Ni and rare earth metal (La, Pr, and Nd) oxides
36 from spent Ni–MH batteries by selective precipitation with formic acid an investigation of
37 photoluminescence properties, *Ionics.* 26 (2020) 311–321. [https://doi.org/10.1007/s11581-](https://doi.org/10.1007/s11581-019-03158-3)
38 [019-03158-3](https://doi.org/10.1007/s11581-019-03158-3).
- 39 [72] D. Fila, Z. Hubicki, D. Kołodyńska, Recovery of metals from waste nickel-metal hydride
40 batteries using multifunctional Diphonix resin, *Adsorption.* 25 (2019) 367–382.
41 <https://doi.org/10.1007/s10450-019-00013-9>.
- 42 [73] A.A.L. Marins, S.G. Banhos, E.J.B. Muri, R.V. Rodrigues, P.C.M. Cruz, M.B.J.G. Freitas,
43 Synthesis by coprecipitation with oxalic acid of rare earth and nickel oxides from the anode
44 of spent Ni–MH batteries and its electrochemical properties, *Materials Chemistry and*
45 *Physics.* 242 (2020) 122440. <https://doi.org/10.1016/j.matchemphys.2019.122440>.
- 46 [74] P. Rasoulnia, R. Barthen, K. Valtonen, A.-M. Lakaniemi, Impacts of Phosphorous Source
47 on Organic Acid Production and Heterotrophic Bioleaching of Rare Earth Elements and
48 Base Metals from Spent Nickel-Metal-Hydride Batteries, *Waste Biomass Valor.* 12 (2021)
49 5545–5559. <https://doi.org/10.1007/s12649-021-01398-x>.
- 50 [75] P. Rasoulnia, R. Barthen, J.A. Puhakka, A.-M. Lakaniemi, Leaching of rare earth elements
51 and base metals from spent NiMH batteries using gluconate and its potential bio-oxidation

- 1 products, *Journal of Hazardous Materials*. 414 (2021) 125564.
2 <https://doi.org/10.1016/j.jhazmat.2021.125564>.
- 3 [76] M. Zielinski, L. Cassayre, P. Destrac, N. Coppey, G. Garin, B. Biscans, Leaching
4 Mechanisms of Industrial Powders of Spent Nickel Metal Hydride Batteries in a Pilot-Scale
5 Reactor, *ChemSusChem*. 13 (2020) 616–628. <https://doi.org/10.1002/cssc.201902640>.
- 6 [77] M. Petranikova, I. Herdzik-Koniecko, B.-M. Steenari, C. Ekberg, Hydrometallurgical
7 processes for recovery of valuable and critical metals from spent car NiMH batteries
8 optimized in a pilot plant scale, *Hydrometallurgy*. 171 (2017) 128–141.
9 <https://doi.org/10.1016/j.hydromet.2017.05.006>.
- 10 [78] L. Li, S. Xu, Z. Ju, F. Wu, Recovery of Ni, Co and rare earths from spent Ni–metal hydride
11 batteries and preparation of spherical Ni(OH)₂, *Hydrometallurgy*. 100 (2009) 41–46.
12 <https://doi.org/10.1016/j.hydromet.2009.09.012>.
- 13 [79] P. Zhang, T. Yokoyama, O. Itabashi, Y. Wakui, T.M. Suzuki, K. Inoue, Recovery of metal
14 values from spent nickel–metal hydride rechargeable batteries, *Journal of Power Sources*.
15 77 (1999) 116–122. [https://doi.org/10.1016/S0378-7753\(98\)00182-7](https://doi.org/10.1016/S0378-7753(98)00182-7).
- 16 [80] D.A. Bertuol, A.M. Bernardes, J.A.S. Tenório, Spent NiMH batteries—The role of selective
17 precipitation in the recovery of valuable metals, *Journal of Power Sources*. 193 (2009) 914–
18 923. <https://doi.org/10.1016/j.jpowsour.2009.05.014>.
- 19 [81] L. Pietrelli, B. Bellomo, D. Fontana, M.R. Montereali, Rare earths recovery from NiMH
20 spent batteries, *Hydrometallurgy*. 66 (2002) 135–139. [https://doi.org/10.1016/S0304-386X\(02\)00107-X](https://doi.org/10.1016/S0304-386X(02)00107-X).
- 22 [82] L. Pietrelli, B. Bellomo, D. Fontana, M. Montereali, Characterization and leaching of NiCd
23 and NiMH spent batteries for the recovery of metals, *Waste Management*. 25 (2005) 221–
24 226. <https://doi.org/10.1016/j.wasman.2004.12.013>.
- 25 [83] C. Liu, Y. Deng, J. Chen, D. Zou, W. Su, Integrated Process To Recover NiMH Battery
26 Anode Alloy with Selective Leaching and Multistage Extraction, *Ind. Eng. Chem. Res.* 56
27 (2017) 7551–7558. <https://doi.org/10.1021/acs.iecr.7b01427>.
- 28 [84] A.R. Alonso, E.A. Pérez, G.T. Lapidus, R.M. Luna-Sánchez, Hydrometallurgical process
29 for rare earth elements recovery from spent Ni-HM batteries, *Canadian Metallurgical*
30 *Quarterly*. 54 (2015) 310–317. <https://doi.org/10.1179/1879139515Y.0000000013>.
- 31 [85] N. Tzanetakis, K. Scott, Recycling of nickel–metal hydride batteries. I: Dissolution and
32 solvent extraction of metals, *Journal of Chemical Technology & Biotechnology*. 79 (2004)
33 919–926. <https://doi.org/10.1002/jctb.1081>.
- 34 [86] P. Zhang, T. Yokoyama, O. Itabashi, Y. Wakui, T.M. Suzuki, K. Inoue, Hydrometallurgical
35 process for recovery of metal values from spent nickel-metal hydride secondary batteries,
36 *Hydrometallurgy*. 50 (1998) 61–75. [https://doi.org/10.1016/S0304-386X\(98\)00046-2](https://doi.org/10.1016/S0304-386X(98)00046-2).
- 37 [87] X. Yang, J. Zhang, X. Fang, Rare earth element recycling from waste nickel-metal hydride
38 batteries, *Journal of Hazardous Materials*. 279 (2014) 384–388.
39 <https://doi.org/10.1016/j.jhazmat.2014.07.027>.
- 40 [88] P. Holmberg, Recycling of Nickel Metal Hydride (NiMH) Batteries - Characterization and
41 Recovery of Nickel, AB5 Alloy and Cobalt, Thesis for the degree of licenciate of
42 engineering, Chalmers University of Technology, 2017.
43 <https://publications.lib.chalmers.se/records/fulltext/249441/249441.pdf>.
- 44 [89] A. Sobianowska-Turek, Hydrometallurgical recovery of metals: Ce, La, Co, Fe, Mn, Ni and
45 Zn from the stream of used Ni-MH cells, *Waste Management*. 77 (2018) 213–219.
46 <https://doi.org/10.1016/j.wasman.2018.03.046>.
- 47 [90] E.E. Abd El Aal, W. Zakria, A. Diab, S.M. Abd El Haleem, Inhibition of the hydrogen
48 evolution reaction on nickel in acidic chloride solutions, *Anti-Corrosion Methods and*
49 *Materials*. 48 (2001) 181–187. <https://doi.org/10.1108/00035590110391030>.
- 50 [91] E.E. Abd El Aal, W. Zakria, A. Diab, S.M. Abd El Haleem, Anodic dissolution of nickel in
51 acidic chloride solutions, *Journal of Materials Engineering and Performance*. 12 (2003)
52 172–178. <https://doi.org/10.1361/105994903770343312>.

- 1 [92] M.L. Kronenberg, J.C. Banter, E. Yeager, F. Hovorka, The Electrochemistry of Nickel,
2 Journal of The Electrochemical Society. 110 (1963) 1007.
3 <https://doi.org/10.1149/1.2425910>.
- 4 [93] A. Bengali, K. Nobe, Electrodissolution Kinetics of Nickel in Concentrated Acidic Chloride
5 Solutions, Journal of The Electrochemical Society. 126 (1979) 1118–1123.
6 <https://doi.org/10.1149/1.2129229>.
- 7 [94] G. Das, M.M. Lencka, A. Eslamimanesh, A. Anderko, R.E. Riman, Rare-earth elements in
8 aqueous chloride systems: Thermodynamic modeling of binary and multicomponent
9 systems in wide concentration ranges, Fluid Phase Equilibria. 452 (2017) 16–57.
10 <https://doi.org/10.1016/j.fluid.2017.08.014>.
- 11 [95] E.P. Lokshin, O.A. Tareeva, K.G. Ivlev, T.G. Kashulina, Solubility of Double Alkali Metal
12 (Na, K) Rare-Earth (La, Ce) Sulfates in Sulfuric-Phosphoric Acid Solutions at 20°C, Russ
13 J Appl Chem. 78 (2005) 1058–1063. <https://doi.org/10.1007/s11167-005-0449-y>.
- 14 [96] J. Lie, J.-C. Liu, Selective recovery of rare earth elements (REEs) from spent NiMH
15 batteries by two-stage acid leaching, Journal of Environmental Chemical Engineering. 9
16 (2021) 106084. <https://doi.org/10.1016/j.jece.2021.106084>.
- 17 [97] D.P. Mantuano, G. Dorella, R.C.A. Elias, M.B. Mansur, Analysis of a hydrometallurgical
18 route to recover base metals from spent rechargeable batteries by liquid–liquid extraction
19 with Cyanex 272, Journal of Power Sources. 159 (2006) 1510–1518.
20 <https://doi.org/10.1016/j.jpowsour.2005.12.056>.
- 21 [98] F. Wu, S. Xu, L. Li, S. Chen, G. Xu, J. Xu, Recovery of valuable metals from anode material
22 of hydrogen-nickel battery, Transactions of Nonferrous Metals Society of China. 19 (2009)
23 468–473. [https://doi.org/10.1016/S1003-6326\(08\)60297-6](https://doi.org/10.1016/S1003-6326(08)60297-6).
- 24 [99] D.A. Bertuol, F.D.R. Amado, H. Veit, J.Z. Ferreira, A.M. Bernardes, Recovery of Nickel
25 and Cobalt from Spent NiMH Batteries by Electrowinning, Chemical Engineering &
26 Technology. 35 (2012) 2084–2092. <https://doi.org/10.1002/ceat.201200283>.
- 27 [100] A. Porvali, V. Agarwal, M. Lundström, REE(III) recovery from spent NiMH batteries as
28 REE double sulfates and their simultaneous hydrolysis and wet-oxidation, Waste
29 Management. 107 (2020) 66–73. <https://doi.org/10.1016/j.wasman.2020.03.042>.
- 30 [101] N.K. Ahn, B. Swain, H.W. Shim, D.W. Kim, Recovery of rare earth oxide from waste NiMH
31 batteries by simple wet chemical valorization process, Metals. 9 (2019).
32 <https://doi.org/10.3390/met9111151>.
- 33 [102] M. Zielinski, L. Cassayre, N. Coppey, B. Biscans, Pilot-Scale Lanthanide Precipitation from
34 Sulfate-Based Spent Ni-MH Battery Leachates: Thermodynamic-Based Choice of
35 Operating Conditions, Crystal Growth & Design. 21 (2021) 5943–5954.
36 <https://doi.org/10.1021/acs.cgd.1c00834>.
- 37 [103] J. Monhemius, Precipitation diagrams for metal hydroxides, sulphides, arsenates and
38 phosphates., Trans Inst Min Metall Sect C. 86 (1977) 202–206.
- 39 [104] N.-K. Ahn, H.-W. Shim, D.-W. Kim, B. Swain, Valorization of waste NiMH battery through
40 recovery of critical rare earth metal: A simple recycling process for the circular economy,
41 Waste Management. 104 (2020) 254–261. <https://doi.org/10.1016/j.wasman.2020.01.014>.
- 42 [105] J. Nan, D. Han, M. Yang, M. Cui, X. Hou, Recovery of metal values from a mixture of spent
43 lithium-ion batteries and nickel-metal hydride batteries, Hydrometallurgy. 84 (2006) 75–
44 80. <https://doi.org/10.1016/j.hydromet.2006.03.059>.
- 45 [106] W. Zhang, A. Noble, B. Ji, Q. Li, Effects of contaminant metal ions on precipitation
46 recovery of rare earth elements using oxalic acid, Journal of Rare Earths. (2020).
47 <https://doi.org/10.1016/j.jre.2020.11.008>.
- 48 [107] K. Korkmaz, M. Alemrajabi, Å.C. Rasmuson, K.M. Forsberg, Separation of valuable
49 elements from NiMH battery leach liquor via antisolvent precipitation, Separation and
50 Purification Technology. 234 (2020) 115812.
51 <https://doi.org/10.1016/j.seppur.2019.115812>.

- 1 [108] H. Zhi, S. Ni, X. Su, W. Xie, H. Zhang, X. Sun, Separation and recovery of rare earth from
2 waste nickel-metal hydride batteries by phosphate based extraction-precipitation, *Journal of*
3 *Rare Earths*. (2021). <https://doi.org/10.1016/j.jre.2021.04.012>.
- 4 [109] N.-K. Ahn, B. Swain, H.-W. Shim, D.-W. Kim, Recovery of Rare Earth Oxide from Waste
5 NiMH Batteries by Simple Wet Chemical Valorization Process, *Metals*. 9 (2019) 1151.
6 <https://doi.org/10.3390/met9111151>.
- 7 [110] P.V.M. Dixini, V.G. Celante, M.F.F. Lelis, M.B.J.G. Freitas, Recycling of the anode from
8 spent Ni-MH batteries for synthesis of the lanthanide oxysulfide/oxysulfate compounds
9 used in an oxygen storage and release system, *Journal of Power Sources*. 260 (2014) 163–
10 168. <https://doi.org/10.1016/j.jpowsour.2014.03.006>.
- 11 [111] S. Luidold, Recovery of rare earth metals from waste material by leaching in non-oxidizing
12 acid and by precipitating using sulphates, EP 2444507 A1, 2012.
- 13 [112] Y. Xia, L. Xiao, J. Tian, Z. Li, L. Zeng, Recovery of rare earths from acid leach solutions
14 of spent nickel-metal hydride batteries using solvent extraction, *Journal of Rare Earths*. 33
15 (2015) 1348–1354. [https://doi.org/10.1016/S1002-0721\(14\)60568-8](https://doi.org/10.1016/S1002-0721(14)60568-8).
- 16 [113] P. Meshram, Abhilash, Recovery and Recycling of Cerium from Primary and Secondary
17 Resources- a Critical Review, *Mineral Processing and Extractive Metallurgy Review*. 41
18 (2020) 279–310. <https://doi.org/10.1080/08827508.2019.1677647>.
- 19 [114] R.D. Abreu, C.A. Morais, Purification of rare earth elements from monazite sulphuric acid
20 leach liquor and the production of high-purity ceric oxide, *Minerals Engineering*. 23 (2010)
21 536–540. <https://doi.org/10.1016/j.mineng.2010.03.010>.
- 22 [115] X. Yang, J. Zhang, X. Fang, Rare earth element recycling from waste nickel-metal hydride
23 batteries, *Journal of Hazardous Materials*. 279 (2014) 384–388.
24 <https://doi.org/10.1016/j.jhazmat.2014.07.027>.
- 25 [116] G. Granata, E. Moscardini, F. Pagnanelli, F. Trabucco, L. Toro, Product recovery from Li-
26 ion battery wastes coming from an industrial pre-treatment plant: Lab scale tests and process
27 simulations, *Journal of Power Sources*. 206 (2012) 393–401.
28 <https://doi.org/10.1016/j.jpowsour.2012.01.115>.
- 29 [117] V. Innocenzi, F. Veglio, Separation of manganese, zinc and nickel from leaching solution
30 of nickel-metal hydride spent batteries by solvent extraction, *Hydrometallurgy*. 129–130
31 (2012) 50–58. <https://doi.org/10.1016/j.hydromet.2012.08.003>.
- 32 [118] K. Funakoshi, S. Yoshizawa, M. Matsuoka, Continuous Precipitation of Nickel Hydroxide
33 by Addition of Ammonium Ions, *Crystal Growth & Design*. 16 (2016) 1824–1828.
34 <https://doi.org/10.1021/acs.cgd.5b00950>.
- 35 [119] D.S. Hall, D.J. Lockwood, C. Bock, B.R. MacDougall, Nickel hydroxides and related
36 materials: a review of their structures, synthesis and properties, *Proceedings of the Royal*
37 *Society A: Mathematical, Physical and Engineering Sciences*. 471 (2015) 20140792.
38 <https://doi.org/10.1098/rspa.2014.0792>.
- 39 [120] V.K. Jha, M. Miyake, Recovery of Nickel Oxide from Primary-type Portable Spent Battery:
40 an Experimental Strategy, *Nepal Journal of Science and Technology*. 12 (2011) 193–200.
41 <https://doi.org/10.3126/njst.v12i0.6499>.
- 42 [121] T. Kanamori, M. Matsuda, M. Miyake, Recovery of rare metal compounds from nickel–
43 metal hydride battery waste and their application to CH₄ dry reforming catalyst, *Journal of*
44 *Hazardous Materials*. 169 (2009) 240–245. <https://doi.org/10.1016/j.jhazmat.2009.03.079>.
- 45 [122] Z.T. Ichlas, M.Z. Mubarok, A. Magnalita, J. Vaughan, A.T. Sugiarto, Processing mixed
46 nickel-cobalt hydroxide precipitate by sulfuric acid leaching followed by selective oxidative
47 precipitation of cobalt and manganese, *Hydrometallurgy*. 191 (2020) 105185.
48 <https://doi.org/10.1016/j.hydromet.2019.105185>.
- 49 [123] K. Byrne, W. Hawker, J. Vaughan, Effect of key parameters on the selective acid leach of
50 nickel from mixed nickel-cobalt hydroxide, *AIP Conference Proceedings*. 1805 (2017)
51 030001. <https://doi.org/10.1063/1.4974412>.

- 1 [124] M. Joulié, R. Laucournet, E. Billy, Hydrometallurgical process for the recovery of high
2 value metals from spent lithium nickel cobalt aluminum oxide based lithium-ion batteries,
3 Journal of Power Sources. 247 (2014) 551–555.
4 <https://doi.org/10.1016/j.jpowsour.2013.08.128>.
- 5 [125] S.H. Joo, J. Kang, K. Woong, S.M. Shin, Production of Chemical Manganese Dioxide from
6 Lithium Ion Battery Ternary Cathodic Material by Selective Oxidative Precipitation of
7 Manganese, Materials Transactions. 54 (2013) 844–849.
8 <https://doi.org/10.2320/matertrans.M2012379>.
- 9 [126] D.G.E. Kerfoot, Nickel, in: Ullmann's Encyclopedia of Industrial Chemistry, John Wiley
10 & Sons, Ltd, 2000. https://doi.org/10.1002/14356007.a17_157.
- 11 [127] J. Ricknell, Recovery of valuable metals from spent HEV NiMH battery leach solutions,
12 Degree project, KTH Royal Institute of Technology, 2017.
13 <http://urn.kb.se/resolve?urn=urn:nbn:se:kth:diva-216397>.
- 14 [128] V. Agarwal, M.K. Khalid, A. Porvali, B.P. Wilson, M. Lundström, Recycling of spent
15 NiMH batteries: Integration of battery leach solution into primary Ni production using
16 solvent extraction, Sustainable Materials and Technologies. 22 (2019) e00121.
17 <https://doi.org/10.1016/j.susmat.2019.e00121>.
- 18 [129] B. Pospiech, J. Gega, Solvent Extraction of Metal Ions from Sulfate Solutions Obtained in
19 Leaching of Spent Ni-MH Batteries, New Trends in Production Engineering. 2 (2019) 214–
20 221. <https://doi.org/10.2478/ntpe-2019-0086>.
- 21 [130] K. Larsson, C. Ekberg, A. Ødegaard-Jensen, Using Cyanex 923 for selective extraction in
22 a high concentration chloride medium on nickel metal hydride battery waste,
23 Hydrometallurgy. 129–130 (2012) 35–42. <https://doi.org/10.1016/j.hydromet.2012.08.011>.
- 24 [131] K. Larsson, C. Ekberg, A. Ødegaard-Jensen, Using Cyanex 923 for selective extraction in
25 a high concentration chloride medium on nickel metal hydride battery waste: Part II: mixer-
26 settler experiments, Hydrometallurgy. 133 (2013) 168–175.
27 <https://doi.org/10.1016/j.hydromet.2013.01.012>.
- 28 [132] M.K. Jha, P.K. Choubey, O.S. Dinkar, R. Panda, R.K. Jyothi, K. Yoo, I. Park, Recovery of
29 Rare Earth Metals (REMs) from Nickel Metal Hydride Batteries of Electric Vehicles,
30 Minerals. 12 (2022) 34. <https://doi.org/10.3390/min12010034>.
- 31 [133] K. Larsson, K. Binnemans, Selective extraction of metals using ionic liquids for nickel metal
32 hydride battery recycling, Green Chem. 16 (2014) 4595–4603.
33 <https://doi.org/10.1039/C3GC41930D>.
- 34 [134] M. Petranikova, B. Ebin, C. Tunsu, Selective recovery of cobalt from the secondary streams
35 after NiMH batteries processing using Cyanex 301, Waste Management. 83 (2019) 194–
36 201. <https://doi.org/10.1016/j.wasman.2018.11.022>.
- 37 [135] A.A. Nayl, Extraction and separation of Co(II) and Ni(II) from acidic sulfate solutions using
38 Aliquat 336, Journal of Hazardous Materials. 173 (2010) 223–230.
39 <https://doi.org/10.1016/j.jhazmat.2009.08.072>.
- 40 [136] L.E.O.C. Rodrigues, M.B. Mansur, Hydrometallurgical separation of rare earth elements,
41 cobalt and nickel from spent nickel-metal-hydride batteries, Journal of Power Sources. 195
42 (2010) 3735–3741. <https://doi.org/10.1016/j.jpowsour.2009.12.071>.
- 43 [137] T.V. Hoogerstraete, K. Binnemans, Highly efficient separation of rare earths from nickel
44 and cobalt by solvent extraction with the ionic liquid trihexyl(tetradecyl)phosphonium
45 nitrate: a process relevant to the recycling of rare earths from permanent magnets and nickel
46 metal hydride batteries, Green Chemistry. 16 (2014) 1594–1606.
47 <https://doi.org/10.1039/C3GC41577E>.
- 48 [138] M.I. Fedorova, Y.A. Zakhodyaeva, A.E. Baranchikov, V.A. Krenev, A.A. Voshkin,
49 Extraction Reprocessing of Fe,Ni-Containing Parts of Ni–MH Batteries, Russ. J. Inorg.
50 Chem. 66 (2021) 266–272. <https://doi.org/10.1134/S003602362102008X>.

- 1 [139] S.J.R. Vargas, N. Schaeffer, J.C. Souza, L.H.M. da Silva, M.C. Hespanhol, Green separation
2 of lanthanum, cerium and nickel from waste nickel metal hydride battery, *Waste*
3 *Management*. 125 (2021) 154–162. <https://doi.org/10.1016/j.wasman.2021.02.038>.
- 4 [140] A. Valadares, C.F. Valadares, L.R. de Lemos, A.B. Mageste, G.D. Rodrigues, Separation
5 of cobalt and nickel in leach solutions of spent nickel-metal hydride batteries using aqueous
6 two-phase systems (ATPS), *Hydrometallurgy*. 181 (2018) 180–188.
7 <https://doi.org/10.1016/j.hydromet.2018.09.006>.
- 8 [141] V. Rychkov, E. Kirillov, S. Kirillov, G. Bunkov, M. Botalov, V. Semenishchev, D.
9 Smyshlyaev, A. Malyshev, A. Taukin, A. Akcil, Rare Earth Element Preconcentration from
10 Various Primary and Secondary Sources by Polymeric Ion Exchange Resins, *Separation &*
11 *Purification Reviews*. 0 (2021) 1–16. <https://doi.org/10.1080/15422119.2021.1993255>.
- 12 [142] A.B. Botelho Junior, D.B. Dreisinger, D.C.R. Espinosa, A Review of Nickel, Copper, and
13 Cobalt Recovery by Chelating Ion Exchange Resins from Mining Processes and Mining
14 Tailings, *Mining, Metallurgy & Exploration*. 36 (2019) 199–213.
15 <https://doi.org/10.1007/s42461-018-0016-8>.
- 16 [143] D. Kołodyńska, D. Fila, Z. Hubicki, Evaluation of possible use of the macroporous ion
17 exchanger in the adsorption process of rare earth elements and heavy metal ions from spent
18 batteries solutions, *Chemical Engineering and Processing - Process Intensification*. 147
19 (2020) 107767. <https://doi.org/10.1016/j.cep.2019.107767>.
- 20 [144] M.S. Gasser, M.I. Aly, Separation and recovery of rare earth elements from spent nickel–
21 metal-hydride batteries using synthetic adsorbent, *International Journal of Mineral*
22 *Processing*. 121 (2013) 31–38. <https://doi.org/10.1016/j.minpro.2013.02.012>.
- 23 [145] F. Odegbemi, G.A. Idowu, A.O. Adebayo, Nickel recovery from spent nickel-metal hydride
24 batteries using LIX-84I-impregnated activated charcoal, *Environmental Nanotechnology,*
25 *Monitoring & Management*. 15 (2021) 100452.
26 <https://doi.org/10.1016/j.enmm.2021.100452>.
- 27 [146] I.G. Sharma, P. Alex, A.C. Bidaye, A.K. Suri, Electrowinning of cobalt from sulphate
28 solutions, *Hydrometallurgy*. 80 (2005) 132–138.
29 <https://doi.org/10.1016/j.hydromet.2005.08.003>.
- 30 [147] C. Lupi, M. Pasquali, A. Dell’Era, Studies concerning nickel electrowinning from acidic
31 and alkaline electrolytes, *Minerals Engineering*. 19 (2006) 1246–1250.
32 <https://doi.org/10.1016/j.mineng.2006.04.002>.
- 33 [148] P. Taxil, L. Massot, C. Nourry, M. Gibilaro, P. Chamelot, L. Cassayre, Lanthanides
34 extraction processes in molten fluoride media: Application to nuclear spent fuel
35 reprocessing, *Journal of Fluorine Chemistry*. 130 (2009) 94–101.
36 <https://doi.org/10.1016/j.jfluchem.2008.07.004>.
- 37 [149] L. Cassayre, P. Palau, P. Chamelot, L. Massot, Properties of Low-Temperature Melting
38 Electrolytes for the Aluminum Electrolysis Process: A Review, *J. Chem. Eng. Data*. 55
39 (2010) 4549–4560. <https://doi.org/10.1021/je100214x>.
- 40 [150] C. Lupi, D. Pilone, Ni–MH spent batteries: a raw material to produce Ni–Co alloys, *Waste*
41 *Management*. 22 (2002) 871–874. [https://doi.org/10.1016/S0956-053X\(02\)00074-0](https://doi.org/10.1016/S0956-053X(02)00074-0).
- 42 [151] V.E.O. Santos, V.G. Celante, M.F.F. Lelis, M.B.J.G. Freitas, Chemical and electrochemical
43 recycling of the nickel, cobalt, zinc and manganese from the positives electrodes of spent
44 Ni–MH batteries from mobile phones, *Journal of Power Sources*. 218 (2012) 435–444.
45 <https://doi.org/10.1016/j.jpowsour.2012.07.024>.
- 46 [152] P.V.M. Dixini, V.C.B. Pegoretti, V.G. Celante, F.S. Betim, M.B.J.G. Freitas,
47 Electrodeposition study of simulated and dissolution solutions of the positive electrode of a
48 spent Ni-MH battery using the electrochemical quartz crystal microbalance and inductively
49 coupled plasma optical emission spectrometry, *Ionics*. 23 (2017) 3235–3243.
50 <https://doi.org/10.1007/s11581-017-2127-5>.

- 1 [153] N. Tzanetakis, K. Scott, Recycling of nickel–metal hydride batteries. II: Electrochemical
2 deposition of cobalt and nickel, *Journal of Chemical Technology & Biotechnology*. 79
3 (2004) 927–934. <https://doi.org/10.1002/jctb.1082>.
- 4 [154] C. Lupi, A. Dell’Era, M. Pasquali, Ni-Co Alloy Production from Secondary Spent Batteries
5 by Electrowinning, *Current Physical Chemistry*. 4 (2014) 324–329.
- 6 [155] S. Blanco, R. Orta-Rodriguez, P. Delvasto, Influence of Na⁺, K⁺, Mn²⁺, Fe²⁺ and Zn²⁺
7 ions on the electrodeposition of Ni-Co alloys: Implications for the recycling of Ni-MH
8 batteries, *J. Phys.: Conf. Ser.* 786 (2017) 012033. [https://doi.org/10.1088/1742-
9 6596/786/1/012033](https://doi.org/10.1088/1742-6596/786/1/012033).
- 10 [156] V. Innocenzi, F. Tortora, M. Prisciandaro, I. De Michelis, F. Vegliò, G. Mazziotti di Celso,
11 Purification of residual leach liquors from hydrometallurgical process of NiMH spent
12 batteries through micellar enhanced ultra filtration, *Journal of Environmental Management*.
13 215 (2018) 377–384. <https://doi.org/10.1016/j.jenvman.2018.03.073>.
- 14 [157] S. Maroufi, R.K. Nekouei, S.S. Mofarah, V. Sahajwalla, Nanoscale design of 1D metal
15 oxides derived from mixed Ni-MH battery/transition metal dust, *Journal of Hazardous
16 Materials*. 415 (2021) 125645. <https://doi.org/10.1016/j.jhazmat.2021.125645>.
- 17 [158] M. Assefi, S. Maroufi, Y. Yamauchi, V. Sahajwalla, Core–Shell Nanocatalysts of Co₃O₄
18 and NiO Shells from New (Discarded) Resources: Sustainable Recovery of Cobalt and
19 Nickel from Spent Lithium-Ion Batteries, Ni–Cd Batteries, and LCD Panel, *ACS
20 Sustainable Chem. Eng.* 7 (2019) 19005–19014.
21 <https://doi.org/10.1021/acssuschemeng.9b04618>.
22