# REE4EU: Integrated High Temperature Electrolysis (HTE) and Ion Liquid Extraction (ILE) for a Strong and Independent European Rare Earth Elements Supply Chain

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## D8.5 Report on the quality of REMA from the NiMH Battery

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## List of abbreviations and definitions

| Abbreviation | Definition |
|---|---|
| BM | Black mass |
| CAGR | Compound annual growth rate |
| HM | Hydrometallurgical |
| HTE | High temperature electrolysis |
| ILE | Ionic liquid extraction |
| MH | Metal hydride |
| Mm | Mischmetal, or rare earth metals mixture |
| NiMH | Nickel metal hydride |
| REA | Rare earth alloy/s |
| REE | Rare earth element/s |
| REMA | Rare earth master alloy/s |
| REO | Rare earth oxide/s |
| SoA | State of art |

# Executive Summary

The flexibility of the REE4EU pilot plant towards different waste streams was demonstrated in the replication activities related to the validation of the REE4EU's technology for rare earth alloy (REA) recovery from nickel metal hydride (NiMH) battery waste.

Then, the same ionic liquid extraction (ILE) and high temperature electrolysis (HTE) pilot units used for the permanent magnet waste were slightly adapted to accommodate the needs of this specific waste material.

Moreover, a pure hydrometallurgical (HM) upgrading process was demonstrated at pilot scale by SNAM. The REA obtained in the HM+HTE pilot units was compared to that obtained in the ILE+HTE pilot runs.

Both REA were characterised in terms of chemical composition and microstructure. The assessment of whether the REA was suited or not to be used in the manufacture of RE-based alloys for metal-hydride hydrogen storage, could only be done from a theoretical rather than a practical point of view, since there is not end-user from the battery value chain in the REE4EU consortium.

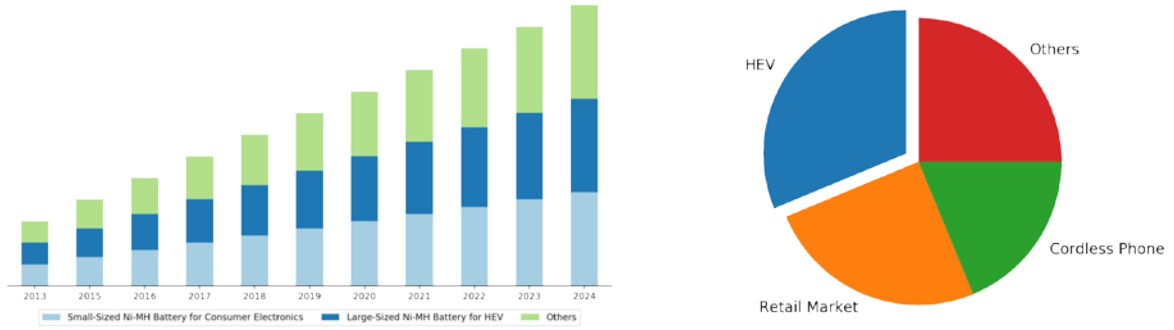
# 1 Introduction

Hydrogen storage alloys are important for a few electrochemical applications, especially in the energy storage area. The scientific principle lies on the fact that when hydrogen enters the lattice of most transition metals, interstitial metal hydride (MH) is formed.

The most important electrochemical application for MH is the negative electrode (anode) material for nickel metal hydride (NiMH) batteries, whose main implementation has shifted from consumer portable devices to hybrid electric vehicle and stationary applications (cf. Figure 1B).

After cadmium has been banned from most batteries because of its toxicity, the NiMH battery is the only alkaline electrolyte battery in widespread use. They have advantages of higher storage capacity compared to lead–acid and nickel–cadmium batteries, less toxicity than lead and cadmium, and lower cost than lithium-ion batteries.

Despite the current focus on Li-ion batteries in applications where high capacity and voltage per unit volume is required, recent data of global NiMH battery market size evolution by product still forecast a slight continuous increase (cf. Figure 1A). The global NiMH battery market is estimated to be of US$ 2120 million in 2019 [1]. However, it is forecasted that the market will be decelerating at a CAGR of nearly 3% [2].



(A) (B)

Figure 1. (A) Global NiMH battery market size evolution and forecast, by product type; (B) Global NiMH battery market share (%) by application. Data from 2019 [3].

The NiMH battery is a secondary battery (rechargeable) and consists of a M/MH electrode, a Nickel Hydroxide/Nickel Oxyhydroxide ($Ni(OH)_2/NiOOH$) electrode and a 20-30% KOH with some LiOH solution as electrolyte. The separators between electrodes are made of alkaline resistant plastics, mainly Polyamide or Polypropylene.

Most of the NiMH battery market are based on $AB_2$-type and $AB_5$-type compounds [4]. The $AB_5$ alloys combine a hydride forming metal A, usually a RE metal (La, Ce, Nd, Pr, Y or their mixture known as mischmetal, Mm), with a non-hydride forming element, usually a transition metal, most common Ni. The latter can be doped with other metals, such as Co, Sn or Al, to improve materials stability or to adjust equilibrium hydrogen pressure and temperature required for its charging/discharging with hydrogen [5].

Typical compositions of the NiMH batteries are shown in Figure 2. Considering the volume in Kg of NiMH in circulation (data from 2005 [6][1]), and that the recycling rate is of ca. 46% [7], the NiMH battery waste generated per year is estimated to potentially be 900 tonnes. Considering that wasted NiMH batteries can lead to 7-15% of black mass, with an average of ca. 12% REE content, 7.5-16 tonnes of REE could be potentially recovered from the spent NiMH battery waste.

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[1] Kg in circulation, data from 2005, Source [6]

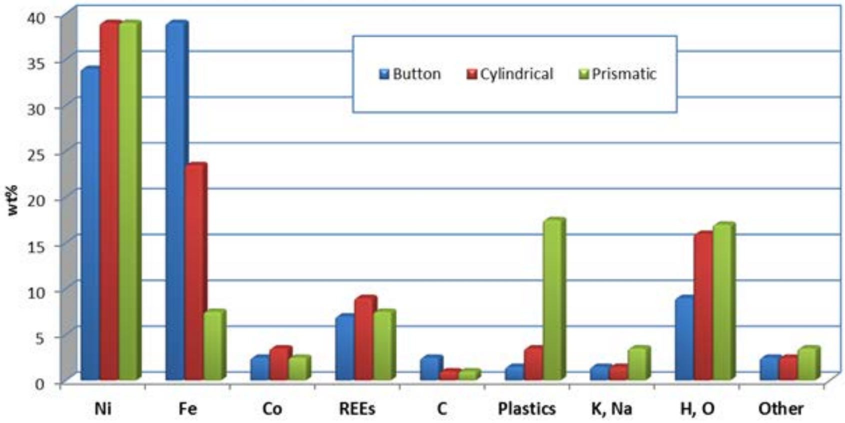

Figure 2. element composition of the different NiMH battery designs

The market potential for the recovery of REE from the NiMH battery waste is very much related to the REE market prices, which in the case of Ce and La is not as high as in the case of Nd or Pr (cf. Table 1). In addition, the prices of Ni and Co, which are valuable by-products in the recovery process, must be considered as well in the overall figures.

Table 1. Evolution of REE market prices. Source MineralPrices.com. Units $/kg (USD/RMB conversion rate from Sept. 2019)

| REE | Price 12 Sept 2019 | Price 31 Dec 2018 | Price difference |
|---|---|---|---|
| **La ( > 99%)** | 5.00 | 5.28 | - 5.3% |
| **Ce ( > 99%)** | 4.86 | 5.14 | - 5.44% |
| **Nd ( > 99.5%)** | 58.55 | 56.01 | + 4.53% |
| **Pr ( > 99%)** | 97.94 | 93.01 | + 5.3% |

## *1.1 $AB_5$ type alloys*

The $AB_5$ alloys combine a hydride forming metal A, usually a RE metal (La, Ce, Nd, Pr, Y or their mixture known as mischmetal, Mm) thus improving the hydrogen storage abilities of the alloy, with a non-hydride forming element, usually a transition metal, most common Ni, thus reducing the metal hydrogen bond strength. Partial substitution of Ni with other elements affects several factors such as structure, metal hydrogen bond strength, volume expansion during absorption, corrosion etc., and since these factors are correlated, it is hard to discuss how substitution of each element are affecting these factors [8]. Table 2 summarizes the effects of the individual elements suggested in the literature [9-15].

Table 2. Effect of individual elements in $AB_5$-type hydrogen storage alloys (from [9-15])

| Element | Effect |
|---|---|
| **RE** | Forms stable hydrides and improves hydrogen storage |
| **Ni** | Forms unstable hydrides and decreases the metal hydrogen bond strength |
| **Co** | Reduces corrosion rates |
| **Mn** | Tunes the metal hydrogen bond strength and improve hydrogen storage |
| **Al** | Reduces corrosion rates |

The most widely reported $AB_5$ composition is $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$. However, after over 40 years of research, many compositions, structures, processes, and electrode fabrication modifications have been performed. Efforts have been focused on reducing/eliminating expensive Co by introducing Fe and Cu, or substituting Ni by Cu, Fe and Mo. A review of the investigations on $AB_5$ alloys is given in a paper from BASF Battery Materials [16].

The Mm composition is a very important parameter in $AB_5$ type alloys. Typical composition is 20-30% La, 40-50% Ce, 10-20% Nd and 5-10% Pr [17]. The REE composition leads to a substantial change in the thermodynamic properties of the MM alloy, particularly in the equilibrium hydrogen plateau pressure, which markedly increases (meaning lower stability of the hydride) as a result of decreasing the La content. This is because the $AB_5$ lattice shrinks when La is replaced by smaller elements like Ce, Nd and Pr. Only a few studies on the Mm composition have been published. However, there has been no convincing literature data with regards to the optimum Mm composition, being proprietary information of the battery manufacturers.

## *1.2 Fabrication of MH electrodes for NiMH batteries*

Conventionally, and according to the available open literature, the $AB_5$ alloy powder undergoes an extensive preparation method consisting on arc melting under inert atmosphere stoichiometric amounts of the metallic elements, followed by annealing, and subsequent ball milling of the alloy powder in a glove box under argon atmosphere. The synthesized material can be then hydrogenated from gas phase at ca. 300 °C. Then the electrodes are prepared by cold pressing the mixture of MH powders with a conductive paste (usually carbon black) containing a thickener and a binder (usually polytetrafluoroethylene, PTFE) [18].

As above mentioned, the electrode fabrication has also undergone modifications through the years, seeking better performances and durability of the batteries. As the electrode composition, the fabrication procedures are proprietary information of the battery manufacturers.

# 2 Results

The flexibility of the REE4EU pilot plant towards different waste streams was demonstrated in the replication activities related to the validation of the REE4EU's technology for REA recovery from NiMH battery waste (cf. Figure 3).

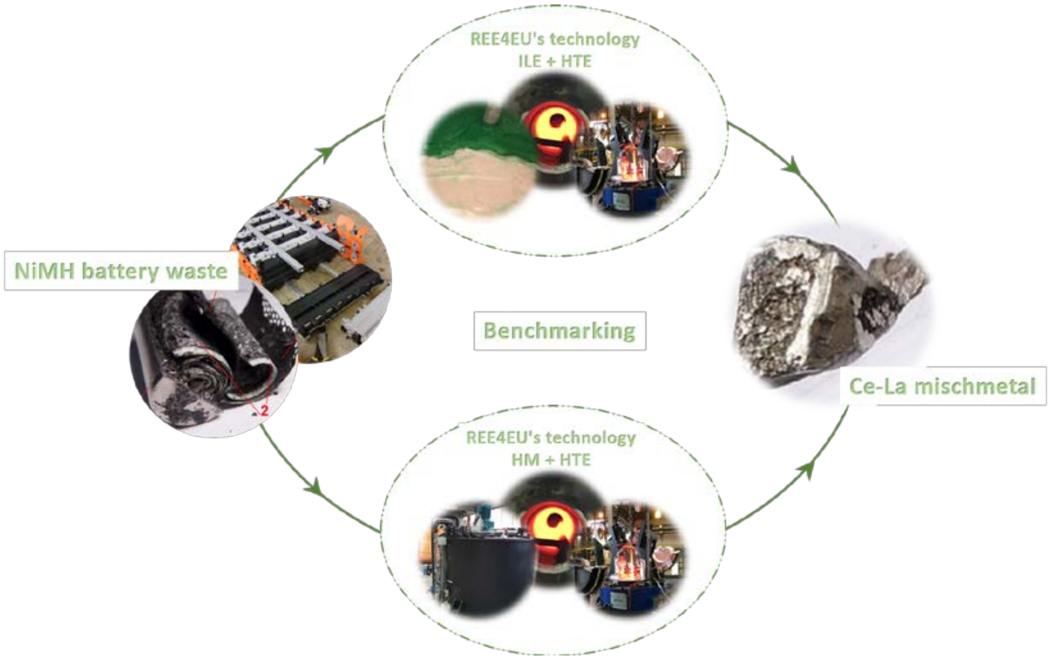

Figure 3. Replication activities of the REE4EU technology to the NiMH battery black mass

The ILE pilot unit previously used in the processing of permanent magnet (PM) waste, was slightly adapted to the new waste stream. A multidisciplinary design optimization (MDO) tool was used in order to predict the optimization of the operating parameters of the ILE pilot unit.

At the same time, the REO mixture obtained after the ILE unit was compared to the REO mixture obtained after the advanced HM up-grading processing of the NiMHB black mass at pilot scale, carried out by partner SNAM in the frame of the REE4EU project.

Both REO mixtures, were used in the HTE pilot unit in order to obtain a pure RE-Mm to be used in the manufacture of electrodes for new batteries, or other suitable applications. In this way, the REA Mm obtained from REO mixtures extracted by both ILE and HM methods were compared and benchmarked with SoA products.

The REE content of the REA obtained in the HTE pilot is given by the operating conditions, mainly working temperature. Moreover, the impurity content is dependent on the quality of the REO-feed obtained after the treatment of NiMH battery black mass by both the ILE and advanced HM process.

The results obtained in the frame of the REE4EU project when applying the REE4EU technology in the treatment of spent NiMH battery black mass showed that both the ILE and HM up-concentration steps need to be further optimized when running at pilot scale. In both cases, the positive results obtained at lab-scale were not possible to achieve at pilot scale, and the efficiencies in the recovery of REE were rather low. Moreover, the impurity content of the REO material obtained was high, especially in terms of Ni, Fe and Mn. This was affecting the HTE process, not only in terms of lowering the current efficiency of REE production, but also in the quality of the REA-Mm product.

## 2.1 REE composition of the Mm alloy obtained

As explained in the Introduction section, the Mm composition is a very important parameter in $AB_5$ type alloys. The final electrode composition is proprietary data of the battery producers, as it has a great impact in the battery performance and its lifetime.

The Mm alloy obtained in the REE4EU replication activities could be potentially used as raw material in the manufacture of electrodes for NiMH batteries, by adjusting the final REE composition according to the client's needs.

## 2.2 Mm alloy quality

The impurity content of the Mm alloy obtained in the HTE process is highly dependent on the quality of the REO obtained in the ILE and HM up-grading processes.

The impurity content of the REO material obtained was high, especially in terms of Ni, Fe and Mn. Due to the fact that there is a certain solubility of the different metal oxides in the molten fluoride electrolyte, and that the REE have a very negative reduction potential, the metallic oxides are dissolved as electroactive species and subsequently co-deposited at the cathode, together with the REA-Mm.

However, considering that the REMA to be used in NiMH battery electrodes has a certain content of Ni, Fe, Mn, Co, and Al, the REA-Mm obtained in the REE4EU pilot could potentially meet the required specifications.

Moreover, further refining of the Mm could possibly be carried out, if needed.

# 3 Conclusions

The flexibility of the REE4EU pilot plant towards different waste streams was demonstrated in the replication activities related to the validation of the REE4EU's technology for REA recovery from NiMH battery waste.

Both REO mixtures obtained after the ILE pilot runs at Elkem and the advanced HM pilot runs at SNAM, were used in the HTE pilot unit in order to obtain a pure REA (REE-Mm) to be used in the manufacture of electrodes for new batteries, or other suitable applications. The REA Mm obtained from both REO mixtures were compared and benchmarked with SoA products.

The Mm composition is a very important parameter in $AB_5$ type alloys used in MH hydrogen storage applications, like negative electrode (anode) material for NiMH batteries. Only a few studies on the Mm composition have been published, and there is no convincing literature data with regards to the optimum Mm composition, being proprietary information of the battery manufacturers.

The Mm alloy obtained in the REE4EU replication activities could be potentially used as raw material in the manufacture of electrodes for NiMH batteries, possibly after adjusting the final REE composition and other metallic elements according to the client's specifications.

However, the fact that there is not an end-user in the consortium (battery producer) hindered the assessment of the REMA by making real products, thus not being able to fully demonstrate a closed-loop battery recycling process, as it was done in the case of permanent magnets.

# 4 References

[1] https://www.marketwatch.com/press-release/ni-mh-battery-market-share-size-2019-global-industry-forecast-analysis-company-profiles-competitive-landscape-and-key-regions-2024-available-at-market-reports-world-2019-08-27 (accessed Sept 2019)

[2] Global NiMH battery market 2018-2022, Technavio (2018)

[3] www.marketintellica.com

[4] P. Ruetschi, F. Meli, J. Desilvestro, Journal of Power Sources, 57 (1-2) (1995) 85-91

[5] Battery Technology Handbook, H.A. Kiehne (Ed), Expert Verlag GmbH, Renningen-Malsheim, Germany, 2003

[6] "Battery recycling: defining the market and identifying the technology required to keep high value material in the economy and out of the waste dump" Report from NIST, 2017

[7] https://ec.europa.eu/eurostat/data/database

[8] T. Sakai, K. Oguro, H. Miyamura, N. Kuriyama, A. Kato, H. Ishikawa, and C. Iwakura, Journal of the Less Common Metals, 161(2) (1990) 193-202

[9] P. Ruetschi, F. Meli, and J. Desilvestro, Journal of Power Sources, 57(1-2) (1995) 85-91

[10] J.J. Reilly, G.D. Adzic, J.R. Johnson, T. Vogt, S. Mukerhee, and J. McBreen, Journal of Alloys and Compounds, 293-295 (20) (1999) 569-582

[11] J.J.G. Willems, and K.H.J Buschow, Journal of the Less Common Metals, 129 (1986) 13-30

[12] T. Sakai, H. Yoshinaga, H. Miyamura, N. Kuriyama, and H. Ishikawa, Journal of Alloys and Compounds, 180(1-2) (1992) 37-54

[13] J. Kleperis, G. Wójcik, A. Czerwinski, J.M. Skowronski, M. Kopczyk, and M. Beltowska-Brzezinska, Journal of Solid State Electrochemistry, 5 (20009 229-249

[14] A. Percheron-Guégan, C. Lartigue, J.C. Achard, P. Germi, and F. Tasset, Journal of the Less Common Metals, 74(1) (1980) 1-12

[15] P.A. Gregoriev, J. Liu, D.K. Ross, K.H. Andersen, and A. Otto, Journal of Alloys and Compounds,349 (2003) 325-333

[16] K-H. Young and J. Nei, Materials, 6 (2013) 4574-4608

[17] T. Sakai, M. Matsuoka and C. Iwakura, in Handbook on the Physics and Chemistry of Rare Earths, K.A. Gschneider Jr. and L. Eyrin (Eds), Vol 21 (1995) Elsevier, pp. 133-178

[18] M.M. Li, C.C. Yang, C.C. Wang, Z. Wen, Y.F. Zhu, M, Zhao, J.C. Li, W.T. Zheng, J.S. Lian, and Q. Jiang, Nature, Scientific Reports, 6, Art. No. 27601 (2016)

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