# Development of a new metallurgical process for closed-loop recycling of discarded Nickel-Metalhydride-Batteries

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## Abstract

The demand on Nickel-Metalhydride-Batteries (Ni-MH) is increasing rapidly since their market launch in the early 1990ies. The market share of this batteries is expected to be significantly expanded in the near future due to their possible application as board batteries in cars respectively as substitute of Ni-Cd-batteries in power tools. Nowadays there is no suitable recycling process existing. Several hydrometallurgical research projects were namely investigated, but none of them has been transferred into industrial application.

Today the discarded batteries are used in the steel industry for alloying because of their Nickel content. Cobalt and Rare Earth (RE) are slagged and lost for recycling. The entire value of the metals in discarded Ni-MH is estimated 4.0-4.8 €/kg.

In a governmental funded research project IME cooperates with two industrial partners for a processing and feasibility study. The goal of the project is the development of a pyrometallurgical closed-loop recycling process for metal recovery from Ni-MH. After comminution the steel shell is separated. The resulting Ni-MH-fraction is smelted in an electric arc furnace. The products are a Nickel-Cobalt alloy and a slag phase highly enriched with RE-oxides. Different fluxes are investigated in order to reach best separation of the two phases and metal yields. Extensive laboratory scale experiments have been successfully implemented. The most suitable slag systems were then tested in a 480 kW pilot-plant electric arc furnace. The results for tests with battery scrap from used batteries as well as production waste will be shown. The slag will be processed and in a molten salt electrolysis and a ‘Mischmetal is produced. Both the Nickel-Cobalt alloy and the ‘Mischmetal’ are suitable for direct reuse in Ni-MH-battery production.

# 1. Introduction

In the recent ten years the demand on light, energy-rich and rechargeable batteries has been grown intensively. This trend is expected to continue due to increasing requirements in relation to mobility within the areas of communication, video and audio applications, and computers. Furthermore the use of rechargeable batteries in the automobile is predicted to increase sharply. Nickel-Metallhydride-Batteries are voltage compatible, high in energy density and compared to Ni-Cad-systems environmental friendly. So far no sustainable closed-loop recycling circle is existing. State of the art is the use of discarded Ni-MH-Batteries in the steel industry using the Nickel content as alloying element. But the contained Cobalt and Rare Earths Metals (RE) are neither used nor recycled. They are lost in the slag. Hence, it is timely to develop a novel technology to enable recycling of all metallic components, thereby also enabling recovery of non-metallic components, such as plastics.

The object of the German government funded project reported here is to develop a simply structured, environmental friendly recycling process for discarded Ni-MH-Batteries. After collection a combination of comminution and metallurgical processing is intended (Figure 1). The greyscale boxes include the working area of the IME while the white boxes show the working area of the industrial partner UVR FIA GmbH, Freiberg, Germany.

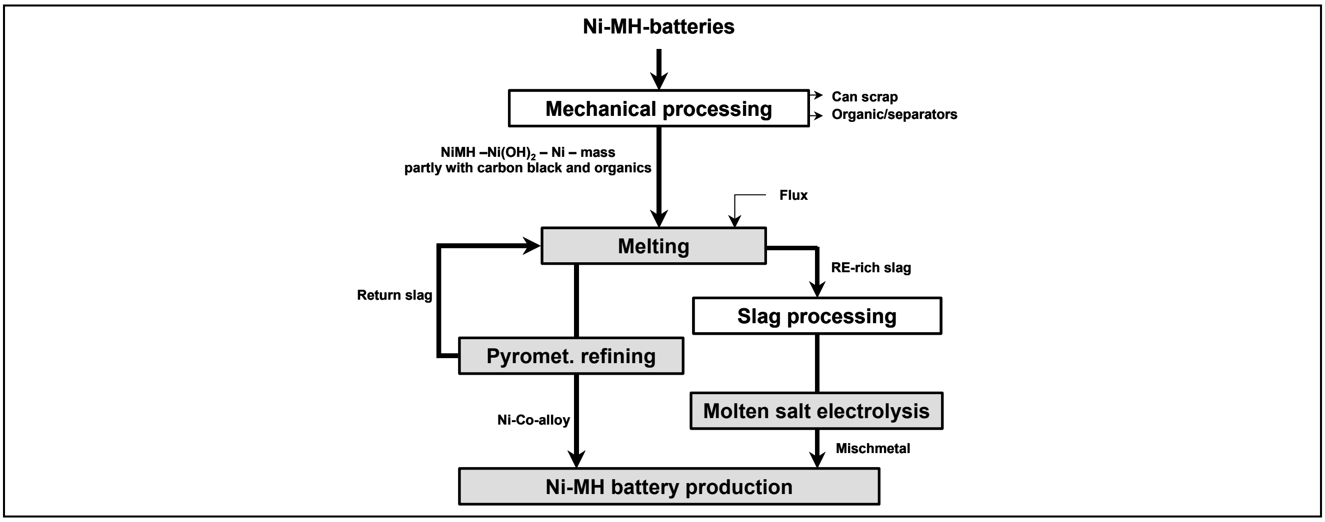


Figure 1: Flowsheet of the intended investigation on NiMH-battery recycling

Within the comminution step it is intended to separate the steel shell and organics from the Ni-MH mass. Using an electric arc furnace and fluxes a Nickel-Cobalt alloy should be generated whereas the Rare Earths Metals should be oxidised and slagged. The Nickel-Cobalt alloy is pyrometallurgically refined and a product directly useable in the battery industry. The slag is processed mechanically and hydrometallurgical in order to transfer the RE-oxides into RE-chlorides, which are fed into a molten salt electrolysis. The produced Mischmetal is also direct usable as a battery alloy component.

# 2. Market situation of NiMH-Batteries

## 2.1. Battery types, design and applications

Batteries are galvanic elements, where chemical energy is transferred into electrical energy. A battery consists of several, parallel galvanic cells; battery packs contain additionally plastic housings and electronic elements. The cell consists of a positive (cathode) and a negative (anode) electrode, which are embedded in a liquid, pastry or solid electrolyte. If the battery is discharged (=used) the cathode is reduced by electrode consumption, whereas the anode is oxidised. The electrons are leaving the cell at the anode entering the outside current circuit.

In general batteries have to be divided into primary and secondary (or rechargeable, accumulator) batteries. In primary cells the discharge reaction is irreversible contrary to secondary cells. Thus secondary cells can be recharged up to 3000 times depending on their type and mode of use. The most popular accumulator battery systems nowadays are Nickel-Cadmium-, Nickel-Metallhydride-, and Lithium-Ion-Batteries.

Cylindrical cells are used in various applications like Walkman, cameras or camcorders. Prismatic cells are designed for use in special devices, where cylindrical cells are limited due to their shape. They are mostly used as battery packs, for instance in mobile phones. Button cells are adapted to computer, phones or televisions devices for bridging operations [1, 2].

## 2.2. Components of Ni-MH-Batteries

The main parts of a battery are an aqueous alkaline electrolyte, the positive and negative electrode, separator and cell cup with lid. The positive electrode is consisting of Cobalt doted Nickel (II)-hydroxide, which is oxidised during charging to Nickel-oxi-hydroxide. The negative electrode can based on a nickel-plated, punched steel sheet or Nickel-foam. The sheet is plated, the foam impregnated with mixture of a hydrogen-storing-alloy/Teflon binder/Carbon- or Nickel-powder.

Two intermetallic alloy types are used for hydrogen-storage in batteries. Due to their larger stability and lower self-discharge is AB5 the most common, very rare is $AB_2$. A is derived from IIIa, IVa group metals and B is derived from Va, VIa, VIIa, VIIIa group metals. For $AB_5$ $LaNi_5$ is mainly used, but improved by substitution of Nickel with Cobalt, Manganese and Aluminium [3]. Lanthanum is partly replaced by the cheaper Mischmetal (Mm), composed e.g. of 50-55 % Cerium, 18-28 % Lanthanum, 12-18 % Neodymium and 4-6 % Praseodymium. A typical alloy nowadays is $MmNi_{3.5}Co_{0.7}Mn_{0.4}Al_{0.3}$.

A typical $AB_2$ alloy is represented by $Zr(Mn_{0.25}Cr_{0.1}V_{0.05}Ni_{0.6})_2$. The separators between the electrodes are made of alkaline resistant plastics, mainly PA or PP. The cell cup is consisting of Nickel or nickel-plated steel, which is resistant in alkaline solutions. [4] The electrolyte is mainly diluted potassium hydroxide (20-30 % KOH) containing some parts of Lithiumhydroxide. During discharge atomic hydrogen is disorbed at the negative electrode and reacts with OH-ions (released at the positive electrode) forming water. This process is reversible and allows thousands of charge/discharge-cycles.

## 2.3. Market situation and economical potential

In the recent years the production of Ni-MH-Batteries has grown steadily (Figure 3a). Nowadays they are established in the market in various applications. About 8970 t Ni-MH-Batteries were sold within Europe in 2001 including 3140 t in Germany (Figure 3b) [5, 6]

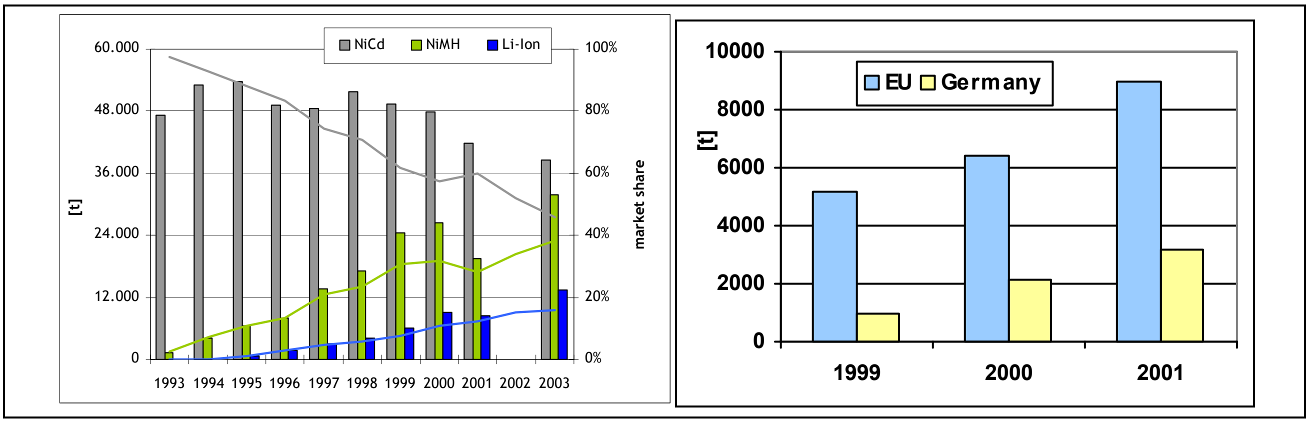


Figure 3: a) World battery production (left), b) sold batteries in 2000 (right) [5,6]

The most important criterion for the evaluation of recycling processes is the raw materials situation and the raw materials price of the recycled material. According to today's knowledge the reserves of Nickel, Cobalt and Rare Earth metals are sufficient for the next 100 years [7,8]. But recycling is economically interesting due to the relatively high metal prices of Nickel, Cobalt and Rare Earth metals. In order to determine the economical content of Ni-MH-battery scrap the composition are summarized in Table 1:

Table 1: Composition of Ni-MH-cell scrap [5]

| **component** | **mass percentage %** | | | |
|---|---|---|---|---|
| | **$AB_5$-button cell** | **$AB_5$-cyln. cell** | **$AB_5$-pris. cell** | **$AB_2$-cyln. cell** |
| Ni | 29-39 | 36-42 | 38-40 | 37-39 |
| Fe | 31-47 | 22-25 | 6-9 | 23-25 |
| Co | 2-3 | 3-4 | 2-3 | 1-2 |
| La, Ce, Nd, Pr | 6-8 | 8-10 | 7-8 | - |
| Zr, Ti, V, Cr | 0.02-0.1 | 0.02-0.1 | 0.02-0.1 | 13-14 |
| Carbon black, Graphite | 2-3 | <1 | <1 | - |
| Organics | 1-2 | 3-4 | 16-19 | 3-4 |
| Potassium | 1-2 | 1-2 | 3-4 | 1-2 |
| Hydrogen and Oxygen | 8-10 | 15-17 | 16-18 | 15-17 |
| Others | 2-3 | 2-3 | 3-4 | 1-2 |

The metal value of 1 kg Ni-MH-Batteries (type $AB_5$) is represented in Table 2. Base of the calculation are the mass percentages of Table 1.

Table 2: Value contained in 1 kg Ni-MH-round cell consumer battery-scrap (type AB$_5$)

| Component | Proportion in AB$_5$-cyln. cell [mass-%] | Metal price [€/t] [9] | Value [€/kg] |
|---|---|---|---|
| Ni (March 2003) | 36-42 | 8460 | 3.0-3.6 |
| Co (March 2003) | 3-4 | 20520 | 0.6-0.8 |
| Mischmetal (June 2002) (La, Ce, Nd, Pr) | 8-10 | 4850 | 0.4-0.5 |
| Sum | | | 4.0-4.9 |

Taking the mass of sold batteries in 2000 (Figure 3b) the total economical potential of Ni-MH-battery scrap is calculated to 8.9-10.9 million Euros for Germany respectively 24.8-30.4 million Euros for Europe. This value is assuming a 100 per cent recovery of the sold batteries. Due to losses during collection, comminution, processing etc. nowadays only a recycling rate of 0.8-1.0 percent is reached, which makes the recycling process not economical at the moment. A statement about the return of production scrap could not be performed due to missing information.

## 3. Processing of used NiMH-batteries

The main design criteria for the comminution is to obtain a powdery fraction not polluted by iron. After sorting respectively pyrolysis at ACCUREC GmbH, Mülheim, Germany the steel shell and the various fractions of battery materials are carefully separated by mechanical processing performed at UVR FIA GmbH, Freiberg Germany. Figure 4 shows the comminution flow sheet.

A hammer mill with one rotor driven by a speed of 46 m/s (rotor diameter 670 mm) and equipped with a perforated discharge grid of 20 mm opening wideness, was found to be suitable for crushing the batteries to release the active mass of electrodes for metallurgical processing. Carrying out the comminution with spraying of water in the mill is recommended because the fine particles of the negative electrode could ignite.

The ground material is wet screened by a mesh size of 0.5 mm, thus obtained a fine fraction with the valuable components Ni, Co, and RE and an oversize fraction consisting of a mix of iron chips, electrodes grids, plastic chips, paper, and flocculent material of separators. The amount of organic components is significant reducible by performing a previously pyrolysis step.

Table 3 shows the results of chemical analysis of fine fractions after shredding and screening of anodes plates and spent batteries. According to these results, nickel is contained in the anode-material with 42 %, cobalt with 10 %, RE-Mischmetal with 37 %, manganese with 6.5 %, chrome with 4.3% and iron with 0.4%.

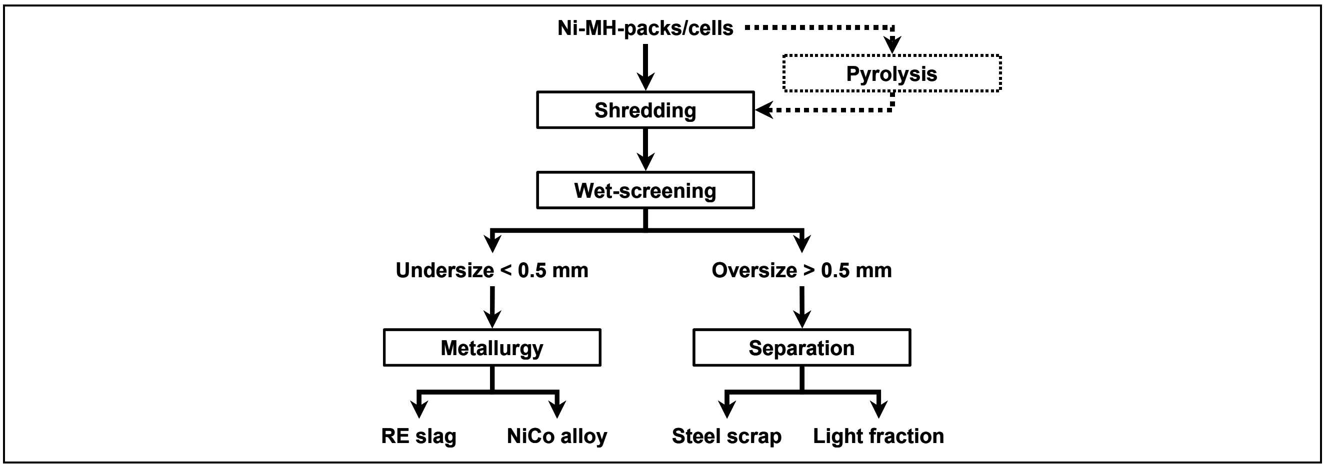


Figure 4: Flow sheet Mechanical Processing

With the mechanical preparation of batteries is nickel with 56 %, cobalt with approximately 9 %, RE-Mischmetal with 19 %, manganese with 5.6 %, chrome with 3.3 % and iron with 0.7%.

Table 3: Results of chemical analysis of fine fractions after shredding and screening in %

| **Composition** | **Anode Mechanical treated** | **Batteries Mechanical treated** |
|---|---|---|
| Ni | 42 | 56 |
| Co | 10 | 9 |
| Fe | 0.4 | 0.7 |
| Mn | 6.5 | 5.6 |
| Al/Ti/V | <0.1 | <0.1 |
| Cr | 4.3 | 3.3 |
| Zn/Cd | | 5 |
| Ca/Mg | 0.5 | 0.9 |
| K/Na | 0.1 | 0.2 |
| RE | 36 | 19 |
| Sum | 99.9 (as metal) | 99.8 (as oxide). |

## 4. Experimental Methodology

Any pyrometallurgical process relies on a suitable slag system. In this specific case it has to allow separation of Nickel and Cobalt as metal from the RE almost quantitavely collecting the RE as well as unnoble impurities e.g. as oxides. Alternatively the RE can be forced to react with compounds or elements into chlorides or fluorides, which might be more suitable than oxides for the subsequent slag treatment and fused salt electrolysis.

The important demands of the slag system are:

- Poor solubility for Nickel and Cobalt
- High solubility for RE as oxide, chloride or fluoride
- Density significant smaller than metal phase density (< 5 g/cm$^3$)
- Low viscosity to allow an easy slag/metal separation

- Moderate melting temperature (< 1500 °C)
- Low reactivity with furnace lining

Extensive lab scale trials proofed that several slag systems are suitable to the mentioned assumptions. A slag system with 45 % $SiO_2$/40 % CaO/15 % MgO has a melting point at 1400°C, a density of 2.6 g/cm$^3$ and a viscosity between 1.8 and 2.5 poise [10]. Pure silica flux is also suitable. Between 1400°C and 1700°C RE-silicates are generated. These RE-silicates are later extractable with hydrochloric acid in order to chlorinate RE-oxides.

Most of metal chlorides and fluorides have got low melting and boiling points. Thus the major part is not suitable as slag base for the expected working temperature of 1500-1700 °C. Calcium fluoride (Bp 2513°C) may be useable as flux in order to generate RE-fluorides respectively RE-chlorides during the melting process. The chlorides are not useable as the boiling point is too low. The boiling point of RE-fluorides is about 2300°C and for RE-chlorides between 1700 and 1800 °C. Within expected working temperature area the RE-chlorides respectively RE-fluorides couldn't be evaporated selectively. Alternatively a mixture of Calcium fluoride and Calciumoxide shows a good potential, as the mixture has got a eutectic melting point of 1360°C (for 15 % CaO, 85 % $CaF_2$). Trial tests were made in a Tamman-type furnace [11]. The experiments were performed in order to screen the slag systems and to find a suitable crucible-material, which resists the aggressive conditions of chlorides and Rare Earth Metals.

# 5. Trials in lab-scale furnace

## 5.1 Furnace description

First trials were performed in a lab-scale DC tilting electric arc furnace with a usable volume of 6 l. Figure 5 shows the schematic construction of the furnace.

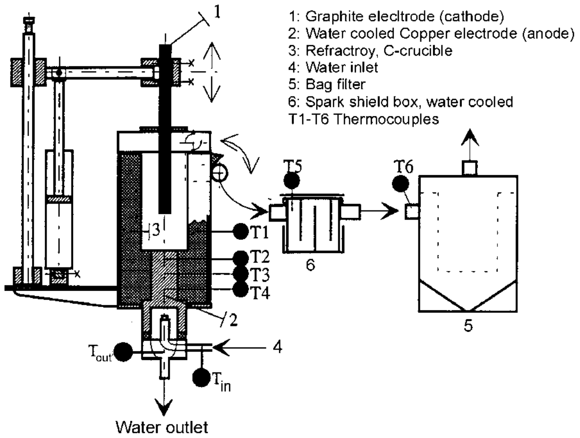


Figure 5: Schematic construction of the lab-scale DC electric arc furnace

The DC electric arc furnace has got a water-cooled bottom electrode made of Copper and a vertical moveable graphite electrode. Several refractories for the inner lining (MgO, SiC, $Al_2O_3$) were tested in the beginning as well as graphite crucible embedded in the refractory. The outer lining consists of $Al_2O_3$ (LINCO®) in order to decrease heat losses as well as to protect the steel shell. The usable volume is about 300 mm in height with a diameter of 160 mm. The used C-crucibles were 150 mm in diameter and the height was 200 mm. The bottom electrode is completely embedded in the refractory. Only the top layer is in contact with the melt. The underpart of the electrode is water-cooled, thus a smelting of the electrode is prevented. The cathodic graphite electrode has got a diameter of 50 mm and a starting length of 1500 mm. A hydraulic system moves both the electrode vertically and the furnace for tilting. Casting is performed with a pouring tundish into a steel mould.

The offgas is collected with a ring suction system and filtered in a bag filter. Additionally a gas washer can be used.

## 5.2 Experimental procedure and working plan

The most promising slag systems from the Tamman furnace trials were investigated in a lab-scale electric arc furnace (Table 4). Objective was to evaluate the technical feasibility of these slag systems in a larger volume of scale. The Ni-MH mass was briquetted with the flux (25 % of charge) in order to avoid dust losses. Alternatively the raw material was pelletized together with the flux. The total input was 6500 g for each trial. Three different furnace refractories (MgO, SiC, $Al_2O_3$) were used, which were identified to resist the chemical aggressive impact of RE. As refractory wear was too high for commercial refractory a graphite crucible was mounted into the furnace. Total input mass was 5000 g in that case. The temperature was measured with a commercial lance. Samples were taken from the cast metal as well as from the slag. Two trials were executed for each slag system. Different raw materials were tested as discharged batteries from production scrap, processed batteries from collection, anode and electrode production scrap.

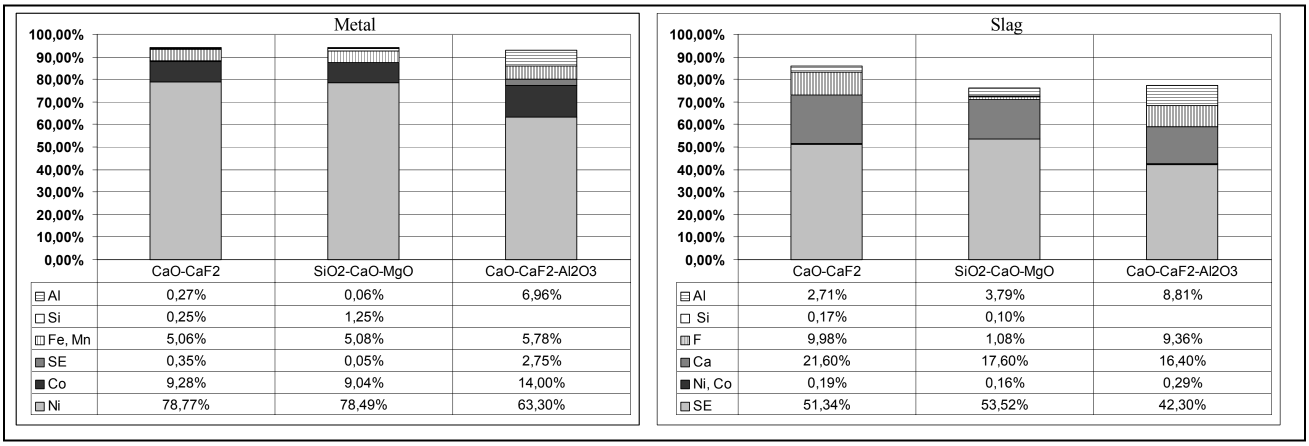
Table 4: Overview electric arc furnace experiments

| Exp. | Flux composition | | | | | charge composition | | | Pouring temperature | Crucible | Material preparation | Material type |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $CaF_2$ | CaO | MgO | $Al_2O_3$ | flux | | Ni-MH | [°C] | - | - | - |
| 1 | 100% | | | | | 25% | | 75% | 1550 | MgO | Briquetts | Anodes |
| 2 | 100% | | | | | | | | 1700 | SiC | | |
| 3 | | 100% | | | | | | | 1350 | | | |
| 4 | | 100% | | | | | | | 1420 | | | |
| 5 | | 65% | 35% | | | | | | 1555 | | | |
| 6 | | 65% | 35% | | | | | | 1592 | | | |
| 7 | 45% | | 40% | 15% | | | | | 1450 | | | |
| 8 | 45% | | 40% | 15% | | | | | 1415 | | | |
| | | $CaF_2$ | CaO | | | CaO | $CaF_2$ | Ni-MH | | | | |
| 9 | | 84,2% | 15,8% | | | 7,5% | 40,0% | 52,5% | 1420 | graphite | Briquetts | Anodes |
| 10 | | 87,0% | 13,0% | | | 7,5% | 50,0% | 42,5% | 1392 | | | |
| 11 | | 84,2% | 15,8% | | | 7,5% | 40,0% | 52,5% | 1520 | | | |
| 12 | | 100,0% | | | | | 50,0% | 50,0% | 1360 | | | |
| 13 | | 66,7% | 33,3% | | | 15,0% | 30,0% | 55,0% | 1430 | | | |
| 14 | | 76,9% | 23,1% | | | 15,0% | 50,0% | 35,0% | 1360 | | | |
| 15 | | 84,2% | 15,8% | | | 7,5% | 40,0% | 52,5% | 1650 | | | |
| 16 | | 100,0% | | | | | 30,0% | 70,0% | 1480 | | | |
| 17 | | 100,0% | | | | | 40,0% | 60,0% | 1360 | | | |
| 18 | | 80,0% | 20,0% | | | 7,5% | 30,0% | 62,5% | 1290 | | | |
| 19 | | 72,7% | 27,3% | | | 15,0% | 40,0% | 45,0% | 1540 | | | |
| 20 | | 84,2% | 15,8% | | | 7,5% | 40,0% | 52,5% | 1420 | | | |
| 21 | | | 15% | | 15% | 30% | | 70% | 1600 | graphite | Briquetts | Anodes |
| 22 | | | 15% | | 15% | | | 70% | 1550 | | | |
| 23 | | 12% | 6% | | 12% | | | 70% | 1760 | | | |
| 24 | | 12% | 6% | | 12% | | | 70% | 1760 | | | |
| 25 | | 16% | 8% | | 16% | 40% | | 60% | - | | | |
| 26 | | 12% | 6% | | 12% | 30% | | 70% | 1580 | | | |
| 27 | | 12% | 6% | | 12% | | | 70% | 1770 | | | |
| 28 | | 12% | 6% | | 12% | | | 70% | 1740 | | | Electrodes |
| 29 | | 65% | 35% | | | 30% | | 70% | 1520 | graphite | Powder | Spent batteries |
| 30 | | 65% | 35% | | | 30% | | 70% | 1450 | | | |
| 31 | | 65% | 35% | | | 30% | | 70% | 1620 | | Pellets | |
| 32 | | 65% | 35% | | | 30% | | 70% | 1760 | | | |
| 33 | | 65% | 35% | | | 15% | | 85% | 1650 | | | |
| 34 | | 65% | 35% | | | 10% | | 90% | 1630 | | | |
| 35 | | 65% | 35% | | | 30% | | 70% | - | | | |
| 36 | | 65% | 35% | | | 15% | | 85% | 1630 | | | |
| 37 | | 65% | 35% | | | 15% | | 85% | 1630 | | | |
| 38 | | 40% | 20% | | 40% | 30% | | 70% | - | | | |
| 39 | 45% | | 40% | 15% | | 30% | | 70% | 1630 | | | |
| 40 | 45% | | 40% | 15% | | 30% | | 70% | 1680 | | | |
| 41 | | 40% | 20% | | 40% | 15% | | 85% | - | | | |
| 42 | 45% | | 40% | 15% | | 15% | | 85% | 1640 | | | |
| 43 | 45% | | 40% | 15% | | 15% | | 85% | 1680 | | | |
| 44 | | 65% | 35% | | | 15% | | 85% | 1560 | | | |
| 45 | | 65% | 35% | | | 15% | | 85% | 1620 | | | |
| 46 | | 65% | 35% | | | 10% | | 90% | 1500 | | | |
| 47 | | 65% | 35% | | | 10% | | 90% | 1600 | | | |
| 48 | | 65% | 35% | | | 10% | | 90% | 1400 | | | Electrodes |
| 49 | | 65% | 35% | | | 10% | | 90% | 1550 | | | |
| 50 | 45% | | 40% | 15% | | 10% | | 90% | 1620 | | | Spent batteries |
| 51 | 45% | | 40% | 15% | | 10% | | 90% | 1750 | | | |
| 52 | 45% | | 40% | 15% | | 10% | | 90% | 1760 | | | Electrodes |
| 53 | 45% | | 40% | 15% | | 10% | | 90% | 1690 | | | |
| 54 | | 65% | 35% | | | 10% | | 90% | 1450 | $Al_2O_3$ | Powder | Spent batteries |
| 55 | | 65% | 35% | | | 10% | | 90% | 1380 | $Al_2O_3$ | | |
| 56 | 45% | | 40% | 15% | | 10% | | 90% | 1650 | $Al_2O_3$ | | |

## 5.3 Results and discussion

With the slag systems used in experiment 1 to 8 (Table 4) the objective of metal-slag separation could not be performed. A clear separation was failed. Also in every case the refractory did not resist the impact of the slags. The melt was high viscose. Decreasing of viscosity by increasing the temperature was not successful. The major part of the melt remained in the furnace after pouring. As the influence of the dissolved refractory material on the slag behaviour could not be clearly described next these slag systems were tested using a graphite crucible. Experiments 9-20 results in a low viscous melt which was easy to pour and lead to a good metal – slag separation for a high $CaF_2$-CaO-ratio. Pure $CaF_2$ as flux did not work properly. In experiments 29-37 and 44-49 the $CaF_2$-CaO-system was optimized with respect to the flux ratio. A good performance was reached with a flux ratio of 10 % consisting of 65 % $CaF_2$ and 35 % CaO. The best result (exp. 48) is included in Figure 6. Both a high Nickel content in the metal parallel to a low content in the slag could be reached as well as high RE content in the slag.

In experiments 39/40 resp. 42/43 and 50-53 the $SiO_2$-CaO-MgO-system was investigated. A good metal – slag separation could be gained. But the slag was high viscous and only liquid in a small temperature range. In some experiments a sudden freezing of the slag was observed. The best result (exp. 51) is added to in Figure 6. A high Nickel content in the metal could be reached as well as a high content of RE in the slag. Some of the $SiO_2$ was reduced and dissolved as silicon in the metal. Hence for this alloy a refining step is required as silicon is undesirable for battery production. However, the Si-content of the slag is conspicuously low. It is possible, that $SiO_2$ was first reduced to SiO and than has got reacted with surplus carbon to form silica carbide SiC, which sublimates at 2300°C to gaseous silicon and solid carbon.



| | CaO-CaF2 | SiO2-CaO-MgO | CaO-CaF2-Al2O3 |
|---|---|---|---|
| ▤ Al | 0,27% | 0,06% | 6,96% |
| ☐ Si | 0,25% | 1,25% | |
| ▥ Fe, Mn | 5,06% | 5,08% | 5,78% |
| ▩ SE | 0,35% | 0,05% | 2,75% |
| ■ Co | 9,28% | 9,04% | 14,00% |
| ░ Ni | 78,77% | 78,49% | 63,30% |

| | CaO-CaF2 | SiO2-CaO-MgO | CaO-CaF2-Al2O3 |
|---|---|---|---|
| ▤ Al | 2,71% | 3,79% | 8,81% |
| ☐ Si | 0,17% | 0,10% | |
| ▥ F | 9,98% | 1,08% | 9,36% |
| ▩ Ca | 21,60% | 17,60% | 16,40% |
| ■ Ni, Co | 0,19% | 0,16% | 0,29% |
| ░ SE | 51,34% | 53,52% | 42,30% |

Figure 6: Best results for lab-scale trials (right:, slag left: metal), Exp. 48, 51, 26

The $CaF_2$-CaO-$Al_2O_3$-system could not be tested successfully in experiments 21-28 resp. 38/41. The slag was even higher viscous than in the $SiO_2$-bearing system and tended to freeze directly when the energy supply from the electric arc was not accessible. From the crucible wall into the middle of the melt a building up of a slag crust was observed. Also metal – slag separation was rather poor leading to a mixed layer of slag and metal within the cast. The best result (exp. 26) is shown in Figure 6. Both the Nickel content in metal as well as the RE content in slag was reasonably lower than in the other two systems. Hence only the $CaF_2$-CaO-system and the $SiO_2$-CaO-MgO-system were determined to be suitable for further investigation in the pilot plant furnace.

The influence of the material preparation has got no significant influence to the used slag system. Both briquettes and pellets did work properly and showed a similar melting behaviour. Also charging of dust was possible, but there have been larger losses due to flue dust. The used material behaved rather similar. The behaviour a anode material was a little bit different due to the high amount of RE, which required a larger flux amount. Thus the slag systems worked with every material if it worked with the pure anode fraction.

# 6. Trials in pilot plant furnace

## 6.1 Furnace description

A first series of three trial has been performed in the IME pilot plant DC electric arc furnace Some technical furnace details are given a max. current 5.2 kA, max. voltage 90 V, max. primary power 480 kW, process temperature up to 1900°C, capacity 200 kg/h pellets (150 kg/h steel), shell cooling water 0.5-1 $m^3$/h, gas cleaning volume max. 5000 $m^3$/h. The furnace was built from Mannesmann Demag Metallurgie, Duisburg, Germany (nowadays SMS Demag). The water-cooled bottom electrode can be operated either as cathode or anode. In these trials the bottom electrode was operated as anode. The cathode was made out of graphite (quality: EL/XN, Conradty GmbH, Nürnberg, Germany) with a diameter of 150 mm.

The furnace vessel was lined with massive chrome – magnesite bricks and has got a water-cooled shell.. The inside furnace height was about 990 mm, the inner diameter at the bottom was 520 mm and on the top the diameter was 650 mm. As the refractory is not usable with the developed slag system a clay-graphite crucible was fixed into the furnace. A ramming mix (ANKOCAST-ZV 97C®) for fixing was used. The crucible dimensions are height 850 mm, outer diameter 450 mm and inner diameter 400 mm. Electric contact to the bottom electrode was improved with an additional coke layer between the electrode top and the crucible bottom.

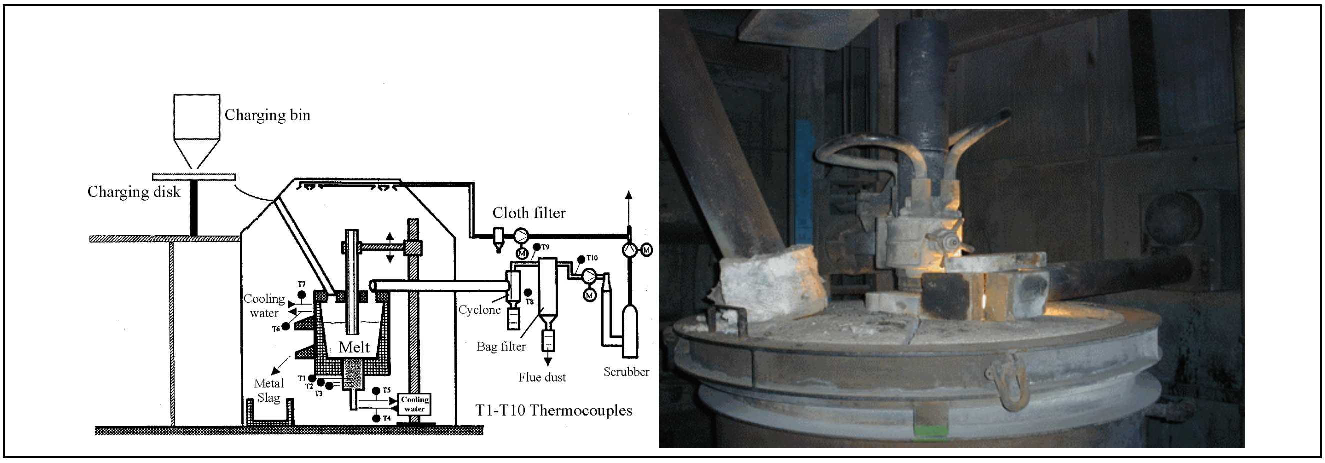


Figure 7: Schematic construction of pilot plant DC EAF (left); operating furnace (right)

The spent NiMH-batteries were prepared after comminution at UVR FIA in a one step mixing-granulation process using an Eirich mixer (Type 08, 75 l mixing volume) The battery powder was mixed together with a binder and the flux components in the mixer producing pellets in the size range of 1–4 mm. Subsequently the pellets were dried at 120°C for 36 hours. The charging system was consisting of a buffer mounted directly over a rotating disc. The revolution of the disc could be varied leading to a feeding rate of 150 to 300 kg/h. The pellets were dropping continuously on the disc and from there transported into the charging pipe. The charging pipe was ending at the charging hole in the furnace lid. The altitude difference between the charging disk and the furnace lid was 2 meters, thus the falling velocity of the pellets was large enough in order to transport them into the furnace.

## 6.2 Experimental procedure and working plan

So far three trials have been performed. In this first series out of three planned for the project different raw materials were tested in order to determine possible differences in the material behaviour. The overview about all planned trials in the pilot plant is given in Table 5.

Table 5: Overview of pilot plant trials planned for the project

| Exp. | Flux composition | | | charge composition | | Pouring temp. | Material preparation | Material type |
|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $CaF_2$ | CaO | flux | Ni-MH | [°C] | - | - |
| 1 | | 65% | 35% | 10% | 90% | 1730 | Pellets | anode scrap |
| 2 | | 65% | 35% | 10% | 90% | 1660 | | production scrap |
| 3 | | 65% | 35% | 10% | 90% | 1600 | | spent batteries |
| 4 | | 65% | 35% | 10% | 90% | - | Pellets | pyrolised spent batteries (planned) |
| 5 | | 65% | 35% | 5% | 95% | - | | |
| 6 | 65% | | 35% | 5% | 95% | - | | |
| 7 | | 65% | 35% | 5% | 95% | - | Powder | mixture of production scrap and spent batteries incl. contamination with other batteries (planned) |
| 8 | 65% | | 35% | 5% | 95% | - | | |
| 9 | | 65% | 35% | 5% | 95% | - | | |

In this first series the input material originated from pure anode scrap from battery production without any further material like steal case or foil. The production scrap included complete battery cells from production, which were hot-wired due to manufacturing failure. Batteries from collection after finishing the use phase were investigated as spent batteries in the third trial. All three trials were carried out using the same slag system on $CaF_2$-CaO base. Input mass was 300 kg in trial 1, 403.8 in trial 2 and 334.1 in trial 3. In each charge 3 % of carbon were included in order to decrease crucible wear. The water content after moderate drying at 120°C for 24 hours was determined to 8-10 %. Charging rate was between 200 and 300 kg/h. With the higher charging rate the furnace has got a capacity up to 1000 t/a at a availability of 90 %. Total consumed power was 363 kWh for trial 1, 230 kWh for trial 2 and 235 kWh for trial 3. Specific energy consumption was 1.2 kWh/kg in trial 1, 0.57 kWh/kg for trial 2 and 0.7 kWh/ kg for trail 3. The smaller energy demand in trial 1 may be explained with the heating of the furnace as only limited preheating was performed. In the next trials additionally pyrolised spent batteries will be investigated as well as the flux ration will be reduced and the second suitable slag system will be tested. Completing an alternative charging system via hollow electrode will be tested with a real material mixture coming form the market including contamination of other battery types like Li-Ion, Ni-Cd-accumulators or alkaline batteries. As the reaction does occur during the melting process no further reaction time is required and the trial was finished after end of charging. Before pouring the temperature of the melt was measured using a commercial lance. The furnace was opened with an oxygen lance and the melt was poured in a conventional ladle.

## 6.3 Results and discussion

Each of the three first trials could be completed successful. The chosen design for the charging did work very well. The pellets were easily fed into the furnace and the melting process was done very fast. Blocking of the charging pipe did not occur. The process temperature was sufficient high with temperature above 1600°C in each trial. Thus the furnace could be poured completely. The melt as well as slag were low in viscosity leading to a very liquid outflow out of the furnace. The input and output flows are listed in Table 6. The occurring losses are mainly through charging failure as some of the material stayed on the edge of the crucible. Furthermore the flue dust weight could be adulterated due to material bound to the filter tubes. After pouring some of the metal remained in the furnace and some of the slag covered the inside of the crucible. Both could not be quantified. All chemical analysis was made using a conventional ICP analyser. The Nickel content in the alloys was 84-88 % whereas Cobalt was 9-11 %. Major accompanying elements were Manganese (3.7-4.2 %) and Iron (0.8-1.9 %). The relatively high amount of Iron eventually requires a refining step in order to fulfil the demands of a battery alloy.

Table 6: Results of first trial series.

| | | 1. Trial | 2. Trial | 3. Trial |
|---|---|---|---|---|
| Input | Material [kg] | 322.8 | 353.4 | 334.1 |
| | C [kg] as $CO_2$ | 9.7 | 10.6 | 10.0 |
| | $H_2O$ [kg] as steam | 32.28 | 35.34 | 33.41 |
| | Metal [kg] | 127.0 | 158.0 | 132.0 |
| Output | Slag [kg] | 66.7 | 78.0 | 84.0 |
| | Flue dust [kg] | 48.4 | 53.0 | 50.1 |
| | Losses [kg] | 39.6 | 18.4 | 24.5 |
| | Recovery [%] | 88 | 95 | 93 |

In Figure 8 the mass balance of Nickel and Rare Earth are presented. It can be clearly seen that the tested slag system fulfils the required tasks. Almost all Nickel is transferred into the metal phase whereas most of the Rare Earths were separated into the slag phase. Overall recovery of Nickel-Cobalt alloy for the process could be close to 96 %.

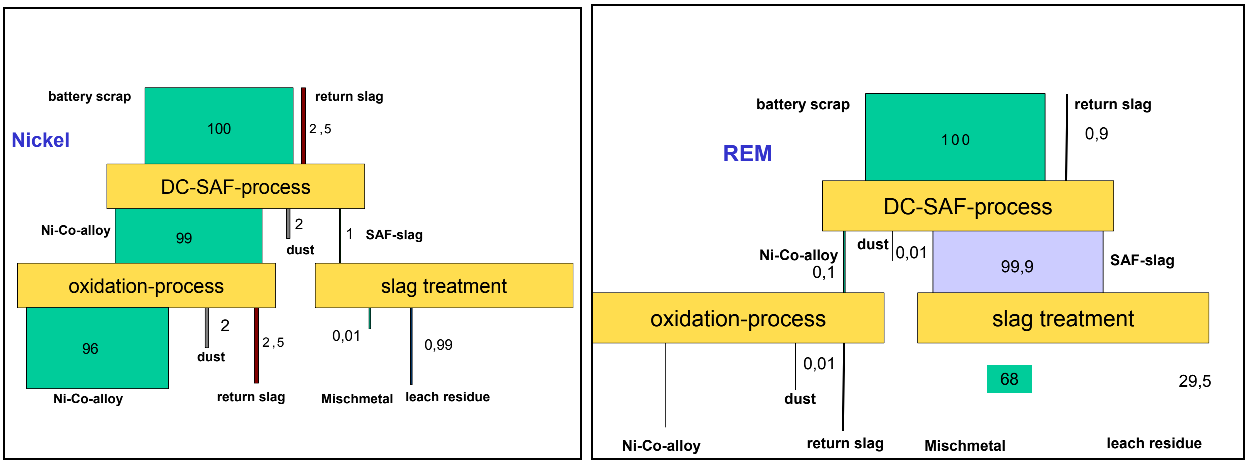


Figure 8: Exemplarily mass balance for Nickel and Rare Earth Metal (REM)

A similar positive picture may be observed for the Rare Earth metals. In two analysis the amount of RE in the metal was smaller than the detection limit. In the other trial the sum of RE was smaller than 0.1 %. The RE content in the slag is up to now between 49 % and 53 % respectively 58-62 % for RE oxides. Other major elements in the slag are Calcium (17-20 %), Fluoride (7-8 %) and Aluminium (2.2-3.1 %). Manganese and Iron were relatively low with 0.3-1.1 % respectively 0.3-1.2 %. The recovery of RE in the overall process is 68 %. The major losses occur during the chemical precipitation – leaching – precipitation process for reacting the RE-oxides from pyrometallurgy into RE-chlorides. The material is crushed in a jaw-crusher and grinded in a ball mill. The part finer 0.1 mm after screening is leached with aqueous sulphuric acid. The solution contains in addition to the RE also further metals, in particular Ni, Co, Mn, Zn and Al. RE are precipitated as double salts of the $(RE)_2(SO_4)_3*Na_2SO_4*xH_2O$ type from the strongly acidic solution by adding NaOH solution. Subsequently RE hydroxide is build by treatment with NaOH solution and washing with $NH_4OH$ solution. The precipitate filtered off is dissolved in hydrochloric acid, and from this solution after adding ammonium chloride, a rare earth chloride is obtained which may be used as raw material for molten salt electrolysis to produce Mischmetal.

# 7. Summary and conclusion

Within a three-year governmental funded research project a closed-looped process for recycling of spent Nickel-Metalhydride batteries is developed. The batteries are mechanical processed after collection in order to separate the steel case, organics and plastics. The product of the comminution – a metal powder – is treated in a DC electric arc furnace process. Aim of the metallurgical process is to separate the valuable metals Nickel and Cobalt from the Rare Earth metals, which should be enriched in the slag. 56 lab-scale experiments investigated different slag systems. Best results are reached for a $CaO-CaF_2$-slag system on the one hand and on the other hand with a $SiO_2$-CaO-MgO-system. In a first series of three trials in a pilot plant scale the technical feasibility of the $CaO-CaF_2$-slag system has been successfully carried out. Both a Nickel-Cobalt alloy and a slag high in RE are produced with almost 100 % metal recovery.

Further input material will be investigated as well as the alternative developed slag system $SiO_2$-CaO-MgO-system will be optimised. At first in lab-scale experiments the necessity of MgO will be proved as well as the possibility to reduce the slag. Based on the lab-scale trials the results will be transferred into the pilot plant scale. The use of the produced alloy as battery alloy will be proved and the hydrometallurgical produced RE chlorides will be tested in a molten salt electrolysis in order to produce Mischmetal for batteries.

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