Feasibility of a new closed loop recycling concept for Nickel-Metalhydride Batteries

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Abstract

The demand on Nickel-Metalhydride-Batteries (NiMH) is increasing rapidly since their market launch in the early 1990ies. Nowadays there is no suitable recycling process existing. 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 value of the metals in discarded Ni-MH is estimated at 3-4 €/kg.

In a german governmental funded research project the IME cooperates since July 2001 with two industrial partners, ACCUREC GmbH (Mülheim)and UVR-FIA GmbH (Freiberg) for processing and a feasibility study. The target of this 3 years project is the development of a new pyrometallurgical recycling process for metal recovery from Ni-MH. After comminution steel and organics are separated. The separated Ni-MH is smelted in an electric arc furnace. Different fluxes are investigated in order to reach best separation of the two phases. First laboratory scale experiments have been successfully implemented. The products are a Nickel-Cobalt alloy and a slag phase enriched with RE-oxides for further treatment to Mischmetal. Both the Nickel-Cobalt alloy and the 'Mischmetal' will be directly used in 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. This market section was dominated in the 80th and beginning 90th by Nickel-Cadmium accumulators [1]. Due to increasing demands of the electronic industry, Nickel-Metal-Hydride Batteries, which perform a 50-100% higher energy density were introduced to the market in the mid 90th. Especially the rapid development and market success of cellular phones boosted the sales of NiMH-cells.

Furthermore the use of rechargeable batteries in the automobile is predicted to increase sharply. 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.

Where ever a high quantity of goods, containing heavy metals and valuable materials enters the market, the producer responsibility and public is interested in new recycling technologies for a sustainable resource management.The object of the German government funded work reported here is to develop a simply structured, environmental friendly recycling process for discarded Ni-MH-Batteries.

Three partners are involved in the project. ACCUREC GmbH is responsible for market research and feasibility study. UVR-FIA GmbH is dealing with mechanical processing whereas IME Process Metallurgy and Metal Recycling is focused on the pyrometallurgical processing.

After collection a combination of comminution and metallurgical processing is intended (Figure 1).

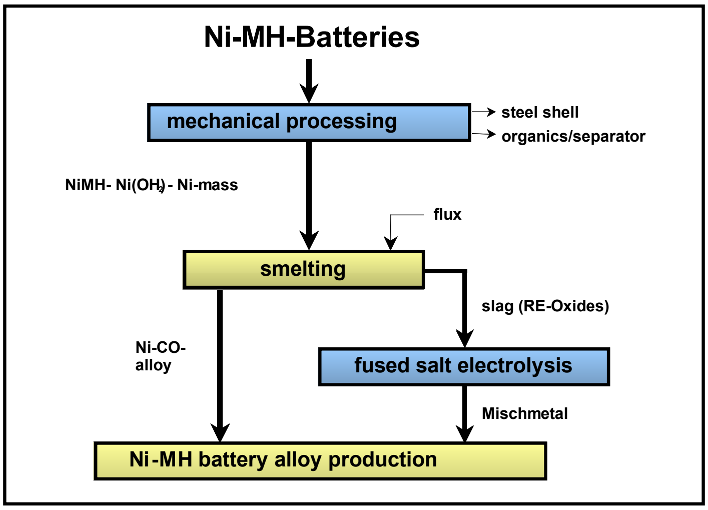


Figure 1: Flowsheet of the intended investigation on NiMH-battery recycling

Within the comminution step it is expected 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 fused salt electrolysis. The produced Mischmetal is also direct usable as a battery alloy component.

2 World-wide Market and Distribution (ACCUREC)

The demand mainly for mobile devices lead to an introduction of NiMH-batteries in 1991. Due to the technical advantages, production of battery cells was expanded yearly around 50-150% . In 1999, shown in Figure 2, the output of cells exceeded 1 billion cells per year, before the sales volume dropped down in 2000 due the world wide economic decline.

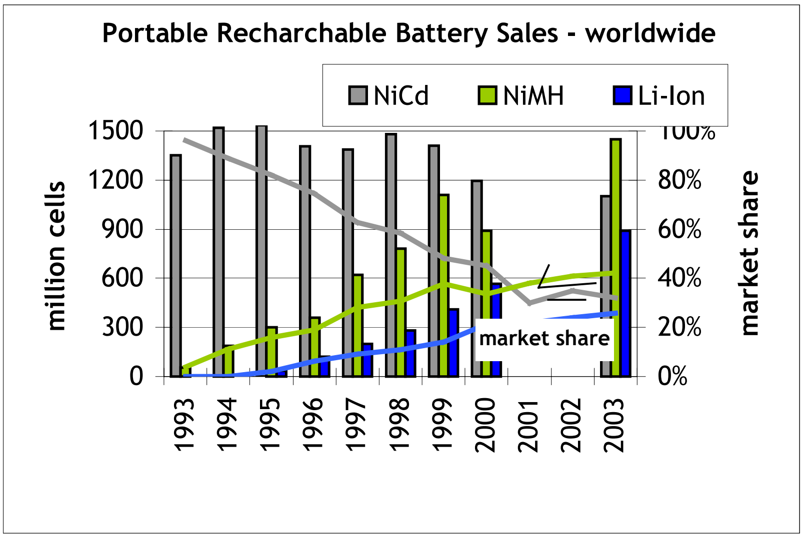


Figure 2: **Sales Quantity of NiMH batteries / million cells**

However, on a world wide basis NiMH-battery production is passing the quantity of produced NiCd-cells currently and will be the dominating battery system in the near future. Lithium-Ion batteries, a battery technology which meets the continuously growing demands of communication industry, develops it´s market chances as fast as NiMH-batteries, and will replace NiMH-batteries , where high capacity and voltage per volume is required.

Taking into account the differing weight per cell between NiMH (average 22 g/unit), NiCd (average 35 g/unit) and Li-Ion (average 15g/unit), Figure 3 expresses that NiCd-cells represent still the majority of batteries-tonnage's introduced to the consumer market. For 2002, a market share of approximately 50% NiCd versus 35% NiMH and 15% Li-Ion is expected. The NiMH-battery production is dominated by japanese companies and takes place at several locations, mainly in Japan and partly in South-Asia. Figure 4 illustrates the product route, where 40% are exported to Europe, 23% to North-America, 8% remain only in Japan and 29% are delivered to Asia [2].

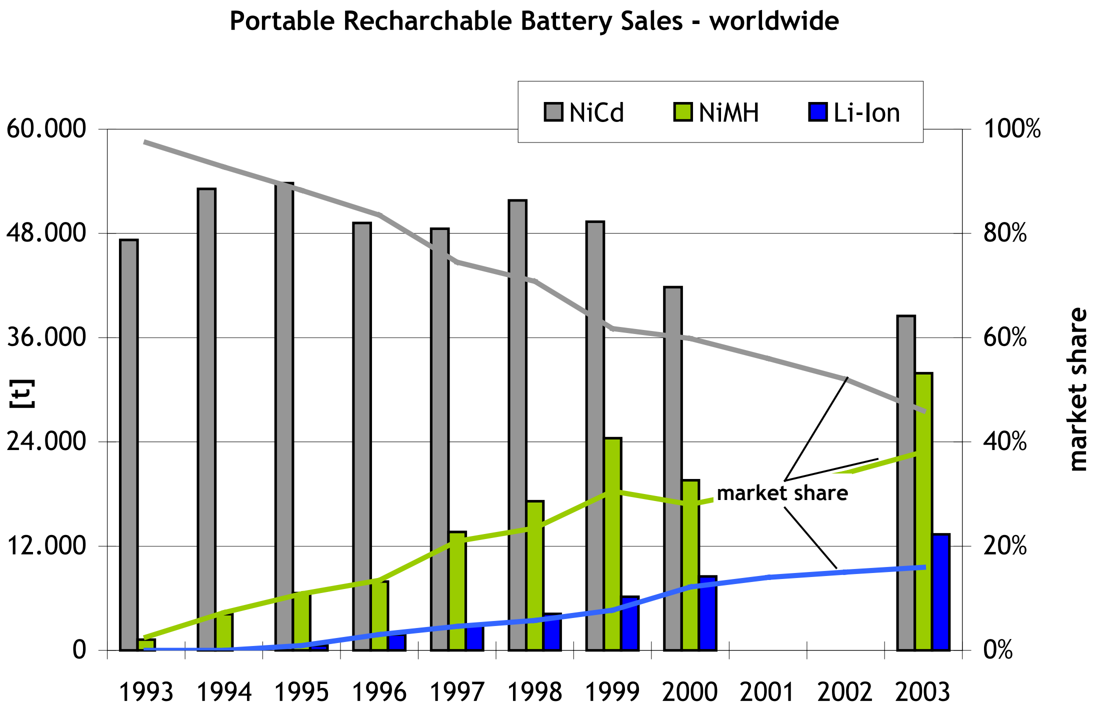


Figure 3: Sales Quantity of NiMH batteries / t

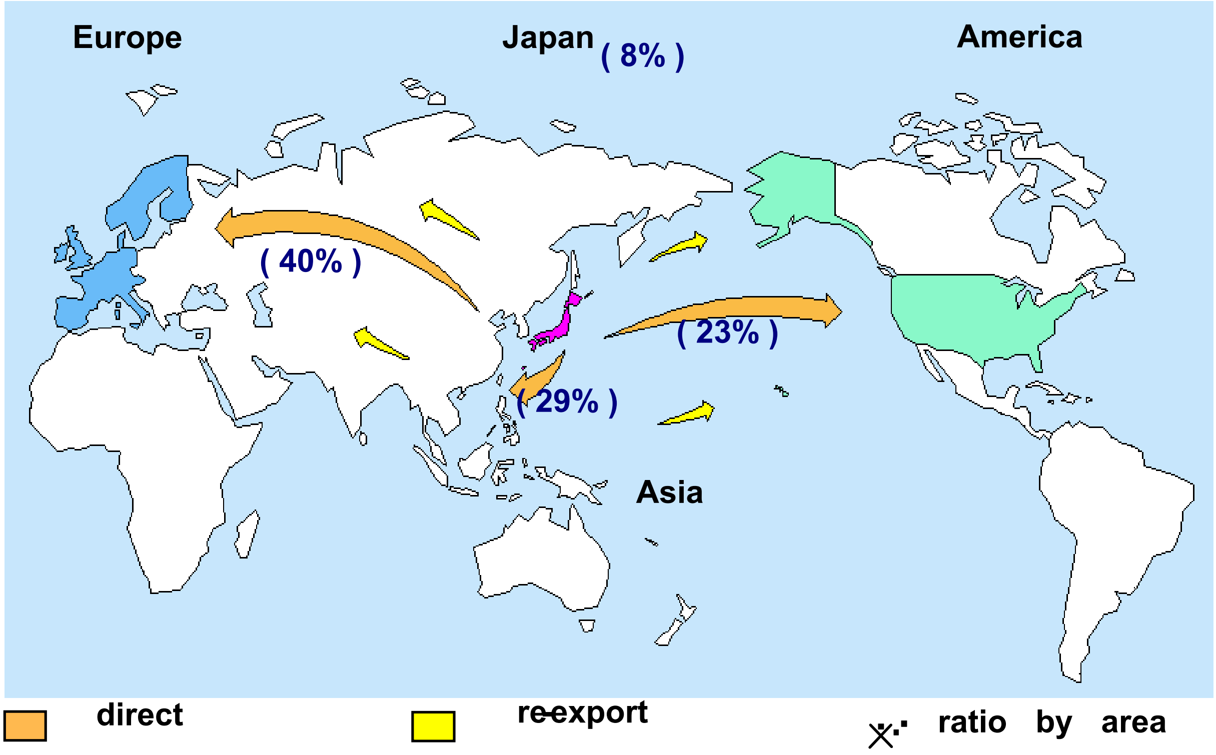


Figure 4: Distribution of NiMH-batteries / % of weight

This considerable amount of battery-cells is used for the electronic industry, where batteries are incorporated into electronic devices. 90% of them are re-exported again to the world market. Considering these premises, a final distribution divided by regions can be calculated for the year 2000 (Table 1).

Table 1: Estimation of NiMH-batteries Consumption by world regions/ t

region	Europe	Asia	Japan	America
[%]	46	5	15	36
[t]	8.970	1.000	2.730	6.850

2.1 Life Cycle of NiMH-Batteries in EU

The use of NiMH-Batteries can be described with 6 main product categories:

- **Home appliances**
- **Office equipment**
- **Communications**
- **Electronic tools and toys**
- **Retail / Replacement**
- **Others**

Due to the individual consumer behaviour and preferences, the distribution differs from country to country, and region to region. Additionally this subdivision changed from year to year. Whereas, for example, the market share for communication and office equipment was around 70-80% in 1995, it turns to the dominating applications retail/replacement and toys/tools (50-60%) in the year 2000.

However, after some years of helpful use, these batteries reach their end of life. Several technical investigations were dedicated to the average life time of NiMH-batteries. The summarizing result is figured out with Figure 5 [3][4]. The front columns show an average life time between 2 years for communication devices and 7 years for single cells. Due to several reasons, the consumer decides to store its waste some time before he dispose of the damaged battery. This behaviour was explained as a kind of hoarding effect [5]. Therefore, a delaying factor regarding each category, is considered (back column). Between 4 and 10 years after introduction to the market, those batteries are expected in the waste stream.

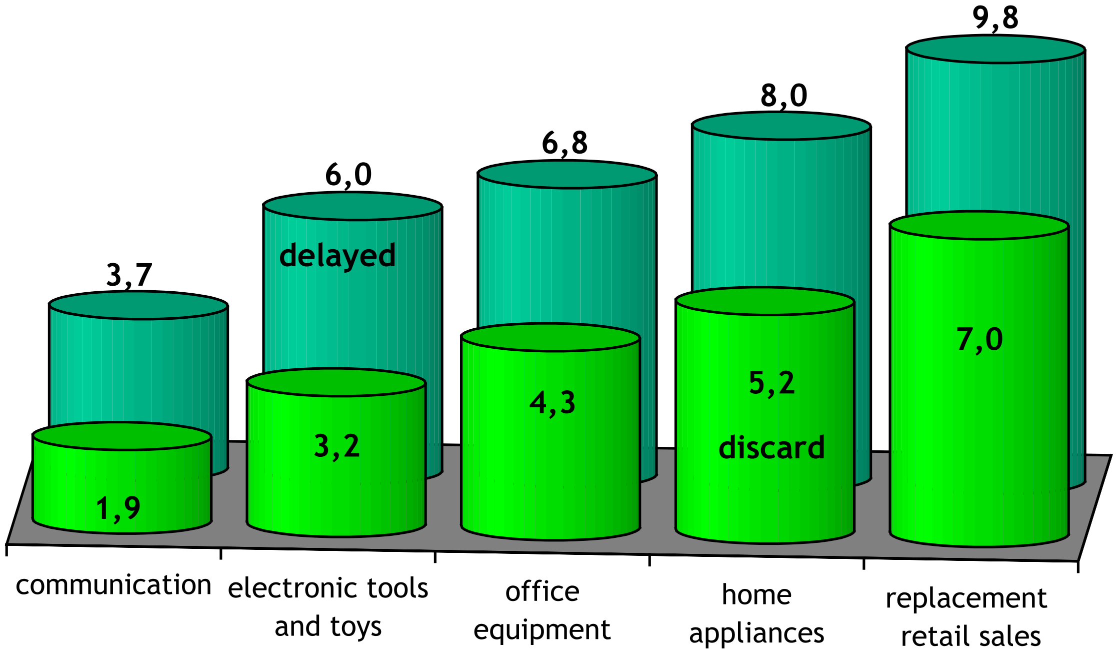


Figure 5: **Average life time of NiMH-Batteries by Application**

2.2 Waste Stream, Collection and Recycling

Focusing on European countries, a model for disposed NiMH-batteries after their end of life was calculated, considering the following experiences and influencing parameters:

- **application categories**
- **average life time**
- **market share in the year of introduction**
- **delaying time (hoarding)**

The back column in Figure 6 shows the tonnage of NiMH-battery scrap by categories in the year 2000. In total, 2.556 t reached their end of life by lost of function in EU-countries. Probably 1.724 t (front column) of damaged batteries were only disposed of by the consumer. In contrast to the batteries which went out of function in the year 2000, this model expresses that the battery scrap collected should came mainly from the communication sector (mobiles). This can be confirmed by the experience of sorting and recycling plants.

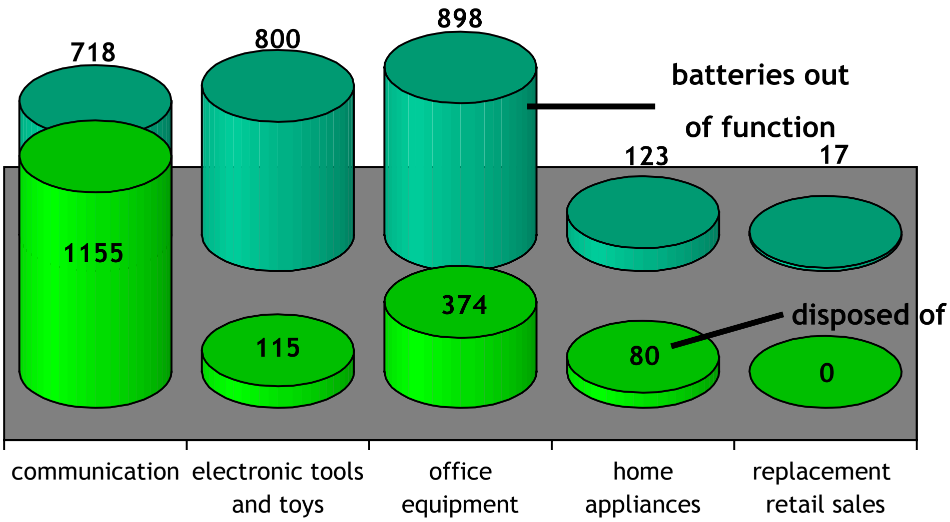


Figure 6: **NiMH-Battery Waste Stream (year 2000 / t)**

In comparison with the waste stream expected, Figure 7 explains the collection of used NiMH-batteries in 2000 in the EU-countries (estimation). In contrast to the expected battery waste, approximately 300 t were collected only. This corresponds to a collection rate of less than 20%.

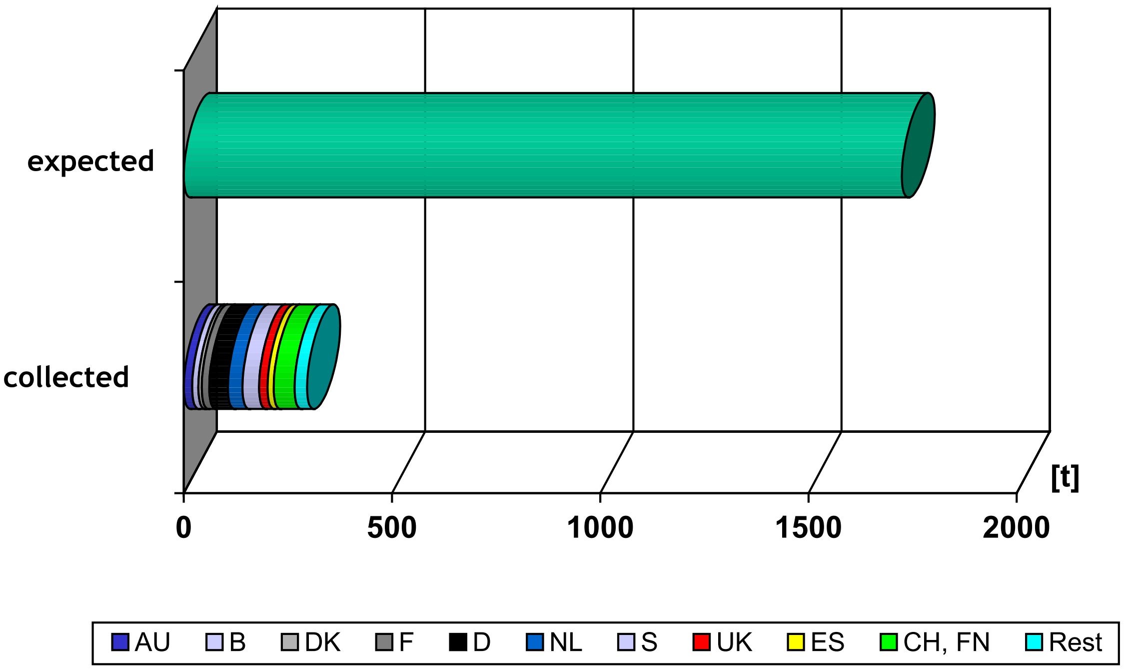


Figure 7: **Amount of NiMH-Battery Waste expected versus collected in EU / year 2000**

Some appropriate reasons and influencing aspects should be mentioned in order to increase the collection rate significantly:

- only 50% of EU-countries installed an efficient collection scheme yet
- existing schemes should exceed the current, partially low collection rate
- consumer of batteries should be motivated to reduce its battery waste stock
- to receive devices with incorporated batteries, the implementation of the WEEE-Directive should be accelerated

Further more, current studies have to reveal the consumer behaviour with a reliable valuation of hoarding effects, to control and improve the disposing habits of battery users. Only considerable amounts of NiMH-battery waste facilitates the economic recover of all contended valuable materials.

3 Mechanical processing of discarded NiMH-Batteries (UVR-FIA)

The Ni-MH batteries consist of a gas-tight can made out of nickel-coated sheet steel, electrodes, separators, seals, and electrolyte. The positive electrode is composed of nickel-plated steel and is covered with active mass composed of a mixture of nickel hydroxide, cobalt oxide, binders and conducting agents. The negative electrode is made of a hydrogen-storing alloy, which is composed of Nickel, Rare-Earths (RE), Cobalt, Manganese and others. RE is representing Mischmetal constisting of La, Nd, Pr and Ce.

Table 2 shows an average composition for cylindrical type of Ni-MH batteries. The percentage distribution of the metals is as-follows: Ni approximately 45%, Co approximately 5%, RE's (Mischmetal) approximately 10%, Fe approximately 35% and small amounts of Zn, Mn and Al.

Table 2: Components of NiMH-Batteries (round type)

Components in %	Total	Casing and Electrode Foils	Active Mass of Electrodes	Plastics	Electrolyte
Casing of steel	22,3	22,3			
Plastic Parts	0,5			0,5	
Separator Fleece	2,2			2,2	
Positive Electrode	32,0				
- Electrode Foil (Ni)		4,7			
- Active Mass ($Ni(OH)_2$)			27,3		
Negative Electrode	30,7				
- Electrode Foil (Ni-NiCrFe-FeNi)		6,8			
- Active mass ($MmNi_5$)			23,9		
Electrolyte	12,3				12,3
Sum	**100**	**33,8**	**51,2**	**2,7**	**12,3**

The main directions for processing of spent batteries in the present investigations are

1. mechanical processing, pyrometallurgy and hydrometallurgy
2. thermal treatment, mechanical processing, pyrometallurgy and hydrometallurgy.

The advantage of an additional thermal step in the second variant is the decomposition of the voluminous organic components.

3.1 Shredding

The main design criteria for the shredding process is to obtain a powder fraction not polluted by iron. After shredding the steel shell and the various fractions of battery materials are carefully separated by mechanical processing. Figure 8 shows the shredding and screening process flow diagram.

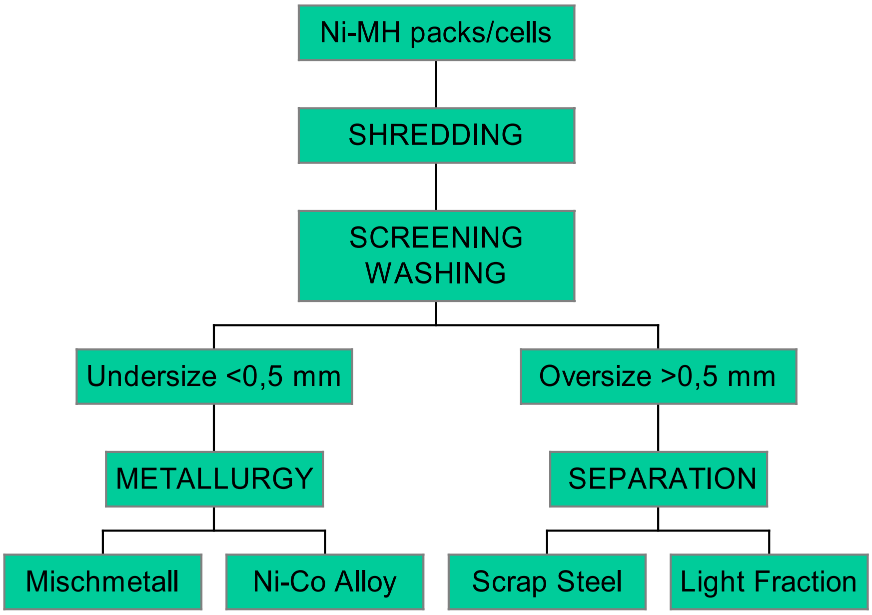


Figure 8: **Flow Diagram Mechanical Processing**

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 used for crushing the batteries to release the active mass of electrodes for metallurgical processing. Comminution with spraying of water into the mill is necessary due to pyrophoric behaviour of the negative electrode's fine particles.

The ground material is wet screened at a mesh size of 0,5 mm producing 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 organic components are avoidable with a first thermal step of processing the batteries. The fine fractions after shredding and screening of anodes plates, spent batteries and thermal treated batteries were analyzed (Table 3).

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

Composition	Anode mechanical treated	Batteries mechanical treated	Batteries thermal +mechanical treated
Ni	42	56	66
Co	10	9	7,5
Fe	0,4	0,7	2,8
Mn	6,5	5,6	4,4
Al/Ti/V	<0,1	<0,1	<0,1
Cr	4,3	3,3	1,9
Zn/Cd		5	2
Ca/Mg	0,5	0,9	0,3
K/Na	0,1	0,2	5,9
RE	36	19	9
Sum	99,9 as metal	99,8 as oxide	99,9 as oxide

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 irons with 0,4%. 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% as well as with the thermal treatment and subsequent shredding nickel with 66%, cobalt with 7,5%, RE-Mischmetal with 9%, manganese with 4,4%, chrome with 1,9%, iron with 2,8% and potassium/sodium from the electrolyte with 5,9% represents.

3.2 Hydrometallurgical Processing

Hydrometallurgical treatments are carried out after the mechanical processing of pyrometallurgical produced slag's. The material is crushed in a jaw-crusher. After removal of coarse metal-pieces a ball-mill is used for grinding. The part finer 0,1 mm after screening was leached.

The hydrometallurgical processing flow diagram in Figure 9 shows the steps to prepare RE-Mischmetal chloride for fused salt electrolysis.

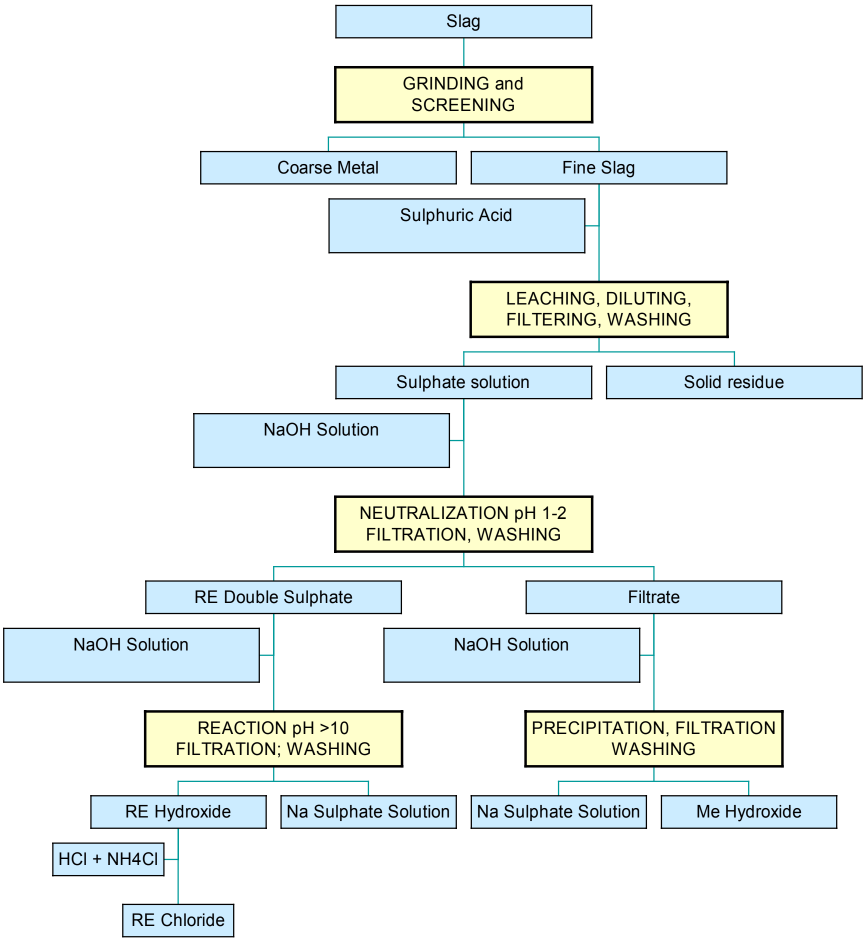


Figure 9: Hydrometallurgical Processing flow

The slag is leached with aqueous sulphuric acid. The concentrations, solid/liquid ratio, temperature and time were modified to optimize process parameters of leaching. The solution contains in addition to the Rare Earths also further metals, in particular Ni, Co, Mn, Zn and Al. Fe also present enters the solution because of an incomplete preliminary separation of the Fe-containing parts. Cd must also be expected for the case where Ni/Cd cells seep in as a result of incorrect sorting, and furthermore, contamination by Ti, Zr, Cr and V must be expected from AB_2 alloys. The proportion of Mn and Zn is possibly increased as a result of adding alkali/manganese primary cells. The pH of the solution is initially in the extremely acid range (pH<<1).

The rare earths 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, in which process the pH rises from approximately 1.5 to 2. In order to ensure that no iron is co precipitated in the pH range favorable for the double sulphate precipitation, it is to reduce to Fe^{2+} by adding a reducer. The filtrate from the double sulphate precipitation now contains all the transition metals not belonging to the rare-earth group, and possibly small residues of rare earths, and furthermore of Al, Ti, Zr, Cr and V.

Next the double sulphates are changed into RE hydroxide 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 of ammonium chloride, a rare earth chloride is obtained which is subjected to an electrometallurgical reduction to the rare earth metal or to a mixture of the same (Mischmetal).

The quantitative recovery of nickel and cobalt is of particular interest for the production of new hydrogen-storage alloys, and also for the production of new nickel hydroxide masses for the positive electrode of nickel/metal hydride cells. The precipitation of hydroxides by adding of NaOH solution leads to a complete separation of the valuable metals Ni and Co, and of the other accompanying metals Zn, Mn, Cd, rare earths, Fe and possibly Cr from the sodium sulphate solutions.

They can now be treated in the pyrometallurgic process.

shows the results of hydrometallurgy of two types of slag's. The slag's were produced with fluxes that yielded a favorable behavior with pyrometallurgic processing.

Table 4: Results of hydrometallurgy slag treatment

Type of slag	A	B
Composition of melt	11,25 % SiO_2 10,00 % CaO 3,75 % MgO 75,00 % NiMH	30,00 % CaF_2 70,00 % NiMH
Material of the crucible	SiC	Graphite
X-ray analysis of slag's	CaO RE-oxide Amorphous silica	CaF_2 CaO RE oxide RE oxide-fluoride
Residue of sulphuric acid leaching (anhydride and others)	19 %	79 %
Na RE double sulphates	158 %	66 %
Content of RE oxides		
- theoretically	69 %	29 %
- experimentally	70 %	30 %

4 Pyrometallurgical processing (IME)

4.1 Economical potential

In the recent years the production of Ni-MH-Batteries has grown steadily as indicated in chapter two. Nowadays they are established in the market in various applications.

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 [6, 7]. But recycling is economically interesting due to the relatively high metal prices of Nickel, Cobalt and Rare Earth metals.

The metal value of 1 kg Ni-MH-Batteries (round cell) is represented in Table 5.

Table 5: Value contained in 1 kg Ni-MH-round cell consumer battery-scrap (type AB_5)

component	proportion in round cell [mass-%]	metal price [€/t] [13]	value [€/kg]
Ni (May 2002)	36-42	7140	2,57-3,00
Co (May 2002)	3-4	17940	0,54-0,72
Mischmetal (January 2000) (La, Ce, Nd,Pr)	*8-10*	8000	0,64-0,80
sum			3,75-4,52

Taking the mass of sold batteries in 2000 (Figure 3) the total economical potential of Ni-MH-battery scrap is calculated to 5.6-6.7 million Euro for Germany respectively 17.1-20.7 million Euro for Europe.

4.2 State of the art in Ni-MH-Battery recycling

4.2.1 Assumption for recycling

Recycling of used products and materials is demanded by the EU-politics because of a raised environmental consciousness in the recent years. Objectives of recycling are to relieve the environment, safe raw materials and energy and to reach a high recycling rate of valuable materials. From today’s point of view recycling is less a technological problem but an economical. In particular metal recycling is depending on economical variations, which often leads to bankruptcy of recycling companies. With expected increasing costs for depositions of wastes the need for recycling is obvious. But recycling has to be always economically feasible.

Assumptions for the mentioned requirements with respect to a recycling process for Ni-MH-Batteries are:

- Knowledge of present and estimation of future rate of returns for discharged Ni-MH-Batteries by installation of suitable collection systems
- sufficient purity of the scrapped battery by sorting technologies to avoid disturbing impurities
- fundamental knowledge about directives, laws, ordinances, regulations
- estimation of future raw material situation on world market
- feasibility study of recycling process and comparison with primary production

A recycling concept for Ni-MH-Batteries is expected to be profitable, if it recovers Nickel, Cobalt and RE-Metals for direct re-use in battery production (closed loop process). A minimum of process steps and of non useable by-products like plastics ore waste water has to be guarantied.

Several hydrometallurgical recycling processes were investigated. The most important processes are described by Yoshida [8], Lyman et al. [9], Pietrelli et al.[10] and Varta [11]. In all described processes the first step is mechanical processing. Subsequently different leaching and solvent extractions steps are necessary in order to obtain Rare Earth metals and Nickel and Cobalt dissolved. The resulting RE salts are useable in a fused salt electrolysis whereas Nickel and Cobalt are won via precipitation, ion-exchange or electrowinning. All described processes were investigated in laboratory scale without transfer into pilot plant tests.

A closed loop pyrometallurgical recycling process for Ni-MH-Batteries is not existing. At the moment Nickel and the steel shell of the batteries are open loop recycled in the steel industry. Cobalt is neither paid nor recovered. The RE are ending in the slag. Besides this no recycling processes or research projects are described in literature.

4.3 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 (< 1450 °C)

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 [12]. 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 they are not suitable as slag base for the expected working temperature of 1500-1700 °C. Calcium fluoride (Bp 2513°C) and Calcium chloride (Bp 1600 °C) may be useable as fluxes in order to generate RE-fluorides respectively RE-chlorides during the melting process. 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 can not be evaporated selectively. Alternatively a mixture of Calcium fluoride and Calciumoxide has potential, as the mixture has got an eutectic melting point of 1360°C (for 15 % CaO, 85 % CaF_2).

4.4 Lab-scale experiments

Trial tests were made in a Tamman-type furnace (Figure 10, left). 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. The input was consisting of pure negative electrode mass originated from production wastes. Type and mass of additive slag was varied as represented in Table 6.

Pouring took place always at 1600 °C measured with a EL18 thermocouple. Different crucibles were tested (graphite, MgO, Al_2O_3).

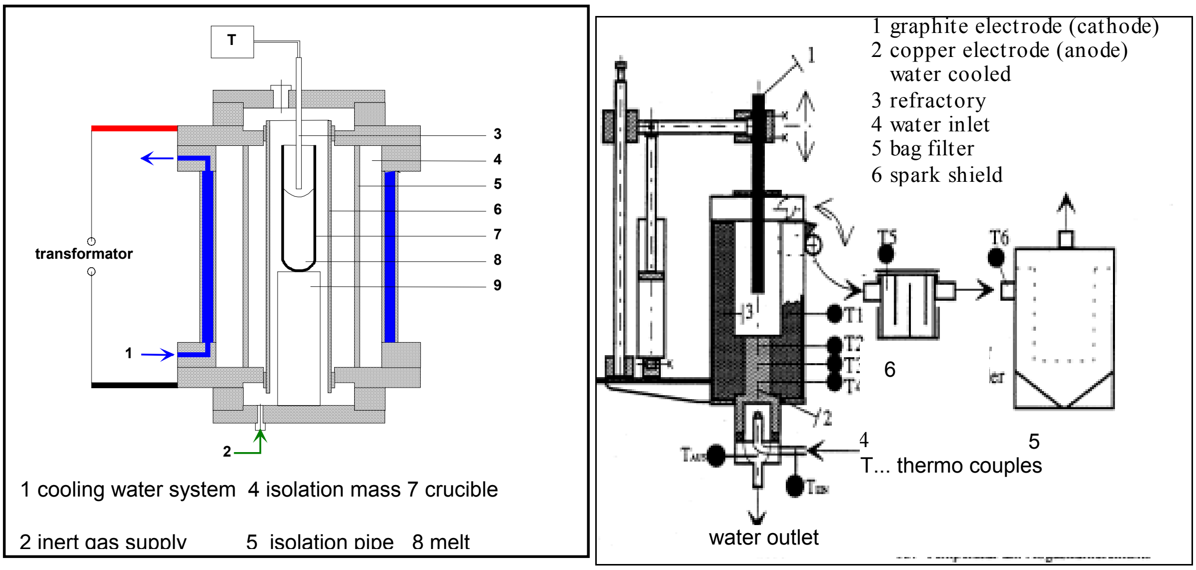


Figure 10: Principle sketch of Tamman furnace (left), electric arc furnace (right)

Table 6: Overview Tamman furnace experiments

exp.	flux composition					charge composition	
	SiO_2	CaO	MgO	CaF_2	$CaCl_2$	flux	Ni-MH
1	45 %	40 %	15 %			33 %	67%
2	45 %	40 %	15 %			29 %	71 %
3	45 %	40 %	15 %			26 %	74 %
4	45 %	40 %	15 %			15 %	85 %
5	45 %	40 %	15 %			23 %	77 %
6	45 %	40 %	15 %			18 %	82 %
7				100 %		23 %	77 %
8				100 %		19 %	81 %
9				100 %		16 %	84 %
10		40 %		60 %		19 %	81 %
11		40 %		60 %		20 %	80 %
12	100 %					11 %	89 %
13	100 %					15 %	85 %
14	100 %					10 %	90 %
15					100 %	21 %	79 %
16					100 %	23 %	77 %

4.5 Experiments electric arc furnace

The most promising slag systems were investigated in a lab-scale electric arc furnace (Figure 10, right). Objective was to evaluate the technical feasibility of these slag systems in a larger volume of scale.

Table 7: Overview electric arc furnace experiments

exp.	flux composition				charge composition			pouring temperature	crucible
	SiO_2	CaF_2	CaO	MgO	flux		Ni-MH	[°C]	
1	100%				25%		75%	1550	MgO
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		84,20%	15,80%		7,50%	40,00%	52,50%	1420	graphite
10		87,00%	13,00%		7,50%	50,00%	42,50%	1392	
11		84,20%	15,80%		7,50%	40,00%	52,50%	1520	
12		100,00%				50,00%	50,00%	1360	
13		66,70%	33,30%		15,00%	30,00%	55,00%	1430	
14		76,90%	23,10%		15,00%	50,00%	35,00%	1360	
15		84,20%	15,80%		7,50%	40,00%	52,50%	1650	
16		100,00%				30,00%	70,00%	1480	
17		100,00%				40,00%	60,00%	1360	
18		80,00%	20,00%		7,50%	30,00%	62,50%	1290	
19		72,70%	27,30%		15,00%	40,00%	45,00%	1540	
20		84,20%	15,80%		7,50%	40,00%	52,50%	1420	

The Ni-MH mass was briquetted with the flux (25 % of charge) in order to avoid dust losses. The total input was 6500 g for each trial. Two different furnace refractories (MgO, SiC) were used, which were identified to resist the chemical aggressive impact of RE. A special emphasis was given to the CaO-CaF_2 system (Table 7). As refractory wear was too high for MgO and SiC a graphite crucible was mounted into the furnace. Total input mass was 5000 g. 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.

4.6 Results and discussion

4.6.1 Tamman furnace

Only the graphite crucible is resisting the thermal and chemical stress. But wear is still occurring after several uses. The crucibles made of MgO and Al_2O_3 are not suitable. According to the chemical reaction

$$2\ RE + MeO \rightarrow RE_2O_3 + 3\ Me \quad (4)$$

the lining oxides (MeO) were reduced by the rare earth metals as it can be expected thermodynamically.

The evaluation of the experiments showed a good separation of metal and the corresponding slag composition is suitable in regard to viscosity. For selected slag systems the final metal and slag analysis are given in Figure 11.

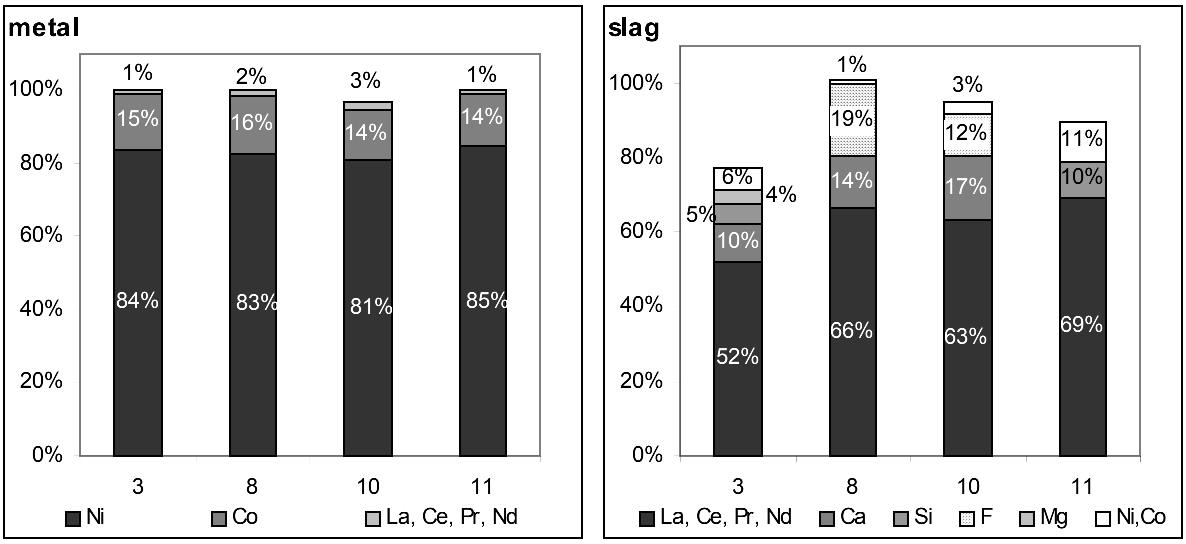


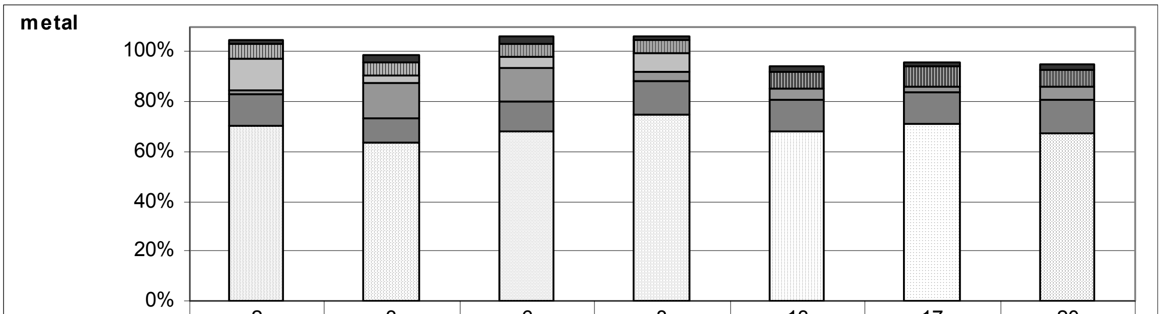
Figure 11: Metal and slag compositions for selected Tamman-furnace experiments

Nickel and Cobalt are mainly collected in the metal phase whereas RE end up in the slag phase. Slag systems containing SiO_2 and/or MgO have got a higher Nickel content in slag in comparison to the CaF_2-CaO systems. The SiO_2 and/or MgO systems are expected to have a higher viscosity and thus the separation by gravity is hindered. Furthermore the volume of flux (slag/metal-ratio) must be sufficient in order to secure separation. From these experiments it can be shown that at least 22,5 % flux are needed for metal-slag separation.

The trials with chloride-based slags are not successful. At temperatures larger than 1500°C calcium chloride is already evaporated due to its high vapor pressure. Intensively smoke development was observed during these experiments. A separation was not visible. Alternatively a slag system based on CaO-CaF_2-Al_2O_3 was tested sussesfully.

4.6.2 Electric Arc Furnace

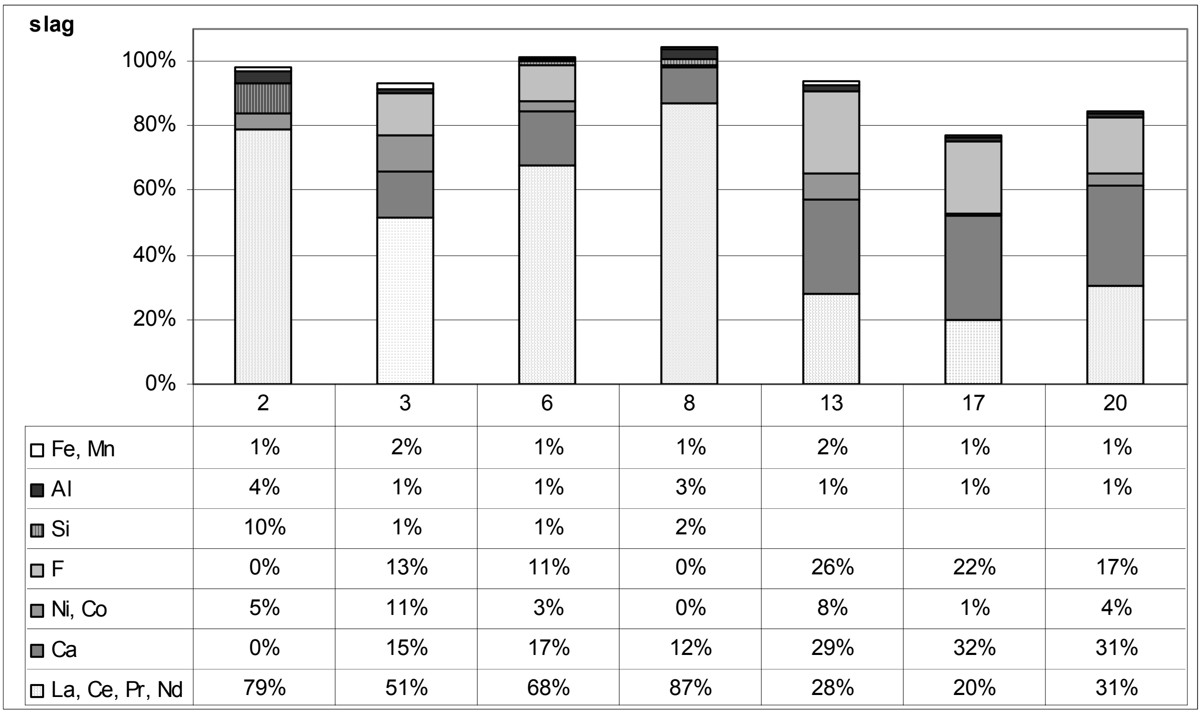
With the slag systems used in experiment 1 to 7 (Table 7) the objective of metal-slag separation could not be performed. A clear separation was failed. In exp. 1 just a single phase was recovered. The melt was high viscose. Decreasing of viscosity by increasing the temperature was not successful. Part of the melt remained in the furnace after pouring. The tested refractory materials were heavily weared by the slag. The exp. 7 and 8 showed expected results. The low viscous melt was poured easily and a clear separation of metal and slag after solidification was observed. The analysis shows for this two experiments the best results follows by experiments 1 and 2 (Figure 12, Figure 13).



	2	3	6	8	13	17	20
■ Al	1%	3%	3%	1%	3%	2%	2%
▥ Fe, Mn	6%	5%	5%	6%	7%	8%	7%
▒ Si	13%	3%	5%	7%			
▨ La, Ce, Pr, Nd	1%	14%	13%	4%	4%	3%	5%
▩ Co	13%	10%	12%	14%	13%	13%	13%
□ Ni	70%	63%	68%	75%	68%	71%	67%

Figure 12: Metal analysis of selected electric arc furnace experiments (best results)

The high silicon content in bullion of experiments 1 to 8 shows (Table 4, Figure 5), that silicon is also reduced and dissolved in the metal phase, which makes a subsequent refining step necessary to meet battery alloy specifications. Thus a silicon free refractory is recommended in order to fulfil process cost and purity requirements.



	2	3	6	8	13	17	20
□ Fe, Mn	1%	2%	1%	1%	2%	1%	1%
■ Al	4%	1%	1%	3%	1%	1%	1%
▥ Si	10%	1%	1%	2%			
▨ F	0%	13%	11%	0%	26%	22%	17%
▨ Ni, Co	5%	11%	3%	0%	8%	1%	4%
▨ Ca	0%	15%	17%	12%	29%	32%	31%
□ La, Ce, Pr, Nd	79%	51%	68%	87%	28%	20%	31%

Figure 13: Slag analysis of selected electric arc furnace experiments (best results)

In exp. 1 the separation of slag and metal was failed. In exp. 4 to 7 the high RE content in metal phase is obvious as well as a the Nickel content in the slag phase. It is assumed that the flux ratio is to less. The chosen ratio of 25 % is close to the lower limit as proven in the Tamman furnace trials. The trials 9-20 with modified CaO-CaF_2 ratio as well as increased flux/metal-ratio showed an improved melting and pouring behaviour. Transferring Nickel and Cobalt in metal on the one hand and on the other hand to collect RE in the slag phase could be reached best in trial no. 12 and 17, where pure CaF_2 flux was used.

Table 8: Distribution coefficient for selected experiments

exp.	Ni_{met}/Ni_{slag}	Co_{met}/Co_{slag}	RE_{met}/RE_{slag}
2	16	22	0,02
3	7	6	0,28
6	29	19	0,19
8	490	135	0,05
13	9	13	0,16
17	177	98	0,13
20	20	58	0,18

The experiments with CaO-CaF_2 flux did not led to a suitable slag system. Metal losses in slag are too high as well as the RE content in the Ni/Co alloy (Table 8). Furthermore the high fluoride content in the slag causes difficulties in the subsequent leaching step due to chemical reaction with hydrogen. A fluoride containing flux is not suitable in the process.

5 Next Steps

The market research will be continued and a the feasibility study will be completed. Used batteries will be used in a higher amount in mechanical processing instead of the so far investigated production scrap. The influence of other battery types (NiCd, Zn/C, Alkaline) polluting the NiMH-scrap will be investigated. The hydrometallurgical trials will be proceeded. In Pyrometallurgy the three alternative slag systems have to be further optimized to fulfill the requirements of the project. Pilot plant trials (1 t) will be executed by end of this year.

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