CLOSED-LOOP RECYCLING OF NICKEL, COBALT AND RARE EARTH METALS FROM SPENT NICKEL-METAL HYDRIDE-BATTERIES

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ABSTRACT

Nickel-metal hydride batteries (Ni-MH) are storers of electrochemical energy, which have a higher specific storage capacity than lead or nickel-cadmium batteries. The demand for Nickel-metal hydride batteries is increasing rapidly since their market launch in the early 1990's. Today there is no suitable and sustainable recycling process to recover nickel, cobalt and rare-earth metals. The discarded batteries are used today in the steel industry as alloy material because they contain nickel. Cobalt and rare-earth metals (RE) are lost; they are non-recycleable.

In a German governmental funded research project, IME Aachen, ACCUREC Mühlheim and UVR-FIA Freiberg are cooperating in processing as well as in creating a feasibility study. The target of this project is the development of a new recycling process for metal recovery from Ni-MH-batteries. The proposed process described in this paper consists of a combination of mechanical, pyrometallurgical and hydrometallurgical processing steps. This process is capable of treating all types of Ni-MH-batteries. After comminution steel and organics are separated. The separated Ni-MH is smelted in an electric arc furnace. The products are a nickel-cobalt alloy and a slag phase enriched with rare-earth oxides for further treatment to ‘mischmetal’. Both the Nickel-Cobalt alloy and the ‘mischmetal’ will be directly used in battery production.

Keywords: Ni-MH-batteries, recycling, mechanical processing, pyrometallurgy, hydrometallurgy

1 INTRODUCTION

In the last ten years, the demand for light, energy-rich, and rechargeable batteries has increased dramatically. 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 80's and early 90's by nickel-cadmium accumulators. Due to increasing demands of the electronic industry, nickel-metal-hydride batteries, which provide a 50-100% higher energy density, were introduced to the market in the mid 90's. The rapid development and market success of cellular phones especially boosted the sales of Ni-MH-cells.

Due to their technical advantages, the yearly production of battery cells was expanded around 50-150%. In 1999, shown in Figure 1, the output of cells exceeded 80,000 tons per year (1 billion cells per year), before the sales volume dropped down in the year 2000 due to the worldwide economic decline. However, on a worldwide basis Ni-MH-battery production is passing the quantity of NiCd-cells currently produced and will be the dominating battery system in the near future. Lithium-Ion batteries, a battery technology which meets the continuously growing demands of the communication industry, are developing market applications as fast as Ni-MH-batteries. Lithium-Ion batteries will replace Ni-MH-batteries, where high capacity and voltage per unit volume is required.

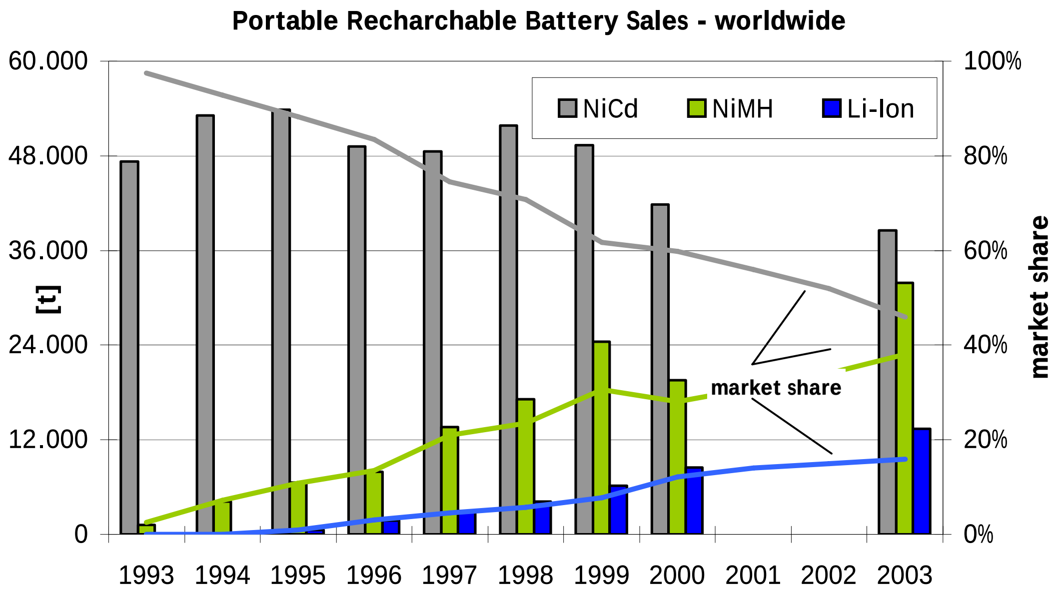

Figure 1: Sales Quantity of Ni-MH-batteries in t

However, after some years of productive use, Ni-MH-batteries reach the end of their life. Several technical investigations have been dedicated to determine the average lifetime of Ni-MH-batteries. The average lifetime is between two years for communication devices and seven years for single cells. For various reasons, the consumer stores his waste for some time before he disposes of the used battery. This behavior has been defined as a kind of hoarding effect. Between four and ten years after introduction to the market, the hoarded batteries are expected to reach the waste stream. The collection rate in Germany was less than 1%, e.g. 17.2 tons collected out of 1833.5 t introduced to the consumer (Schultmann et al. 2002).

Two intermetallic alloy types are used for hydrogen-storage in batteries. Due to their higher stability and lower self-discharge, AB5 is the most common; AB2 is very rare. A is derived from IIIa and IVa group metals and B are derived from Va, VIa, VIIa, VIIIa group metals. For AB5, LaNi5 is mainly used, but can be improved by substitution of nickel with cobalt, manganese and aluminium (Srivastava et al. 2000). Lanthanum is partly replaced by the cheaper 'mischmetal' (RE), composed e.g. of 50-55% cerium, 18-28% lanthanum, 12-18% neodymium and 4-6% praseodymium. A typical alloy today is $RENi_{3.5}Co_{0.7}Mn_{0.4}Al_{0.3}$. A typical AB2 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 Polyamide or Polypropylene. The cell cup consists of nickel or nickel-plated steel, which is resistant in alkaline solutions. The electrolyte is mainly diluted potassium hydroxide (20-30 % KOH) containing some parts of lithium hydroxide. The reactions occurring at the electrodes are:

Negative Electrode: $MH + OH^- \overset{\text{discharge}}{\underset{\text{charge}}{\longleftrightarrow}} M + H_2O + e^-$ (1)

Positive Electrode: $NiOOH + H_2O + e^- \overset{\text{discharge}}{\underset{\text{charge}}{\longleftrightarrow}} Ni(OH)_2 + OH^-$ (2)

Overall: $MH + NiOOH \overset{\text{discharge}}{\underset{\text{charge}}{\longleftrightarrow}} M + Ni(OH)_2$ (3)

During discharge atomic hydrogen is released at the negative electrode and reacts with hydroxide ions (released at the positive electrode) forming water. This process is reversible and allows thousands of charge and discharge cycles.

The most important criterion for the evaluation of recycling processes is determining the raw materials situation and the price of raw materials in comparison with the recycled material. According to today’s knowledge, the natural reserves of nickel, cobalt and rare-earth metals are sufficient for the next 100 years

(Milbank 1997). However recycling is economically interesting due to the relatively high prices of nickel, cobalt and rare-earth metals. The economic feasibility of using Ni-MH-battery scrap is summarized in Table 1 below.

Table 1: Composition of Ni-MH-cell scrap (Fricke and Knudsen 2002)

Component	**Mass Percentage %**			
	AB5-button cell	**AB5-cyln. cell**	**AB5-pris. cell**	**AB2-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	-	-	-	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 recycling concept for Ni-MH-batteries is expected to be profitable, if it possesses the capability to recover nickel, cobalt and rare-earth metals for direct reuse in battery production (closed-loop process). Minimum process steps and useless by-products such as plastics or wastewater must be guaranteed.

Several hydrometallurgical recycling processes have been investigated. The most important processes are described by Yoshida et al. (1995), Lyman et al. (1995), Kleinsorgen et al. (1997), and Pietrelli et al. (1999). The first step is mechanical processing (Czerny and Reichel, 1999) in all of described processes. Subsequent different leaching and solvent extraction steps are necessary in order to obtain rare-earth metals and nickel and cobalt in solution. The resulting rare-earth salts are applicable to fused salt electrolysis whereas nickel and cobalt are produced via precipitation, ion exchange or electrolysis. All the described processes have been investigated in laboratories but have not been transferred into pilot plant tests.

A closed-loop pyrometallurgical recycling process for Ni-MH-batteries does not exist. At the moment the nickel and the steel shell of batteries are open-loop recycled in the steel industry. Cobalt is neither paid nor recovered. The rare-earths metals end in slag. No other recycling processes or research projects are described in today's literature.

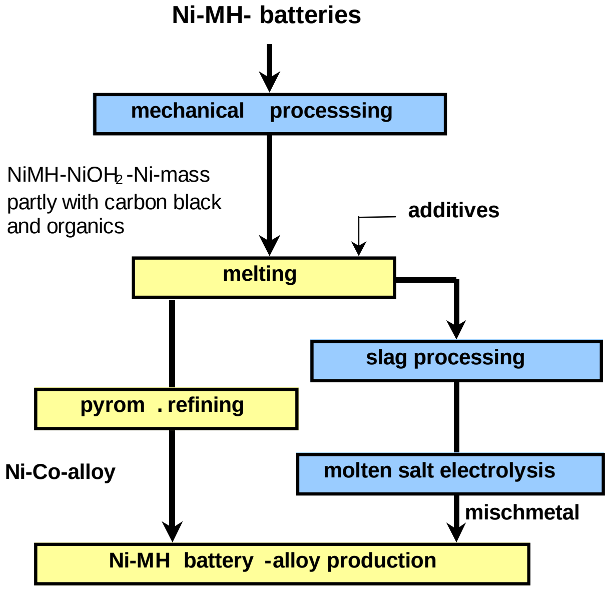

Figure 2: Flow sheet of the intended investigation of Ni-MH-battery recycling

Whenever a high quantity of goods containing heavy metals and valuable materials enters the market, the producers and the public are interested in new recycling technologies. The objective of the German government funded work is to develop a simple-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 studies. UVR-FIA GmbH deals with mechanical processing and hydrometallurgy and IME Process Metallurgy and Metal Recycling focuses on pyrometallurgical processing.

After collection, a combination of mechanical and metallurgical processing is intended (Figure 2). The comminution step is expected to separate the steel shell and organics from the Ni-MH mass. With the use of an electric arc furnace and specific fluxes nickel-cobalt alloy should be generated and the rare-earths metals should be oxidized and slagged. Nickel-cobalt alloy is pyrometallurgically refined and as a product directly usable in the battery industry. The slag is processed mechanically and hydrometallurgically in order to transfer the rare-earth oxides into rare-earth chlorides, which are fed into a fused salt electrolysis. The product 'mischmetal' is also directly usable as a battery alloy component.

2 MECHANICAL PROCESSING OF DISCARDED NI-MH-BATTERIES

The Ni-MH-batteries consist of a gas-tight can made out of nickel-coated sheet steel, electrodes, separators, seals, and an electrolyte. The positive electrode is composed of nickel-plated steel and is covered with an 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 represents 'mischmetal' consisting of La, Nd, Pr and Ce.

Table 2 shows an average composition for cylindrical type of Ni-MH-batteries.

Table 2: Components of Ni-MH-batteries (cylindrical type)

Components in %	Total	Casing and Electrode Foils	Active Mass of Electrodes	Plastics	Electrolyte
Casing 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 design criterion for the shredding process is to obtain a powdery fraction not polluted by iron. After shredding the steel shell, the various fractions of battery materials are carefully separated by mechanical processing. Figure 3 shows the shredding and screening process flow diagram.

A hammer mill with one rotor driven at a speed of 46 m/s (rotor diameter 670 mm), equipped with a perforated discharge grid of 20 mm opening, 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 can ignite.

The ground material is wet screened at a mesh size of 0.5 mm; thus a fine fraction is obtained with valuable components such as Ni, Co, and RE and an oversized fraction consisting of a mix of iron chips, electrodes grids, plastic chips, paper, and flocculent material of separators. The organic components are avoidable when there is a thermal step at the beginning of processing batteries.

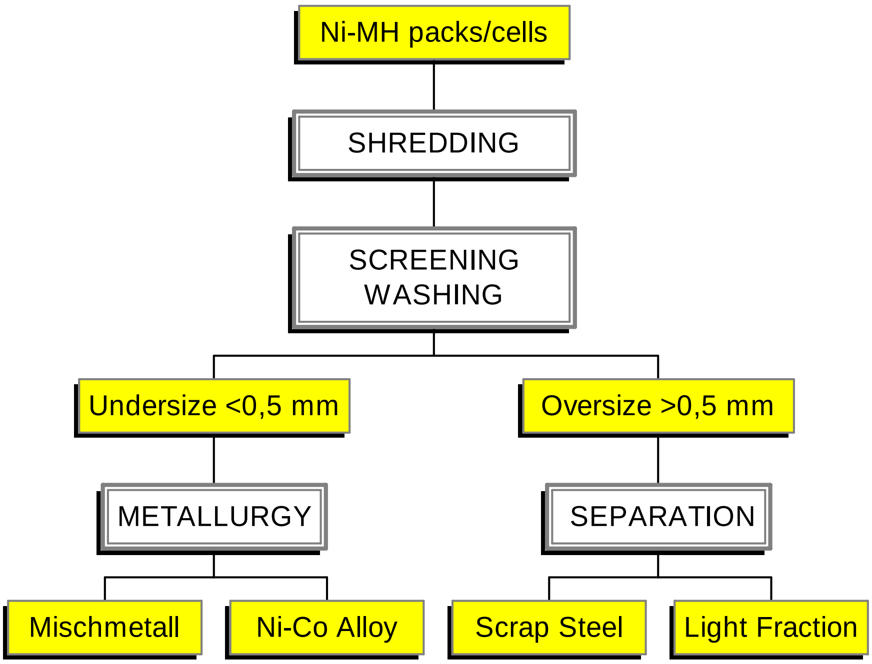

Figure 3: Flow Diagram Mechanical Processing

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, the anode-material contained 42% nickel, 10% cobalt, 37% rare-earth 'mischmetal', 6.5% manganese, 4.3% chrome, and 0.4% iron. In mechanical preparation of batteries, there is 56% nickel, approximately 9% cobalt, 19% rare-earth 'mischmetal', 5.6% manganese, 3.3% chrome, and 0.7% iron.

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)

3 PYROMETALLURGICAL PROCESS

Any pyrometallurgical process relies on a suitable slag system. In this specific case, the process has to allow separation of nickel and cobalt as metal from the rare-earths almost quantitatively, collecting the rare-earths as well as impurities e.g. as oxides. Alternatively, the rare-earths 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 rare-earths as oxide, chloride, or fluoride
- density significantly lower than metal phase density (<5 g/cm³)
- low viscosity to allow an easy slag/metal separation
- moderate melting temperature (<1450 °C).

Several slag systems are suitable for the stated requirements. A slag system with 45% SiO_2/40% CaO/15% MgO has a melting point of 1400 °C, a density of 2.6 g/cm³ and a viscosity between 1.8 and 2.5 poise (Schlackenatlas, 1995). Pure silica flux is also suitable. Between 1400°C and 1700°C, rare-earth silicates are generated. These silicates are later extractable with hydrochloric acid in order to change rare-earth oxides into chlorides.

Most metal chlorides and fluorides have 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 respectively calcium chloride (Bp 1600 °C) may be usable as fluxes in order to generate rare-earth fluorides and rare-earth chlorides during the melting process. The boiling point of rare-earth fluorides is about 2300 °C and for rare-earth chlorides between 1700 °C and 1800 °C. Within this expected working temperature range, the rare-earth chlorides and, respectively, rare-earth-fluorides couldn't be evaporated selectively. Alternatively a mixture of Calcium fluoride and Calcium oxide has potential, as the mixture has a eutectic melting point of 1360 °C (for 15% CaO, 85% CaF_2).

Trial tests were made in a Tamman-type furnace (Figure 4, left). The experiments were performed in order to screen the slag systems and to find a suitable crucible-material, which would resist the aggressive conditions of chlorides and rare-earth metals. The input consisted of pure negative electrode mass originating from production wastes. Type and mass of additive slag was varied as represented in Table 4. Pouring took place always at 1600 °C measured with an EL18 thermocouple. Different crucibles were tested (graphite, MgO, Al_2O_3). Only the graphite crucible resists the thermal and chemical stress. However wear occurs after several uses. Therefore, crucibles made of MgO and Al_2O_3 are not suitable.

The evaluation of these experiments shows good separation of metal and also the corresponding slag composition is suitable in regard to viscosity. Nickel and cobalt are collected mainly in the metal phase, whereas rare-earth metals are found in the slag phase. Slag systems containing SiO_2 and/or MgO have higher nickel content in slag in comparison to CaF_2-CaO systems. The SiO_2 and MgO systems are expected to have a higher viscosity; 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 is needed for metal-slag separation.

The trials with chloride-based slags were not successful. At temperatures greater than 1500 °C, calcium chloride evaporates due to its high vapor pressure. Intense smoke development was observed during these experiments. Separation was not visible.

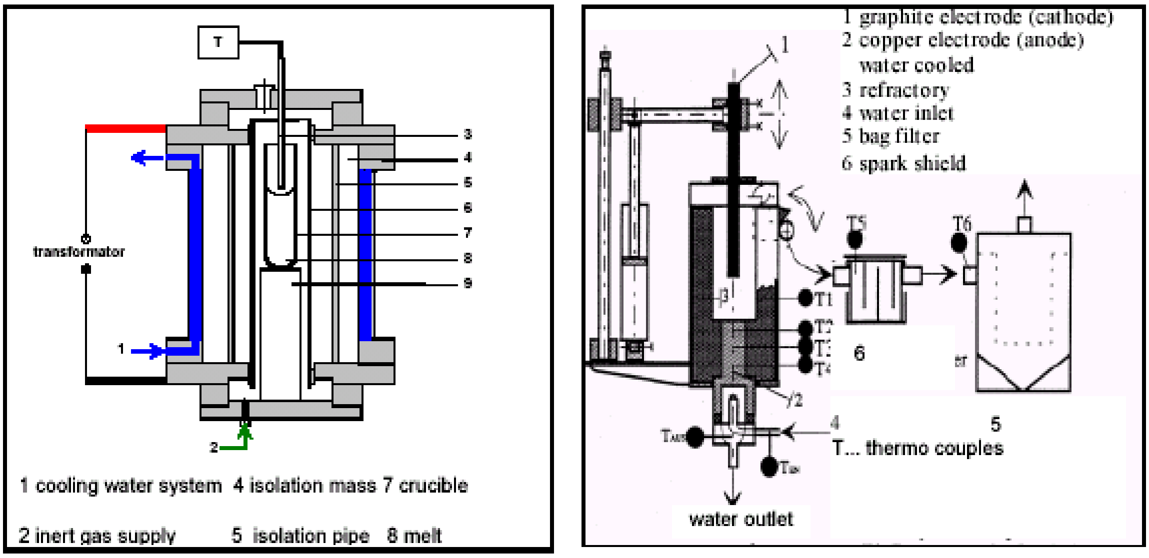

Figure 4: Principle sketch of Tamman furnace (left), electric arc furnace (right)

Table 4: Type and content of additive in slag in %

No	Flux Composition					Charge Composition		Number of Experiments
	SiO_2	CaO	MgO	CaF_2	$CaCl_2$	Flux	Ni-MH	
Tamman Furnace Experiments								
1	45	40	15			15-33	67-85	6
2				100		16-23	77-84	3
3		40		60		19-20	80-81	2
4	100					10-15	85-90	3
5					100	21-23	77-79	2
Electric arc furnace experiments								
6	100					25	75	2
7				100		25-50	50-75	5
8		13-35		65-87		25-65	35-75	11
9	45	40	15			25	75	2

The most promising slag systems (Table 4) were investigated in a lab-scale electric arc furnace (Figure 4, right). The objective was to evaluate the technical feasibility of these slag systems on a larger scale (5-6.5 kg). The Ni-MH mass was briquetted with the flux in order to avoid dust losses. Two different furnace refractories (MgO, SiC) were used, that resisted the chemical aggressiveness of rare-earths. When refractory wear was too high for MgO and SiC, a graphite crucible was mounted in the furnace. The temperature was measured with a commercial lance. Samples were taken from the cast metal as well as from the slag.

When the slag systems used a charge composition of 25% flux (Table 4) the objective of metal-slag separation could not be performed; a clear separation failed. In experiments with pure silica only a single phase was recovered. The melt was highly viscous. Decreasing viscosity by increasing the temperature was not successful. Therefore, part of the melt remained in the furnace after pouring. The tested refractory materials were heavily attacked by the slag. The experiments with a higher content of flux in the mixture showed expected results. The low viscous melt was poured easily and a clear separation of metal and slag after solidification was observed. A high silicon content in many of the experiments shows, that silicon is also reduced and dissolved in the metal phase. This reduction makes a subsequent refining step necessary to meet battery alloy specifications. Thus, a silicon free refractory is recommended in order to fulfill process cost and purity requirements. Table 5, with the distribution coefficient for selected experiments, shows that if the flux ratio is too low, a high rare-earth content in the metal phase is observable as well as nickel content in the slag phase. The chosen ratio of 25% is close to the lower limit as proven in the Tamman Furnace Trials. The trials, with modified CaO-CaF_2 ratio as well as increased flux/metal-ratio, showed an improved melting and pouring behavior; transferring nickel and cobalt in metal on the one hand and collecting rare-earth metals on the other. The slag phase could be reached best in trials using pure CaF_2 flux and content of 40% was used.

Table 5: Distribution coefficient for selected experiments

Charge composition					Ni_{met}/Ni_{slag}	Co_{met}/Co_{slag}	RE_{met}/RE_{slag}
NiMH	SiO_2	CaF_2	CaO	MgO			
75	25				16	22	0.02
75		25			7	6	0.28
75			16.25	8.75	29	19	0.19
75	11.25	10	3.75		490	135	0.05
55		30	15		9	13	0.16
60		40			177	98	0.13
52.5		40	7.5		20	58	0.18

The experiments with CaO-CaF2 flux did not lead to a suitable slag system. Metal losses in slag and the rare-earth content in the Ni/Co alloy (Table 5) were too high. Furthermore the high fluoride content in the slag creates difficulties in the subsequent leaching step. A fluoride containing flux is not suitable in this process.

4 HYDRO-METALLURGICAL PROCESSING

Hydro-metallurgical treatments are carried out after the mechanical processing of pyrometallurgical slags. The material is crushed in a jaw-crusher. After removal of coarse metal-pieces, a ball-mill is used for grinding. The part finer than 0.1 mm after screening was leached.

The hydro-metallurgical processing flow diagram in figure 5 shows the steps to prepare rare-earth chloride for manufacture of rare-earths metal by the electrochemical method.

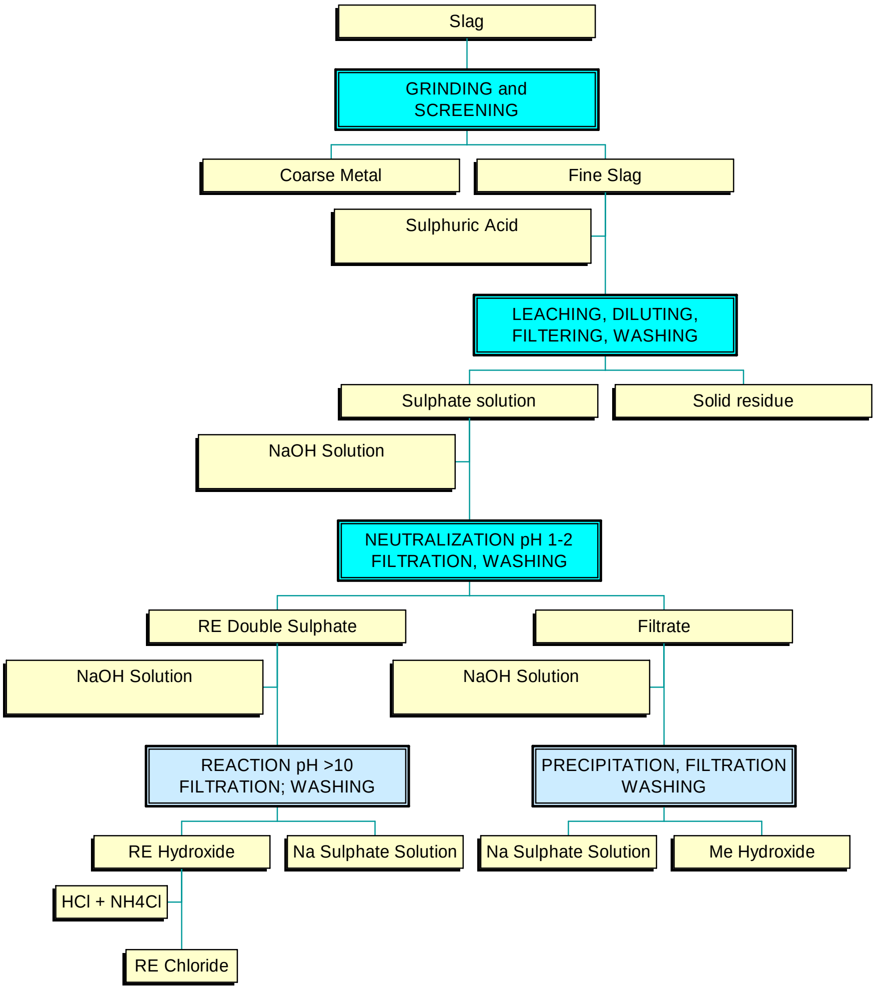

Figure 5: Hydro-metallurgical processing flow

Accordingly leaching with aqueous sulfuric acid dissolves the slag. The concentrations, solid/liquid ratio, temperature, and time were changed to optimize process parameters of leaching. The solution contains in addition to the rare-earths other metals; in particular, Ni, Co, Mn, Zn and Al.

Iron also present, enters the solution because of an incomplete preliminary separation of the Fe-containing components. Cadmium must also be expected when Ni/Cd cells seep in due to incorrect sorting. 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 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 sulfate precipitation, it is reduced to Fe^{2+} by adding a reducer. The filtrate from the double sulfate precipitation now contains all the transition metals not belonging to the rare-earth group, and possibly small residues of rare-earths, and furthermore Al, Ti, Zr, Cr and V.

The step following the double sulfate precipitation is the changing of double sulfate to rare-earth 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 and 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 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 sulfate solutions. These can be melted in elemental form from the latter by pyrometallurgic processes.

Table 6: Results of hydrometallurgy of slags

Type of slag	A	B
Composition of melt	11.25 % SiO_2 10.00 % CaO 3.75 % MgO 75.00 % Ni-MH	30.00 % CaF_2 70.00 % Ni-MH
Material of the crucible	SiC	Graphite
X-ray analysis of slag's	CaO Rare-earth oxide Amorphous silica	CaF_2 CaO Rare-earth oxide Rare-earth oxide-fluoride
	% material mass in relation to input-mass of slag	
Residue of sulfuric acid leaching (anhydride and others)	19 %	79 %
Na-RE-double sulfates	158 %	66 %
Content of rare-earths oxides		
- theoretically	69 %	29 %
- experimentally	70 %	30 %

Table 5 shows example of the results of hydrometallurgy of two types of slags. The slags were produced with fluxes that yielded a favorable behavior with pyrometallurgic processing.

4 CONCLUSIONS AND NEXT STEPS

In this paper, the results of experiments for the process of recovering metals from used nickel-metal hydride storage batteries are presented. The storage battery scrap is mechanically comminuted and divided into at least a coarse fraction and a fine fraction. The separated fine fraction is the input for pyro-metallurgical processing to a cobalt-nickel alloy and a slag with rare-earth metals as the main component. The process is comprised of a digesting step, dissolving the slag with sulfuric acid, performing a double sulfate precipitation of the rare-earths by raising the pH, and changing the double sulfate to rare-earth hydroxide by digestion with NaOH solution and washing with NH_4OH solution. The precipitate filtered off is dissolved in acid and from this solution a rare-earth chloride is obtained. It is then subjected to an electrometallurgical reduction to the rare-earth metal or to a mixture of a plurality of the same ('mischmetal'). The next steps are: Market research will be continued and the feasibility study will be completed. The influence of other battery types (NiCd, Zn/C, Alkaline) polluting the NiMH-scrap will be investigated. The mechanical processes and the hydrometallurgical trials will proceed. In pyrometallurgy the three alternative slag systems will be further optimized to fulfill the requirements of the project. Pilot plant trials on a scale of 1 ton will be carried out.

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