Available online at www.sciencedirect.com
ScienceDirect
Journal of Power Sources 158 (2006) 1498–1509
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Development of a recycling process for nickel-metal hydride batteries

Tobias Müller *, Bernd Friedrich

IME Process Metallurgy and Metal Recycling, Department of RWTH Aachen University, Germany

Received 19 April 2005; accepted 13 October 2005
Available online 28 November 2005

Abstract

In a governmental funded 3-year research project a recycling process for nickel-metal hydride batteries (NiMH) has been developed. Today the discarded batteries are used in the steel industry as a cheap nickel-source. Cobalt is not paid for and rare earths (RE) are slagged and lost for reuse. Spent NiMH batteries contain 36–42% nickel, 3–4% cobalt and 8–10% mischmetal consisting of lanthanum, cerium, praseodymium and neodymium. The dismantled and processed NiMH are melted in a dc electric arc furnace producing a nickel–cobalt alloy and a slag phase highly enriched with RE-oxides. The key for success in this process was to find a suitable slag system which ensures best separation of NiCo alloy from the rare earth oxides. Different oxidic and halogenic slag systems are investigated on a laboratory and technical scale. The slag systems $CaO–CaF_2$ and $CaO–SiO_2$ were determined to be suitable for subsequent pilot plant trials. In these trials, the $CaO–CaF_2$ system has shown a better melting behaviour than the $CaO–SiO_2$ system. Nickel and cobalt were found nearly completely in the metal phase whereas the rare earths were transferred into the slag as oxides. Pyrometallurgical refining of the nickel–cobalt alloy did not make sense as investigated in technical scale trials. Within the scope of a scenario calculation the economical feasibility was demonstrated for a model scenario.
© 2005 Published by Elsevier B.V.

Keywords: Battery recycling; Nickel-metal hydride; Rare earths; Slag system

1. Introduction

In the past 30 years, the European metallurgy has moved away dramatically from primary production towards recycling of secondary raw materials. In the same period the product variety has also changed. More and more complicated products have been and are still being-produced using newest, complex materials. Examples are computer, CD-player, Walkman, cellular phone, PDA and so on. Most of this technically complicated equipment needs to be used mobile. Thus, a flexible power source is used in this field. In the last 15 years secondary battery systems such as nickel-cadmium (NiCd), nickel-metal hydride (NiMH) or lithium-ion batteries have been developed for the mentioned applications. Disposal of used batteries is neither ecologically nor economically useful due to their high metal content. Furthermore, these batteries are a complex, polymetallic deposit.

2. Development and construction of NiMH

NiMH are secondary batteries with a high capacity combined with an ecologically friendly disposal behaviour in comparison to the cadmium containing NiCd batteries. Since their market launch in 1991, up to 1500 tonnes in 2003 have been sold in Germany [1].

The main parts of a NiMH battery are cathode, anode, electrolyte, separator and the steel case. The cathode is made of nickel coated with nickel hydroxide whereas the anode consists of a hydrogen storage alloy based on mischmetal (mainly cerium, lanthanum, praseodymium and neodymium) and nickel including substituents. A typical alloy is $MmNi_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}$. The electrolyte used is a potassium solution. Usually polyamide or polypropylene fleece or gauze are used as a separator between the two electrodes. The assembled battery is fitted into a steel case (Fig. 1).

In cylindrical cells strips of anode, cathode and separator are laminated and are coiled to a helix. The electrolyte is filled into the centre of the cell and afterwards the cell is sealed. Essentially the main difference of prismatic cells is the shape. Single sheets of anode, cathode and separator are laminated or coils

* Corresponding author. Tel.: +49 6181 353672; fax: +49 6181 355318.
E-mail addresses: batteries@ime-aachen.de, tobias.mueller@Heraeus.com (T. Müller).

0378-7753/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.jpowsour.2005.10.046

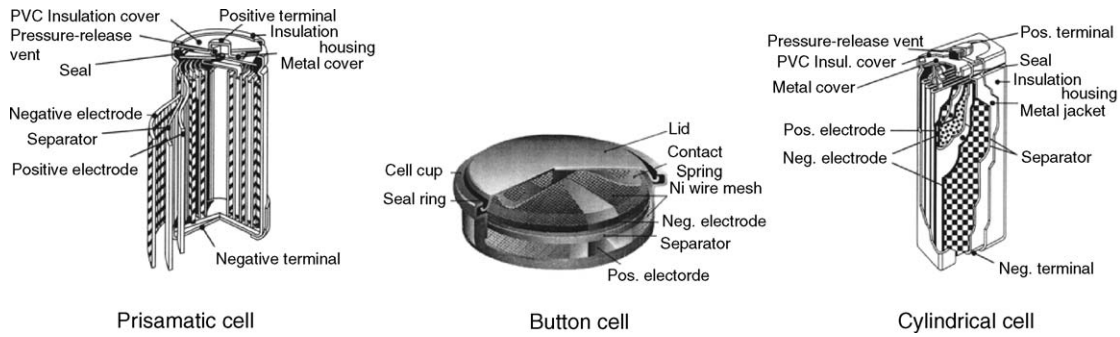

Fig. 1. Schematic assembly of NiMH batteries [2].

are pressed flat. In button cells the electrodes are a tablet-like, compact component.

3. Economic review of the base metals Ni, Co and RE

A typical composition of NiMH is shown in the following Table 1. The most interesting elements are nickel, cobalt and the rare earth metals (RE). Iron may be neglected as the major part is mechanically separated in a prior battery processing step.

The world nickel production in 2003 was about 1.2 million tonnes whereas the monthly average (LME) was equal to €9.62 kg^{-1}. In 2003 worldwide cobalt production was reported to be 40,800 tonnes. The price increased dramatically in late 2003 settling at €45.00 kg^{-1} in December. Typically REs are produced as oxide concentrate. Today China has a 95% market share of the 95,000 tonnes production in 2003. The price for mischmetal was about €5–6 kg^{-1}.

4. Current status of NiMH battery recycling

4.1. Legal framework

The legal basis of battery recycling is the European directive EU 98/1901/EG (latest version). The national implementation in Germany is the so-called "Batterieverordnung" (BattV) enacted on 27.03.1998. According to the BattV all producers and importers of batteries are committed to take back used batteries free of charge and they must treat the batteries according to the recycling management law "Kreislaufwirtschafts- und Abfallgesetz". The costs for the recycling system (including the individual operations collection, sorting, recycling and disposal) must be accepted by the producers or importers. Thus, several battery related companies (e.g. Philips, Sanyo, Sony, Varta, . . .) founded the "Stiftung Gemeinsames Rücknahmesystem Batterien" (GRs Batterien), which is responsible for the fulfilment of the laws.

4.2. Recycling potential

Since their market launch in 1991, the amount of NiMH sold has been increasing steadily up to 10,000 tonnes in the EU for 2003 (Fig. 2). Besides the legal basis the parameters average lifetime, hoarding by the consumer and the application area are determine for the NiMH return. The average lifetime varies between 2 years for communication up to 5–7 years for household applications and spare batteries. About 65% of the used batteries are not disposed of but kept by the user (so-called hoarding). This is a direct consequence of the user, who does not regard used batteries as disposable.

Furthermore, the user keeps the batteries and is hoping for a kind of self-healing process. Average hoarding time is about 2–4 years depending on the application area. Accordingly, the amount of NiMH available for recycling is increasing very slowly. In 2003, about 97 tonnes of NiMH were recycled in Germany. Up to 2007, an increase to 1000 tonnes per annum is expected.

Table 1
Chemical composition of different NiMH [2]

Element	Button cell	Mass percentage	
		Cylindrical cell	Prismatic cell
Nickel	29–39	36–42	38–40
Iron	31–47	22–25	6–9
Cobalt	2–3	3–4	2–3
La, Ce, Nd, Pr	6–8	8–10	7–8
Graphite	2–3	<1	<1
Plastics	1–2	3–4	16–19
Potassium	1–2	1–2	3–4
Hydrogen, oxygen	8–10	15–17	16–18
Other	2–3	2–3	3–4

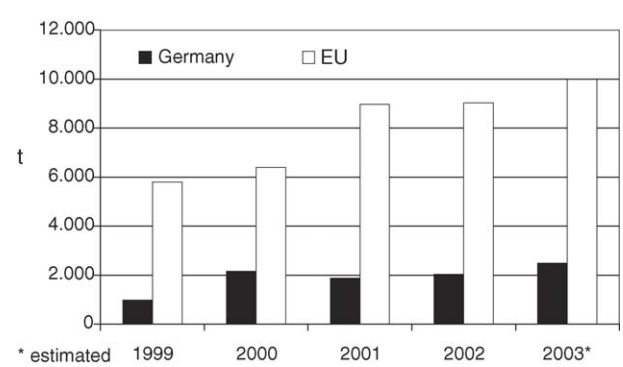

Fig. 2. NiMH batteries sold [1,3,4].

Table 2
Comparative literature overview for NiMH recycling processes

	Lyman [5–7]	Patent EP 585701 B1 [8]	Yoshida [9]	Patent EP 0806 059 B1 [10]	Patent DE 19727880 A1 [11]	Zhang [12]	Pietrelli [13]	Tenorio [14]
Comminution	–	X	X	X	X	–	–	X
Hand separation	X	–	–	–	–	X	X	X
Separation of fine/coarse fraction	–	X	X	X	X	–	–	X
Leached material	Complete cell without shell	Fine fraction	Fine fraction	Fine fraction	Iron free fine fraction	Anode/cathode separated	Anode/cathode separated	–
Separation of RE	Different approaches	–	Precipitaion as salt	Precipitaion as salt	–	Solvent-extraction	Solvent-extraction	–
Sepration of impurities from leach	–	–	Solvent-extraction	Solvent-extraction	–	Solvent-extraction	Ion exchange	–
Recovery of Ni + Co	Electrolysis	Electrolysis suggested	Electrolysis	Electrolysis	–	Cobalt- and nickeloxalate		–
Scale	Laboratory	–	Laboratory	–	–	Laboratory	Laboratory	Laboratory
Publication year	1993–1995	1993	1995	1995	1997	1998	1999	2002

5. State of research and best available technology

As the NiMH are a rather new product the recycling is also still under development. In the literature, no crucial proposal is made for the pyrometallurgical recycling of NiMH. Most of the research work done has focused on hydrometallurgical treatment (Table 2).

Recapitulating, none of the processes described has been transferred to an industrial scale. The hydrometallurgical processes are difficult to put into practice due to their high complexity.

The use of mechanical processing as preliminary stage for a new process is possible.

Best available technology (BAT) is nowadays the use of NiMH as a cheap source in stainless steel production. However, the cobalt is not paid for and the REs are slagged and therefore useless.

6. Development of an alternative recycling process

Consequently, the aim of an alternative recycling process is the production of high grade and marketable products. Industrial processes are available for both battery sorting and battery processing. The significant improvement in comparison to both the literature work and the BAT is the complete use of the raw materials potential of NiMH. Therefore, the following approach (Fig. 3) was developed, which is investigated in the scope of this thesis.

The mechanically processed NiMH will be melted in an electric arc furnace. The produced Ni–Co alloy might already be a saleable product. Possibly a refining step will have to be performed in order to improve the alloy quality. As electrolysis for Ni and Co separation is state of the art, this process is not within the scope of this work. The slag produced is ideally enriched in RE and thus an accepted raw material for the chemical industry.

7. Theory of slag system selection

7.1. Slag requirements

The selection of a suitable slag system was the crucial point within the focus of this research. As the RE are partly metallic they are highly aggressive for common refractory material. Beside this the following needs must be fulfilled:

- liquid at tap temperature of at least 1460 °C (melting point of expected Ni–Co alloy);
- low vapour pressure of slag components;
- possibly low viscosity;
- probably high density difference between slag and metal (minimum 2 g cm^{-3});
- high capacity for RE oxides (minimum 20 wt.%);
- high capability for Mn, Si and other impurities;
- low solubility for Ni and Co (maximum 1 wt.%);
- minimised content of Fe and other disturbing impurities in the slag components.

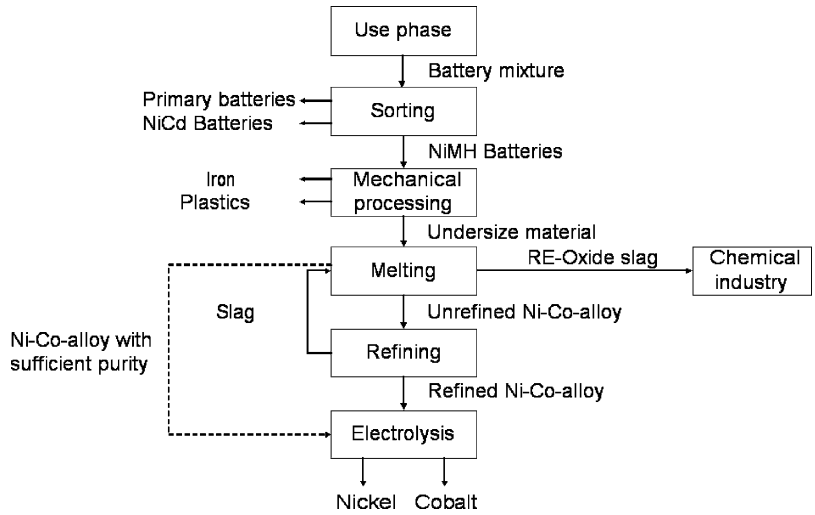

Fig. 3. Flow sheet of an alternative recycling process.

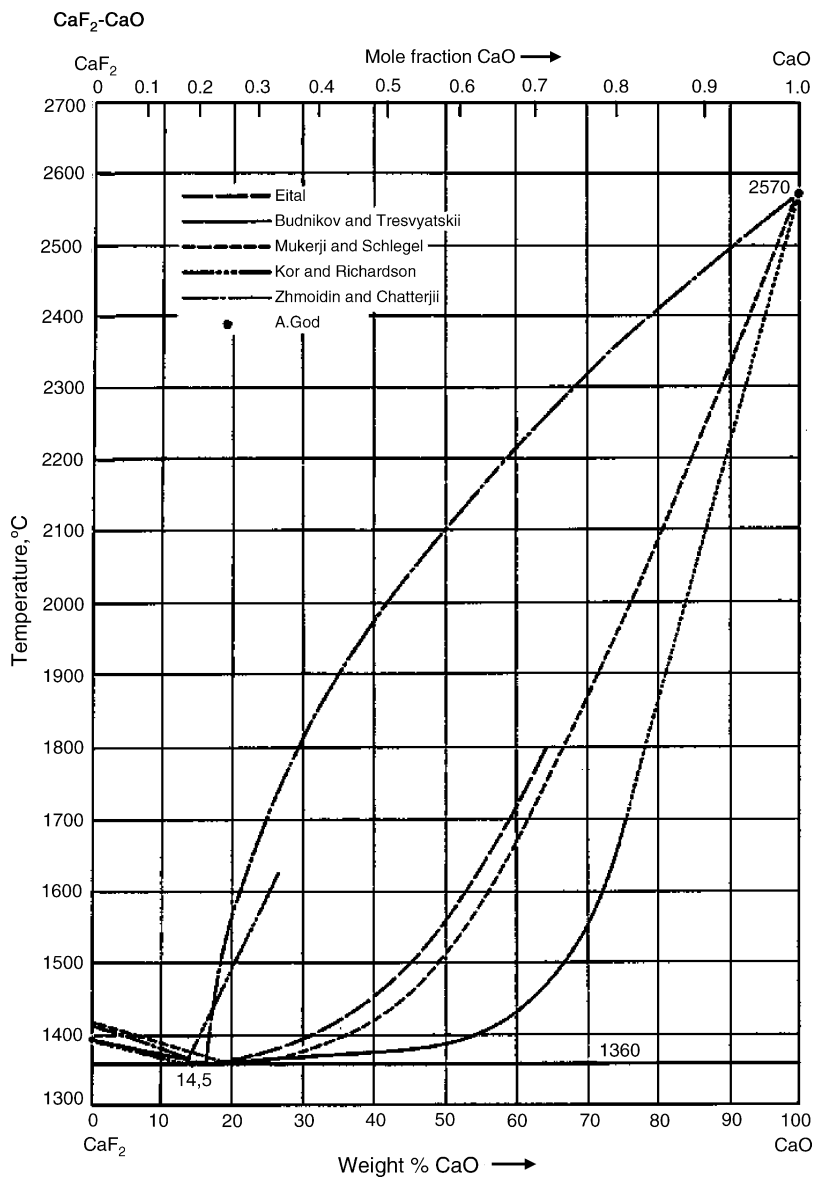

Fig. 4. Phase diagram CaO–CaF_2 [15].

7.2. Slag structure

In general, one distinguishes between the molecular and the ion theory for the explanation of slag structure and reactions [15]. The basis of the molecular theory is that liquid slags are imagined to consist of single oxides or sulphides. These molecules react to compounds such as $2CaO{\cdot}SiO_2$. This theory has been proven very useful for the description of formal slag reactions. However, an investigation of electrical conductivity or viscosity leads to another interpretation which has led to the development of the ion theory. In this theory, slags are expressed as cations and anions. Thus, all slag components may be expressed as charged molecules or atoms and the slag behaviour is derived from the interactions between them. Slag components are either basic (e.g. Ca^{2+}, Fe^{2+}, Mn^{2+}, Mg^{2+}), acid (O^-, F^-, $[SiO_4]^{4-}$, $[PO_4]^{3-}$) or amphoteric components (Al^{3+}, Pb^{2+}, Zn^{2+}). Basic components are able to donate oxygen ions whereas acid components can affiliate oxygen ions. Usually basic oxides have more or less ionic bonds whereas the acid oxides are dominated by strong covalent bonds. Due to the oxygen ion exchange, the strong structure of acidic slag can be destroyed. According to these definitions the RE oxides may be categorised as basic oxides.

7.3. Selection of the slag systems

In non-ferrous metallurgy, several slag systems are generally investigated. Basically slag systems consisting of mixtures CaF_2, MgO, CaO, Al_2O_3 and SiO_2 are suitable for the proposed process. The $CaO–CaF_2$ system shows a eutectic point at 1360 °C according to Fig. 4 for a CaO ratio of 15–20 wt.%. Depending on the various investigations up to 40 wt.% CaO could still be usable as a slag system.

Pure CaF_2 could also be usable as a slag system. Pure CaO is not helpful as there is a eutectic point with La_2O_3 at 1910 °C. A similar behaviour is expected for the other RE due to the chemical and physical similarity. A ternary diagram $RE_2O_3–CaO–CaF_2$ does not exist in the common literature. Thus, no clear interpretation can be made for the RE behaviour in this slag system. Presumably, RE will show a behaviour analogous to CaO as they both have basic character and similar melting points (2200–2300 °C) leading to a higher melting point of the slag system. On the other hand, it is possible that RE fluorides will occur which could behave similarly to CaF_2. Here again the melting points of RE are near the melting point of CaF_2 and the fluorides show full miscibility. Realistically spoken, RE oxides and fluorides will occur simultaneously. Thus, very similar slag behaviour is expected in comparison to the $CaO–CaF_2$ system.

The ternary system $CaO–MgO–SiO_2$ has a eutectic point for a composition of 40 wt.% CaO, 45 wt.% SiO_2 and 15 wt.% MgO at 1430 °C (Fig. 5, dot). Also the binary system $CaO–SiO_2$ seems to be useful for 65 wt.% SiO_2 and 35 wt.% CaO (Fig. 5, arrow) with a melting point of 1436 °C.

Again, a similar behaviour of RE oxides to CaO is assumed. RE are able to form compounds of the type $RE_4(SiO_4)_3$ which could substitute the Ca_2SiO_4 species of the slag system giving a eutectic point at 1770 °C.

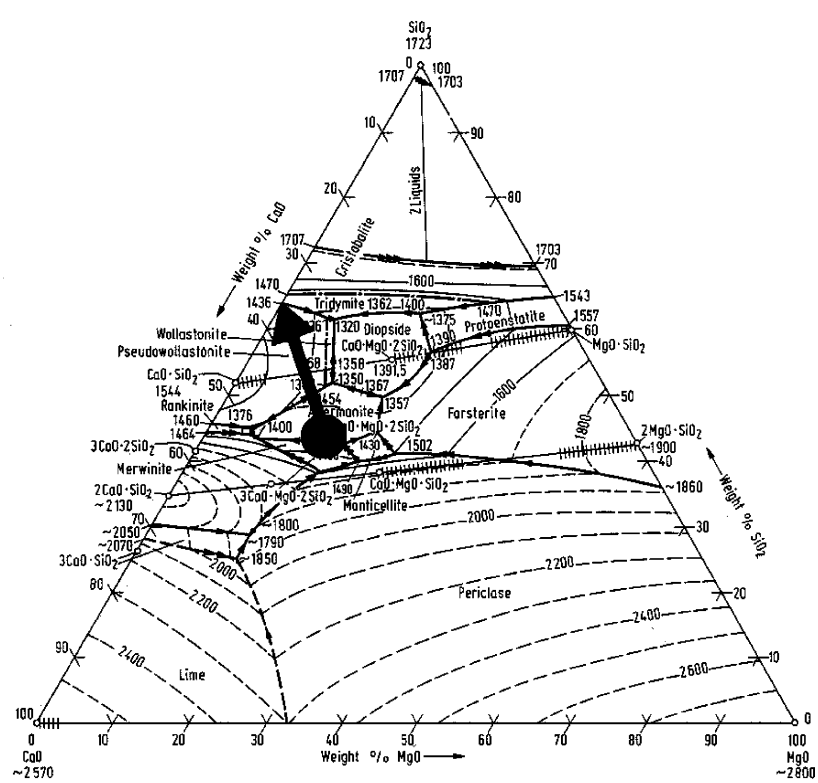

Fig. 5. Phase diagram $CaO–MgO–SiO_2$ [15].

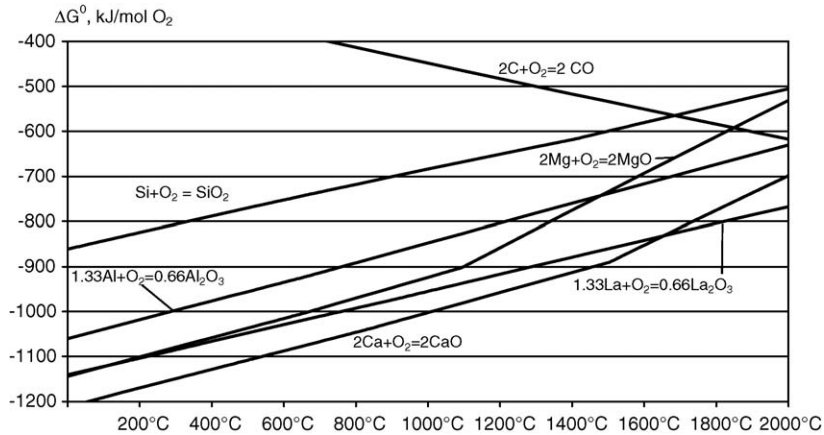

Fig. 6. Richardson–Ellingham diagram for selected metal-oxide systems (standard conditions, pure substances, calculated using FactSage™ [16]).

7.4. Methodology for the characterisation of the selected slag systems

Especially the behaviour of the slag components with the RE is interesting. It is assumed that neither oxides nor metals are dissolving and that the process temperature is high enough for complete melting of all components. For several metal-oxide systems, the equilibrium reaction has been calculated using a software tool (Fig. 6). The real phase mixture and the correlated activity change have been neglected. Lanthanum is used to represent the other RE as their reactions show a very similar behaviour (Fig. 7).

As the Gibbs free energy of the RE oxides is significantly lower than that of CO a carbothermic reduction will not occur. Accordingly, graphite crucibles should be suitable. By reduction of SiO_2 coming either from a refractory or slag component metallic Si could be generated according to:

$$3SiO_2 + 4La \rightarrow Si + 2La_2O_3$$

This would affect the Ni–Co alloy quality as it would be dissolved or form intermetallic compounds. A similar reaction may be expected for MgO:

$$3MgO + 2La \rightarrow 3Mg + La_2O_3$$

Due to the low evaporation point of Mg it will evaporate. Its behaviour as a slag component should be investigated as it could be stabilized in connection with other slag components. Generally spoken, magnesia is not suitable as a refractory material.

In principle, the same is valid for alumina. However, because of its high oxygen affinity a direct reoxidation is possible. In fact, this will not occur completely due to formation of intermetallic phases.

Up to 1700 °C CaO is more stable than RE oxides. Thus, it will not be reduced by metallic RE. With higher temperatures, the following reaction takes place:

$$CaO + La \xrightarrow{\text{above } 1700^\circ C} Ca + La_2O_3$$

With fluorine the metallic RE react to RE fluorides according to:

$$2RE + 3F_2 \rightarrow 2REF_3$$

Calcium fluoride is relatively more stable in comparison to RE fluorides. It is only reduced by lanthanum at temperatures above 1750 °C. Other RE metals are not able to reduce CaF_2. Other fluorides based on potassium, sodium or magnesium would be reduced by the RE and evaporate at the expected process temperature.

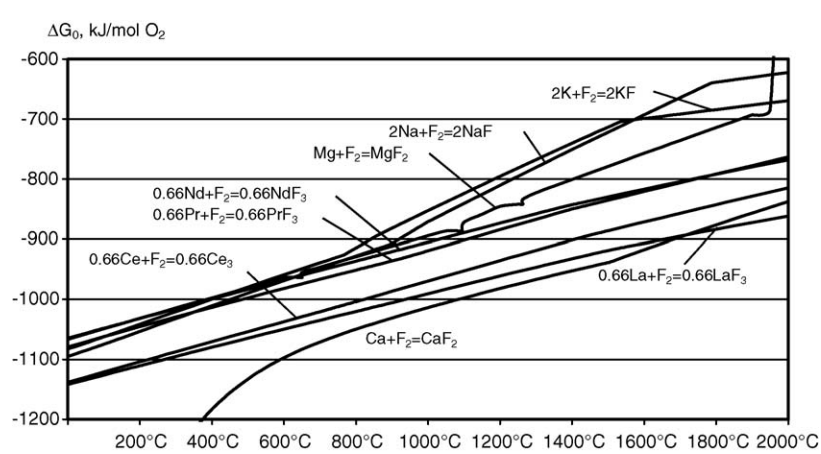

Fig. 7. Richardson–Ellingham diagram for selected metal–fluorine systems (standard conditions, pure substances, calculated using FactSage™ [16]).

Table 3
Composition of the different battery masses for the pilot plant trials, wt.%

Material	Al	Mn	Fe	Ni	Co	La	Ce	Pr	Nd	Cd	Li	Zn
Anode residues	1.15	2.50	0.31	44.04	6.94	9.07	5.96	0.97	2.78	[a]	[a]	[a]
Production scrap	0.98	2.38	0.31	43.95	6.79	8.25	5.52	1.00	2.85	[a]	[a]	[a]
Spent batteries	0.94	2.58	0.26	41.84	6.10	6.93	5.93	0.96	2.72	[a]	[a]	[a]
Pyroly. production scrap	1.05	2.94	1.01	48.16	6.36	6.36	6.44	0.82	2.75	[a]	[a]	[a]
Pyroly. battery mixture	1.02	2.82	0.74	50.35	6.60	6.12	6.53	0.82	2.75	[a]	[a]	[a]
Pyroly. battery mixture with 10% other batteries	1.18	3.36	0.53	45.48	7.45	8.17	5.80	0.74	2.41	0.59	0.15	1.65

[a] Not analysed.

A calculation of the system $CaO–CaF_2–RE_2O_3$ was not possible due to lack of basic data.

A common figure for slag comparison is the so-called basicity, the ratio of base to acid compounds. For the selected slag systems the RE oxides were grouped as bases whereas the RE fluorides were supposed to be acidic. This leads to the following formula for the basicity:

$$B = \frac{CaO + MgO + RE_2O_3}{SiO_2 + Al_2O_3 + CaF_2 + REF_3 + RECl_3}$$

Ni and Co are assumed to be slagged to a very limited amount significantly below 1 wt.% and were neglected. In addition, the proportion of Mn and Fe is very low in the batteries and they were not taken into account.

8. Trials for slag system selection

At first, the selected slag systems were investigated in laboratory scale using a Tamman furnace (300–500 g). With a proportion of 22.5 wt.% of $CaO–SiO_2–MgO$ or $CaO–CaF_2$, RE were slagged at 1600 °C with simultaneous enrichment of Ni and Co in the metal. Only a graphite crucible could be accepted. For validation of the laboratory scale trials more than 60 trials were conducted in technical scale (5–6 kg). A dc electric arc furnace was used. Different battery scraps, e.g. anode residues, production scrap or spent batteries were used after mechanical processing. The battery mass was partly pyrolysed. It could be shown that only $CaO–SiO_2$ and $CaO–CaF_2$ were suitable. For both systems the CaO content is 35 wt.%. By using these systems Ni and Co were transferred almost completely into the metal phase and RE into the slag phase. The required amount of slag was determined as 10 wt.%. The ideal temperature was 1600 °C for $CaO–CaF_2$ and 1700 °C for $CaO–SiO_2$.

The further parameters obtained were validated in nine pilot plant trials (Tables 3 and 4). The pilot plant furnace was a dc electric arc furnace (SMS Demag AG, Duisburg, maximum 5.2 kA, maximum 94 V). Either full or hollow electrodes (150 mm diameter, 60 mm inside diameter) were used. The steel shell of the furnace was water-cooled. A graphite crucible was used. Slag and metal were tapped simultaneously at the bottom tap. Two different charging systems were tested using either powder or granulated battery mass.

In seven trials, the $CaO–CaF_2$ system was investigated. No differences between the different raw materials were observed.

Table 4
Overview of pilot plant trials

Slag system										
	CaO	35								
	CaF_2	65						-		
	SiO_2	-						65		
Share of slag	w.-%	10				5			10	5
Tap temperature	°C	1730	1675	1680	1675	1712	1680	1624	1730	1724
Material processing		Granulation					Powder		gran.	Pow.
Type of material										
Anode residues		X								
Productions scrap			X							
Spent batteries				X						
Pyroly. production scrap					X				X	
Pyroly. battery mixture						X				X
Pyroly. battery mixture with 10 % other batteries							X			
Input	kg	323	357	334	320	310	382	381	320	390
∅ Current	kA	2.7	2.6	2.4	2.8	3.4	3.2	2.9	3.4	3.2
∅ Voltage	V	52	56	49	51	51	43	48	52	49
∅ Power	kW	137	145	121	142	173	150	140	178	152
Power consump.	kWh	396	397	353	385	350	485	549	395	528
	kWh/kg	1,23	1,11	1,06	1,2	1,13	1,27	1,44	1,23	1,35
Melting time	min	20	15	17	18	14	13	15	25	38

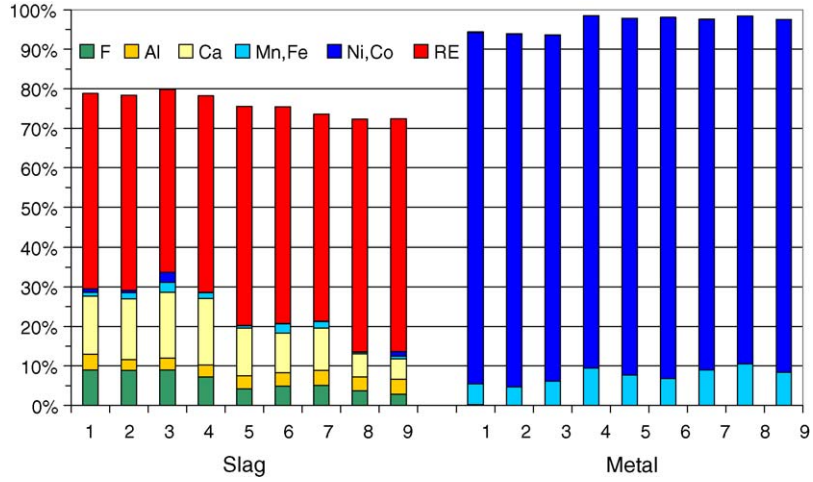

Fig. 8. Chemical assay of pilot plant trials.

Metal–slag separation was very good for all attempts. In contrast to the technical scale trials the RE content in the metal phase was below the analytical limits.

Except for trial 3, all Ni and Co contents were below 0.8 wt.% in the slag (Fig. 8). Obviously, no Al was dissolved in the metal as observed in the technical scale experiments.

The reduction of the slag amount to 5 wt.% (starting with trial 5) leads to a reduced Ca and F content in the slag without influencing product quality or process stability. Furthermore, the RE recovery was improved up to 6 wt.%. The basicity showed a very distinctive behaviour for trials with pyrolysed battery mass (4–7) compared with untreated battery mass. For trials 1–3, the basicity (Fig. 9) is approximately 1.1 and thus slightly base. The reduced slag amount is responsible for this fact. As less CaF_2 is used as less SEF_3 may be react and thus the share of RE_2O_3 is enlarged.

The mass balance shows a poor overall recovery for the first three trials. As these trials were performed in one campaign a 70 kg metallic plate was found afterwards in the bottom of the crucible. The metal content of the plate could not be clearly divided to correspond to the corresponding trials. Thus, for the trials one to three only an overall mass balance (Table 5) was calculated. The mass distribution shows no significant difference with respect to the different raw materials (Fig. 10). The losses are mainly directed by the raw material, which could not be transported into the area of reaction. This is shown by the uniform distribution of the main components Ni, Co and RE.

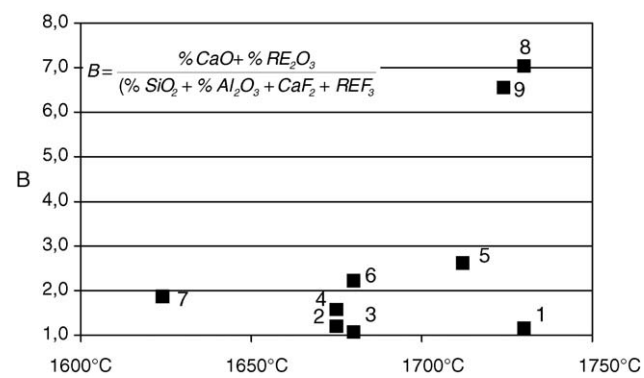

Fig. 9. Basicity of $CaO–CaF_2$-slag in pilot plant trials.

After finishing the trials a certain, non-quantifiable amount was detected around the charging hole, on top of the furnace shell as well as in the air cleaning system. Obviously, the solubility of Fe and Mn in the slag is smaller for the $CaO–SiO_2$ system. Apparently, the dissolution of Si in the metal phase is the major disadvantage of this system. This is not overcome by the very small higher amounts of RE in slag.

However, using the hollow electrode technology resulted in an increased raw material loss as displayed in Fig. 11, left. Up to 15 wt.% was lost in comparison to granulated material. Furthermore, the energy requirement was increased by about 20%, which must be taken into account. A very positive result was

Table 5
Mass balance of pilot plant trials, kg

Trial	Input	Input, H_2O free	Metal	$Metal_{in\ slag}$	Slag	Flue dust	Losses	Recovery (%)
1–3	1010	869	487	14.1	228.8		185	84
4	320	301	156	15.7	96.1		22.6	89
5	311	292	205	6.3	69.5		3.5	96
6	382	382	199	7.5	105.9		58.1	82
7	381	381	166	6.7	97.9	42.3	51.4	82
8	320	301	185	3.4	61.6		44.8	83
9	390	390	181	13.4	99.1		88.3	75

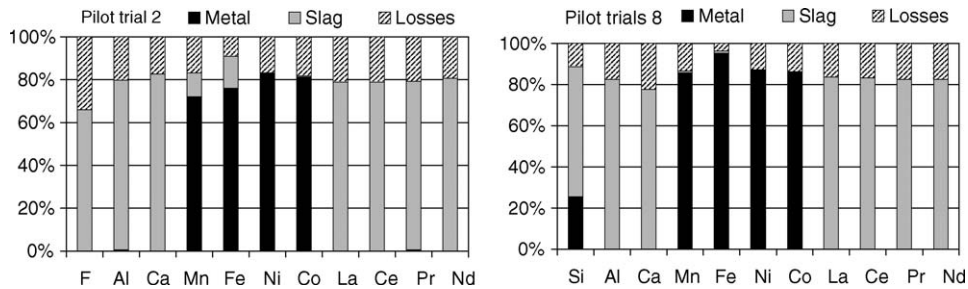

Fig. 10. Mass distribution of selected elements for pilot trial 2 ($CaO–CaF_2$ system, massive electrode, left) and pilot trial 8 ($CaO–SiO_2$ system, massive electrode, right).

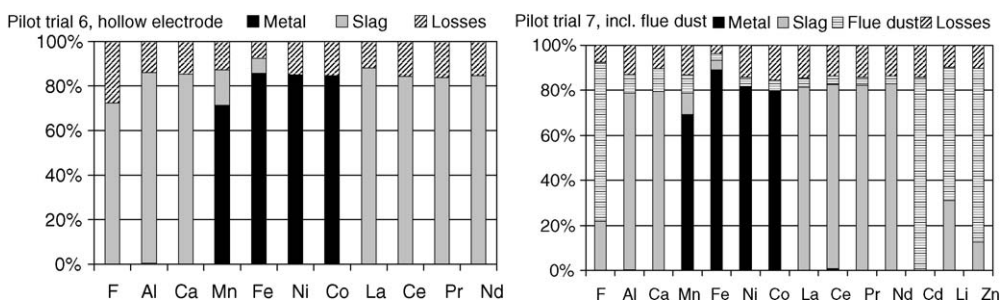

Fig. 11. Mass distribution of selected elements for pilot trial 6 ($CaO–CaF_2$ system, hollow electrode, left) and pilot trial 7 ($CaO–CaF_2$ system, hollow electrode, flue dust collection, right).

obtained for the contaminated raw material (Fig. 11, right). The amount of Li and Zn was very limited in the slag. The major part was found in the flue dust as just the whole Cd. Thus, the process seems to be stable against missed battery disposal in the raw material. Whether there will be an enrichment in a closed-loop process or not must be investigated in further trials.

In order to refine the Ni–Co alloy produced, technical scale trials were conducted. Theoretically, Fe and Mn could be removed from the alloy by selective oxidation (Fig. 12). An oxygen amount of 0.4 mol 100 g^{-1} alloy and a temperature of 1600 °C would be good conditions. Mn would be completely oxidised whereas Fe would be removed to 90 wt.%. However, it must be said that high Ni and Co losses will occur. In four trials (Table 6) a top blown oxygen lance was used for selective oxidation. The operating temperature was 1560 °C using a 50 kW crucible induction furnace and between 200 and 300 l h^{-1} air was blown into the melt (equal to 40–60% required for the oxidation of all elements).

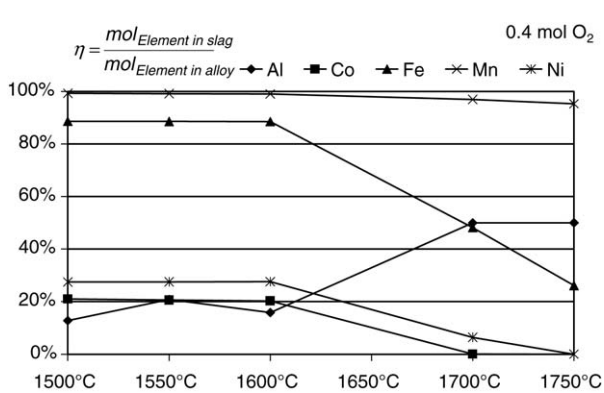

Fig. 12. Refining efficiency at 0.4 mol oxygen.

Neither the required blowing time of 180 min could be achieved nor could the necessary amount of air be transferred into the melt. In all trials, the chosen lance failed after maximum 67 min.

Accordingly, the selective oxidation of Fe and Mn was not successful as shown in Fig. 13. The partly increasing content is related to high melting losses due to melt spills. The reasons for the failed oxidation are the limited amount of oxygen blown into the melt as well as unlikely thermodynamic conditions. At least Al and C could be removed from the melt as illustrated in Fig. 14. The reaction of the ambient oxygen could not be taken into account. Nevertheless, this reaction took place as larger amounts of Ni and Co were oxidised. Summarising, the experiments conducted were not sufficient to draw conclusions for the alloy behaviour on a larger scale. Apparently up to 50 wt.% of the used alloy was splashed and could not be remelted. However, based on these results selective oxidation does not seem to be useful for the refining of the produced alloy.

Table 6
Analysis of Ni–Co alloy for refining trials, wt.%

No.	Al	Mn	Fe	Ni[a]	Co	C	Cu	Cr
1	0.30	4.0	1.9	78.7	13.2	1.9	0.04	0.03
2	0.30	3.9	1.8	78.9	13.3	1.7	0.04	0.02
3	0.26	3.8	1.9	79.4	13.1	1.5	0.03	0.04
4	0.22	3.6	1.3	80.6	12.5	1.6	0.04	0.14

[a] Calculated as balance.

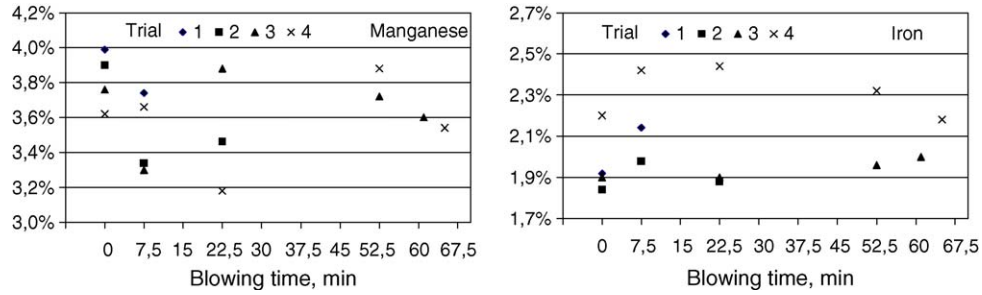

Fig. 13. Mn (left) and Fe content (right) of refined alloy depending on blowing time.

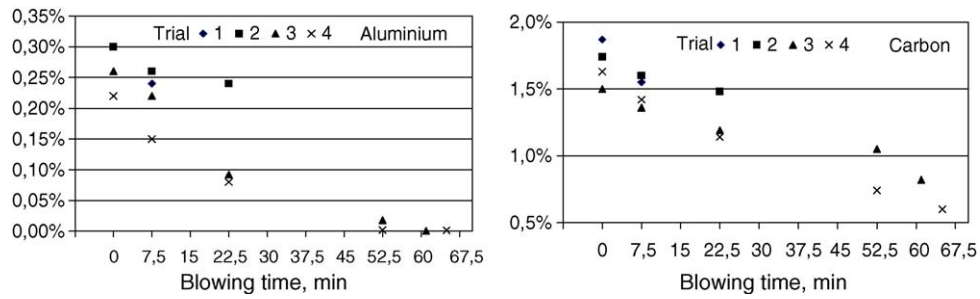

Fig. 14. Al (left) and C content (right) of refined alloy depending on blowing time.

9. Feasibility study of the recycling process

The basis for the feasibility study was a scenario calculation for a green field plant with a nominal capacity of 1000 tonnes per annum. From four different raw material sources (collection systems, battery producer, hybrid vehicles and others) a yearly increasing amount of batteries up to 1000 tonnes in 2009 could be acquired. Using historical raw material prices and taking typical reduced prices for recycled material into account an average sales revenue of €3400 tonnes^{-1} products could be estimated. Labour costs were calculated proportional to the increasing number of employees required. Cost of sales included battery purchase, battery transportation and processing, energy consumption, auxiliary materials (e.g. slag components, refractory), furnace rent and depreciation, electrodes, analysis and quality assurance and were calculated to be €2650 tonnes^{-1}. The investment costs were based on a rented furnace and office building for the first 3 years. Then a new furnace would have

Table 7
Profit and loss account

	2004	2005	2006	2007	2008	2009
Sales (€)	0	432562	1185280	1844905	4134865	6730204
Sales cost (€)	0	297925	775410	1263072	2750048	4514120
Earnings (€)	0	134637	409870	581833	1384817	2216085
Costs (€)						
Labour costs (total) (€)	36300	156090	181500	209378	238564	348190
Non-wage labour costs (€)	13800	33000	34800	34800	34800	38400
Operational costs	11400	22800	22800	22800	22800	22800
Consultancy	18000	36000	36000	36000	36000	36000
Marketing	6000	12000	12000	12000	12000	12000
Further costs	6498	16110	17148	8400	8400	8760
Total costs	91998	276000	304248	323378	352564	466150
EBITDA	−91998	−141363	105622	258454	1032253	1749935
Depreciation, amortisation	1750	4750	48635	163735	166235	166235
EBIT	−93748	−146113	56987	94719	866018	1583700
Interests	0	0	40000	150000	0	0
EBT	−93748	−146113	16987	−55281	866018	1583700
Taxes	0	0	0	0	389708	712665
Earnings	−93748	−146113	16987	−55281	476310	871035

to be purchased as well as a suitable production site including the construction of a building for the furnace and offices. In total an investment of €1,610,000 would be needed of which €900 are related to the furnace. The operating costs were calculated to be €4800 tonnes^{-1} including office material, insurances, phone, travel expenditures, special literature, marketing, consultancy and a company car. The resulting profit and loss account is given in Table 7.

10. Summary

Since the early 1990s, the market for accumulators has been growing steadily in line with the increase in mobile communication markets. The nickel-metal hydride battery was introduced as part of this development. State of the art in battery recycling for NiMH is the use in stainless steel production as a cheap nickel source. However, by this route neither the valuable share of cobalt is paid for nor are the contained RE recycled. Furthermore, the RE are lost in the slag phase. This investigation is focused on the development of a new, alternative recycling process with almost complete recycling of Ni, Co and RE as saleable products.

Initially, the history of NiMH as well as its function, composition and use were described. The major components are Ni, Co, Fe and a mischmetal based on La, Ce, Pr and Nd. The value of the metals contained is about €4–5 kg^{-1}.

Subsequently, important boundary conditions were described including legal framework, market share and recycling potential. The battery recycling of several European countries Europe was compared and a literature review summarised the state of the art and state of research. The existing recycling route was critically evaluated and, from the results, the requirements were derived for a new process. The crucial point for the process development was the selection of a suitable slag system which fulfils demands such as high density difference, low viscosity, pour capacity for Ni, etc. Based on the structure model of liquid slags as well as the related properties of potential slag formers the $CaO–CaF_2$ and the $CaO–SiO_2–MgO$ systems were selected. A new definition for the basicity was introduced for reviewing. RE oxides were selected as basic components whereas RE fluorides were taken as the acid component. The slags were compared on the basis of the basicity and distribution coefficients. Due to basic gaps in the data, especially for RE compounds, no further thermodynamic calculations were conducted.

In the experimental part of this work the selected slag systems were investigated at first on a laboratory and technical scale. For both systems the CaO proportion was determined to be 35 wt.% according to a slag ratio of 10 wt.%. Ni and Co, respectively, RE were transferred to almost 100 wt.% into the metal phase, respectively, slag phase. The trials showed that the MgO share in the $CaO–SiO_2–MgO$ system might be neglected. The ideal melting temperature was determined to 1600 °C for the $CaO–CaF_2$ system and accordingly to 1700 °C for the $CaO–SiO_2$ system. In pilot plant trials this results were evaluated in 320–390 kg scale. With the $CaO–SiO_2$ system an enrichment of Si in the metal phase was observed. Furthermore, the slag with these components was highly viscous and had very poor separation behaviour for slag–metal liberation. In contrast the $CaO–CaF_2$ system produced an excellent slag–metal separation and thus has been recommended. The required slag ratio was decreased to 5 wt.%. The metal consisted of some 80 wt.% Ni, 12 wt.% Co, 4 wt.% Mn, 2 wt.% Fe and 2 wt.% C. The slag consisted of 50–60 wt.% RE. The different battery masses investigated showed very similar behaviour. The mass could be charged using either agglomerated material or hollow electrode technology. Using the hollow electrode led to higher flue dust production and an increased specific power consumption. The process stability against other battery types has been successfully shown. The used graphite crucible might be used for up to 15 charges.

The NiCo alloy produced was refined in order to remove impurities such as Fe, Mn, Al or C. Due to processing and scale difficulties, only the elimination of C and Al could be successfully accomplished. Neither Fe nor Mn could be removed in contrast to the theoretical calculations. For complete refining, far too little oxygen was blown into the melt mainly as a consequence of processing limits. Based on the results the general use of this method seems to be questionable.

By means of a scenario calculation the feasibility of the process could be shown for an assumed mass of 1000 tonnes raw materials in the year 2009. This was determined to be the lower limit for covering the calculated investment costs. However, an industrial implementation as a green field plant seems to be unlikely now because of limited access to NiMH. The major reason for this effect is related to the positive market value of NiMH. As consequence, a non-quantified amount of NiMH is handled outside the official recycling systems. Alternatively, the transfer into an existing enterprise seems to be feasible as far the investment costs can be kept low and the existing infrastructure can be used.

References

[1] J. Fricke, GRs Jahresbericht, Stiftung Gemeinsames Rücknahmesvstem Batterien, Hamburg, 2000.
[2] J. Hejdecke, H.-A. Kiehne, Ni-Cd- und Ni-MH-Batterien für mobile Kommunikation, Spezial Report, Hannover, Varta AG, 1997.
[3] J. Fricke, GRs Jahresbericht, Stiftung Gemeinsames Rücknahmesvstem Batterien, Hamburg, 1999.
[4] J. Fricke, GRs Jahresbericht, Stiftung Gemeinsames Rücknahmesystem Batterien, Hamburg, 2003.
[5] J.W. Lyman, G.R. Palmer, in: H.Y. Sohn (Ed.), Recycling of Nickel-Metal Hydride Battery Alloys in Metallurgical Processes for Early Twenty-First Century, The Minerals, Metals and Materials Society, Warrendale, 1994.
[6] J.W. Lyman, G.R. Palmer, in: P.B. Queneau, R.D. Peterson (Eds.), Hydrometallurgical Treatment of Nickel-Metal-Hydride Battery Electrodes in Third International Symposium on Recycling of Metals and Engineered Materials, The Minerals, Metals and Materials Society, Warrendale, 1995.
[7] J.W. Lyman, G.R. Palmer, Investigating the recycling of nickel hydride battery scrap, J. Met. (1993) 32–35.
[8] Patent No. EP 0585 701 B1, Verfahren zum Entsorgen von Nickel-Cadmium-oder Nickel-Hydrid-Zellen, Anmelder, Enviro EC AG, Zug (CH), 1996.
[9] T. Yoshida, H. Ono, R. Shirai, in: P.B. Queneau, R.D. Peterson (Eds.), Recycling of Used Ni-MH Rechargeable Batteries in Third International Symposium on Recycling of Metals and Engineered Materials, The Minerals, Metals and Materials Society, Warrendale, 1995.

[10] Patent No. EP 0806 059 B1, Process for recovery of metals from used nickel/metalhydride storage batteries, Anmelder, Varta Batterie AG, Hannover, 1997.
[11] Patent No. DE 197 27 880 A1, Verfahren zur Werkstoffrückgewinnung aus Nickel-Metallhydridzellen, Anmelder, Varta Batterie AG, Hannover, DE, Kali-Umwelttechnik GmbH, Sonderhausen, 1999.
[12] P. Zhang, T. Yokoyama, O. Itabashi, Y. Wakui, T.M. Suzuki, K. Inoue, Recovery of metal values from spent nickel-metal hydride rechargeable batteries, J. Power Sources 77 (1999) S.116–S.122.
[13] L. Pietrelli, B. Bellomo, Metal Recovery from NiMH Batteries: Characterization and Leaching Tests in Fifth International Battery Recycling Congress, Deauville, France, 1999.
[14] J.A.S. Tenorio, D.C.R. Espinosa, Recovery of Ni-based alloys from spent NiMH batteries, J. Power Sources 108 (2002) S.70–S.73.
[15] N.N. Schlackenatlas, Düsseldorf: Verlag Stahleisen, 1981/1995.
[16] FactSage^{TM}, Interactive Programs for Computational Thermochemistry, GTT-Technologies, Herzogenrath.