Development of a CaO-CaF$_2$-slag system for high rare earth contents

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In a German governmental funded three-year research project, a closed loop recycling process for Nickel-Metalhydride-Batteries (NiMH) is under development. Today the discarded batteries are used in the steel industry as a cheap nickel source. Cobalt and rare earth (RE) are slagged and lost for reuse. The entire value of the metals in discarded Ni-MH is estimated to be 4–-4.5 €/kg. Spent NiMH-batteries containing 36–42 per cent Ni, 3–4 per cent Co and 8–10 per cent rare rarth (Ce, La, Pr, Nd). The dismantled and processed NiMH-batteries are melted in a DC electric arc furnace producing a nickel-cobalt alloy and a slag phase highly enriched with RE-oxides. The key to success in this process is to find a suitable slag system, which ensures best separation of NiCo-alloy from the rare earth oxides and high concentration of RE in the slag. Different oxidic and halogenic slag systems are investigated in the melting process. So far a slag system based on 65 per cent CaF$_2$ and 35 per cent CaO delivers the best separation of the two phases and metal yields. A slag with a composition of 20–25 per cent La, 13-16 per cent Ce, 1.5–2.5 Pr, 4.5–6.5 per cent Nd is obtained and further treated to misch metal hydro-/electrometallurgically. The first results of the influence of rare earth oxides on the density of CaO-CaF$_2$ slag system are shown at 1600°C.

Keywords: battery recycling, CaF$_2$, CaO, rare earth oxides, slag characterization, density measurement

Introduction

In metal production and processing the recycling of used products has been established since the beginning of metallurgy. Nowadays new products are becoming more complex and a wide range of elements and compounds are used. Accordingly, the demands on recycling this multi-component material are increasing. At the present time different battery systems are used for various applications. Well established is the use of lead starter batteries in vehicles. Also the recycling of lead batteries has been operating for several decades. But many consumer applications need special battery systems in terms of size, voltage and shape. Nickel-cadmium-, nickel-metalhydride- and lithium-ion-batteries are currently used for most mobile applications like laptops, PDA or mobile phones. Only for nickel-cadmium batteries has an environmentally sound industrial recycling process has been developed in the last ten years. This process has been operating successfully since 1996 in Germany[1]. The zenith of nickel-cadmium-batteries is exceeded and production is decreasing due to environmental problems of disposal. The application area of nickel-cadmium-batteries is taken over by nickel-metalhydride (NiMH) and lithium-ion-batteries. A sustainable industrial recycling process has not yet been developed for these.

The development of a new pyrometallurgical process is directly related to the slag system used. Hence, now is the time to develop a novel technology to enable recycling of all metallic components, thereby also enabling recovery of non-metallic components, such as plastics. The slag system needs to separate the metals from the accompanying elements. State of the art in NiMH battery recycling is the use of discarded NiMH batteries in the steel industry for their nickel content as an alloying element. But the contained cobalt and rare earth metals (RE) are neither used nor recycled. They are lost in the slag.

The object of the German government funded work reported here is to develop a simply structured, environmental friendly, closed loop recycling process for discarded NiMH batteries. After collection, a combination of comminution and metallurgical processing is intended. In the investigated project, spent NiMH are recycled in order to produce both a nickel-cobalt alloy and a rare earth bearing slag as a concentrate for a subsequent misch metal recovery (Figure 1)[2,3].

After mechanical processing, a typical NiMH battery scrap consists of 45–50 per cent Ni, 9–11 per cent Co and 13–16 per cent rare earth mischmetal (La, Ce, Nd, Pr). All given percentages are weight percentages, if not otherwise indicated. Further ingredients are 2–3 per cent graphite, 1–2 per cent manganese and 0.5–1 per cent iron. Several slag systems containing SiO$_2$, CaO, MgO, CaF$_2$, CaCl$_2$ were investigated in order to find the best separation conditions[2]. Two suitable slag systems were found based on CaO. The first slag system is composed of 65 per cent CaF$_2$ and 35 per cent CaO. The second slag system is a mixture of 65 per cent SiO$_2$ and 35 per cent CaO. The latter is not part of the subsequent investigations of this study. The NiMH material is mixed with 5–10 per cent of the slag system and melted in a DC electric arc furnace. The produced Ni-Co-alloy is pyrometallurgically refined and can be used in battery alloy production again. The obtained slag is highly enriched in the rare earth oxides (RE). In order to show the significant influence of RE on the slag behaviour several physical

Table I
Overview of slag development experiments

Exp.	SiO_2	CaF_2	CaO	MgO	Al_2O_3	flux		Ni-MH	Pouring temperature [°C]	Crucible	Material preparation	Material type
1	1								1550	MgO		
2	1								1700			
3		1							1350			
4		1				0.25		0.75	1420	SiC	Briquetts	Anodes
5		0.65	0.35						1555			
6		0.65	0.35						1592			
7	0.45		0.4		0.15				1450			
8	0.45		0.4		0.15				1415			
		CaF_2	CaO			CaO	CaF_2	Ni-MH				
9		0.842	0.158			0.075	0.4	0.525	1420			
10		0.87	0.13			0.075	0.5	0.425	1392			
11		0.842	0.158			0.075	0.4	0.525	1520			
12		1					0.5	0.5	1360			
13		0.667	0.333			0.15	0.3	0.55	1430			
14		0.769	0.231			0.15	0.5	0.35	1360	graphite	Briquetts	Anodes
15		0.842	0.158			0.075	0.4	0.525	1650			
16		1					0.3	0.7	1480			
17		1					0.4	0.6	1360			
18		0.8	0.2			0.075	0.3	0.625	1290			
19		0.727	0.273			0.15	0.4	0.45	1540			
20		0.842	0.158			0.075	0.4	0.525	1420			
21			0.15		0.15	0.3		0.7	1600			
22			0.15		0.15	0.3		0.7	1550			
23		0.12	0.06		0.12	0.3		0.7	1760			
24		0.12	0.06		0.12	0.3		0.7	1760	graphite	Briquetts	Anodes
25		0.16	0.08		0.16	0.4		0.6	-			
26		0.12	0.06		0.12	0.3		0.7	1580			
27		0.12	0.06		0.12	0.3		0.7	1770			
29		0.65	0.35			0.3		0.7	1520		Powder	
30		0.65	0.35			0.3		0.7	1450			
31		0.65	0.35			0.3		0.7	1620			
32		0.65	0.35			0.3		0.7	1760			
33		0.65	0.35			0.15		0.85	1650			
34		0.65	0.35			0.1		0.9	1630			
35		0.65	0.35			0.3		0.7	-			
36		0.65	0.35			0.15		0.85	1630			
37		0.65	0.35			0.15		0.85	1630			
38		0.4	0.2		0.4	0.3		0.7	-			Spent batteries
39	0		0.4	0.15		0.3		0.7	1630			
40	0		0.4	0.15		0.3		0.7	1680			
41		0.4	0.2		0.4	0.15		0.85	-	graphite		
42	0		0.4	0.15		0.15		0.85	1640		Pellets	
43	0		0.4	0.15		0.15		0.85	1680			
44		0.65	0.35			0.15		0.85	1560			
45		0.65	0.35			0.15		0.85	1620			
46		0.65	0.35			0.1		0.9	1500			
47		0.65	0.35			0.1		0.9	1600			
48		0.65	0.35			0.1		0.9	1400			Electrodes
49		0.65	0.35			0.1		0.9	1550			
50	0		0.4	0.15		0.1		0.9	1620			Spent batteries
51	0		0.4	0.15		0.1		0.9	1750			
52	0		0.4	0.15		0.1		0.9	1760			Electrodes
53	0		0.4	0.15		0.1		0.9	1690			
54		0.65	0.35			0.1		0.9	1450	Al_2O_3		
55		0.65	0.35			0.1		0.9	1380	Al_2O_3	Powder	Spent batteries
56	0		0.4	0.15		0.1		0.9	1650	Al_2O_3		
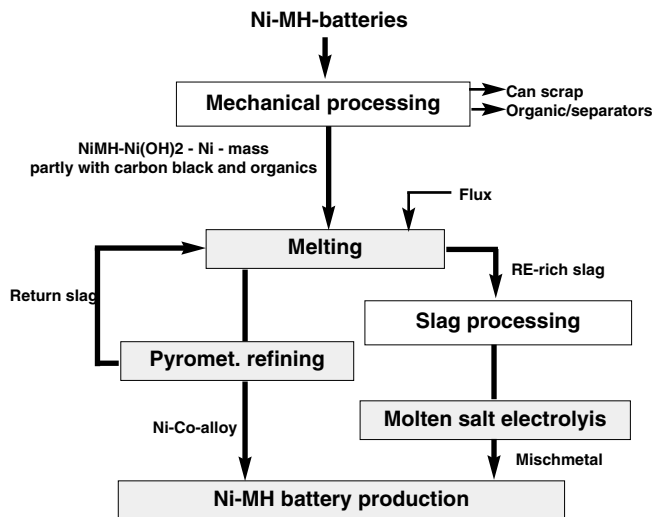
Figure 1. Flowsheet of the intended investigation on NiMH battery recycling

Figure 2. Phase diagram CaO-CaF$_2$

properties should be investigated. In this study the first results of the RE impact on slag density are shown. In the future tviscosity and surface tension will be determined as well. For viscosity the oscillation method will be used, whereas for the surface tension the maximum bubble pressure method will be conducted.

Slag development

During the process development, more than 50 lab-scale tests (5 kg scale) were conducted for the CaO-CaF$_2$-slag system (Table I). The starting ratio was 15% CaO and 85% CaF$_2$ according to the eutectic point derived from literature (Figure 2).

With the slag systems used in experiments 1 to 8 the objective of metal-slag separation could not be performed. A clear separation failed. Also, in every case the refractory did not resist the impact of the slags. The melt was highly viscose. Decreasing viscosity by increasing the temperature was not successful. The major part of the melt remained in the furnace after pouring. As the influence of the dissolved refractory material on the slag behaviour could not be clearly described, these slag systems were then tested using a graphite crucible. Experiments 9–20 resulted in a low viscous melt which was easy to pour and lead to a good
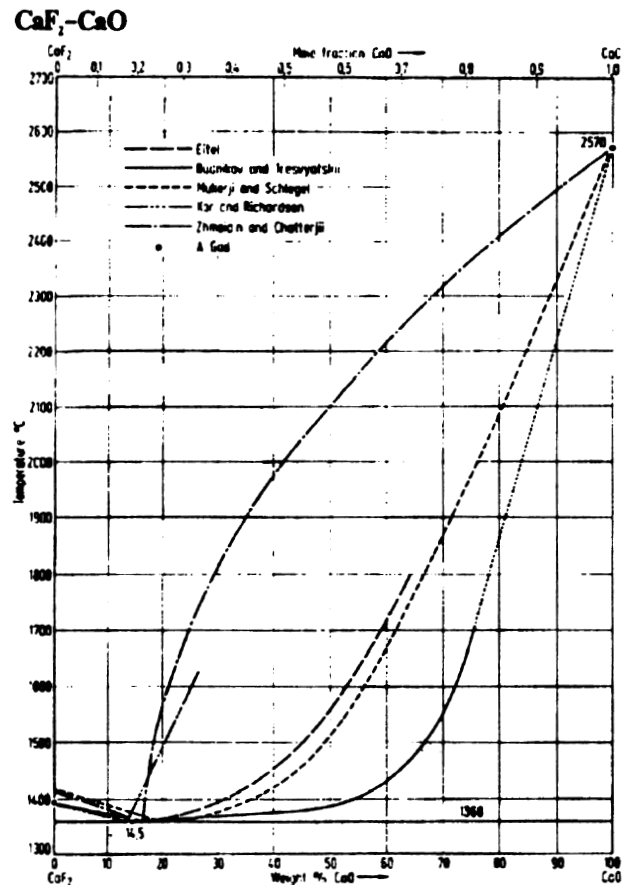
metal–slag separation for a high CaF$_2$-CaO-ratio. Pure CaF$_2$ as flux did not work properly. In experiments 29–37 and 44–49 the CaF$_2$-CaO-system was optimized with respect to the flux ratio. The best performance was reached with a flux ratio of 10% consisting of 65% CaF$_2$ and 35% CaO. Both a high nickel content in the metal parallel to a low content in the slag could be reached, as well as high RE content in the slag.

In experiments 39,40 resp. 42,43 and 50–53 the SiO$_2$-CaO-MgO-system was investigated. A good metal–slag separation could be gained. But the slag was highly viscous and only liquid in a small temperature range. In some experiments a sudden freezing of the slag was observed.

Table II
Overview of pilot plant experiments

Nr.	Material	Flux composition			Charge composition		Pouring temperature °C	Material preparation
		SiO$_2$	CaF$_2$	CaO	Flux	Ni-MH		
1	Anode scrap		65 %	35 %	10 %	90 %	1730	
2	Production scrap		65 %	35 %	10 %	90 %	1660	
3	Spent batteries		65 %	35 %	10 %	90 %	1600	Pellets
4	Pyrolysed spent batteries		65 %	35 %	10 %	90 %	1675	
5	Pyrolysed spent batteries		65 %	35 %	5 %	95 %	1710	
6	Pyrolysed spent batteries	65 %		35 %	5 %	95 %	1730	
7	Mixture		65 %	35 %	5 %	95 %	1545	
8	Mixture	65 %		35 %	5 %	95 %	1720	Powder
9	Polluted Mixture		65 %	35 %	5 %	95 %	1520	

The best result was obtained in experiment 51. A high nickel content in the metal could be reached, as well as a high content of RE in the slag. Some of the SiO$_2$ was reduced and dissolved as silicon in the metal. Hence, for this alloy a refining step is required as silicon is undesirable for battery production. However, the Si-content of the slag is conspicuously low. It is possible that SiO$_2$ was first reduced to SiO and than reacted with surplus carbon to form silica carbide SiC, which sublimates at 2300°C to gaseous silicon and solid carbon.

The CaF$_2$-CaO-Al$_2$O$_3$ system could not be tested successfully in experiments 21–28, 38 and 41. The slag was even more viscous than in the SiO$_2$-bearing system and tended to freeze directly when the energy supply from the electric arc was not accessible. From the crucible wall into the middle of the melt a building up of a slag crust was observed. Also metal–slag separation was rather poor, leading to a mixed layer of slag and metal within the cast. Both the nickel content in metal as well, as the RE content in the slag, was reasonably lower than in the other two systems. Hence, only the CaF$_2$-CaO-system and the SiO$_2$-CaO-MgO-system were determined to be suitable for further investigation in the pilot plant furnace.

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

Nine pilot plant tests were carried out (Table II). In each test about 300 kg battery scrap was fed to the furnace. The results from the lab-scale experiments could be confirmed. However, the required slag ratio could be decreased to 5 per cent. Both tested slag systems were suitable, even when the CaO-CaF$_2$-system was easier to handle because the slag was relatively low in viscosity.

For all slags produced in the pilot plant test, a different slag composition was observed, depending on both the flux and the charge composition. Nevertheless, the slags contained generally more than 50 per cent rare earth oxides (Table III).

Experimental procedures

The **density** was determined following the buoyancy method (Archimedes principle). The crucible was made out of boron nitride. The resistance-heated furnace was
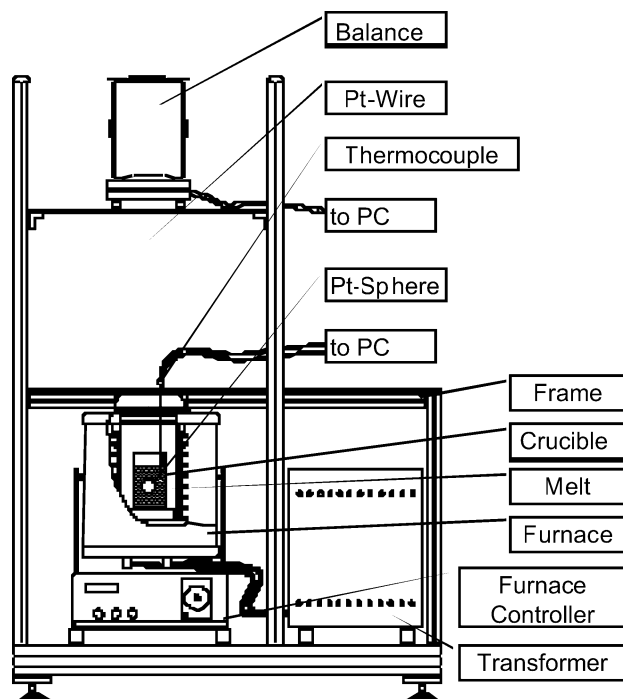

Figure 3. IME density measurement experimental set-up

controlled using a Eurotherm temperature controller. A massive molybdenum cylinder (7 g) was used as a bob as well as a platinum sphere (11 g). Different wires made of Pt/Rh 70/30, molybdenum and W5/Re were tested. On top of the furnace, an analytical balance (Ohaus Adventurer™) was placed. The wire was connected to the balance with a hook in weight below operation. The furnace was heated to 1600°C. After a holding time of 30 minutes for homogenization, the bob was placed in the melt. The weight was measured continuously online. Between the balance and the furnace, a heat shield was placed in order to avoid overheating the balance. The experimental set-up is shown in Figure 3.

In this study the **hydrostatic weighing method** was used. This method is based on Archimedes' principle. An object submerged into a liquid generates a force equal to the displaced volume of liquid. Accordingly, the object weighs less under a liquid media than in the air. It is necessary to know the volume of the submerged body, as well as its dependence on the temperature. The density of the submerged body can be lower or higher than the density of the liquid.

Table III
Composition of the investigated slags

Nr.	Material	RE-Oxide	Ca	Mg	Fe	Al	Co	Ni	Mn	SiO$_2$	F
1	Anode scrap	55.6	14.6	0.93	0.74	4.03	0.12	0.73	0.31		8.95
2	Production scrap	59.1	15.3	0.24	0.37	2.8	0.10	0.59	1.17		8.83
3	Spent batteries	53.3	16.6	0.33	1.77	3.08	0.31	2.25	0.70		8.95
4	Pyrolysed spent batteries	55.3	16.8	0.35	0.49	2.97	0.017	0.10	0.94		7.29
5	Pyrolysed spent batteries	66.1	12.1	0.70	0.29	3.32	0.009	0.04	0.34		4.18
6	Pyrolysed spent batteries	69.0	5.81	1.69	0.18	3.59	0.008	0.03	0.16	10.8	
7	Mixture	63.8	10.1	0.21	0.36	3.44	0.015	0.05	1.93		4.81
8	Mixture	64.1	5.12	0.93	0.38	3.85	0.155	1.00	0.37	10.8	
9	Polluted Mixture	65.8	10.8	0.33	0.33	3.74	0.027	0.12	1.27		5.10

The density of the melt can be determined according to the following equation derived from Arsentev et al.[5].

$$\rho_m - \rho_a = \frac{m_a - m_m}{V} \qquad [1]$$

where:

ρ_m: density of molten slag, g/cm³
ρ_a: air density, g/cm³
V: bob volume, cm³
m_a: bob mass in air, g
m_m: bob mass in molten slag, g

The air density can be neglected. The volume of the bob can be firstcalculated by the same equation using deionized water as liquid. The bob mass in air is measured with the balance. The influence of the surface tension can be taken into account by Equation [2].

$$\rho_m = \frac{m_a - m_m}{V} + \frac{\pi d \sigma \cos\theta}{gV} + \rho_a \qquad [2]$$

where:

d: wire diameter, m
θ: contact angle, grad
g: gravity acceleration, m s⁻²
σ: surface tension, N/m

Several authors have investigated the surface tension of the CaO-CaF₂-system[6]. No information about the influence of rare earth oxides on the surface tension for this slag system was found in literature. It has been shown that the surface tension increases with higher CaO share and decreases with higher temperature. It is assumed that the rare earth oxide will have the same influence on the slag system as pure CaO addition.

In terms of error analysis, the thermal expansion is considered according to Equations 3 and 4:

$$d = d_o(1 + \varepsilon) \qquad [3]$$

$$V = V_o(1 + \varepsilon)^3 \qquad [4]$$

where:

ε: linear coefficient of expansion
d_0: wire diameter at room temperature, m
V_0: volume of the bob at room temperature

The linear coefficient expansion of molybdenum was 0,0104 at 1600°C according to literature[7].

This leads to the final Equation [6] for the calculation of the density:

$$\rho_m = \frac{m_a - m_m}{V_o(1 + \varepsilon)^3} + \frac{\pi d_o(1 + \varepsilon)\sigma \cos\theta}{gV_o(1 + \varepsilon)^3} + \rho_a \qquad [6]$$

As the surface tension was unknown, the density was measured twice with two bodies of different volumes. The wire diameter was the same:

$$m_{a1} - m_{m1} = (\rho_m - \rho_a)V_1(1 + \varepsilon)^3 - \frac{\pi d_o(1 + \varepsilon)\ \sigma \cos\ \theta}{g} \qquad [7]$$

$$m_{a2} - m_{m2} = (\rho_m - \rho_a)V_2(1 + \varepsilon)^3 - \frac{\pi d_o(1 + \varepsilon)\ \sigma \cos\ \theta}{g} \qquad [8]$$

Where m_{a1}, m_{m1}, m_{a2}, m_{m2} are weights of the first and the second bob in air and in the melt, and V_1, V_2 are the volumes of the first and the second bob. Solving the two equations results in:

$$\rho_m - \rho_a = \frac{(m_{a1} - m_{m1}) - (m_{a2} - m_{m2})}{(V_1 - V_2) \cdot (1 + \varepsilon)^3} \qquad [9]$$

In addition, the density of solid slag samples was determined with the same method.

Results and discussions

Throughout the experiments some problems occurred. Neither the molybdenum nor the Pt/Rh/Pt wire worked properly in the rare earth slag. Several diameters were tested. Molybdenum wire with both 0.2 mm and 0.5 mm diameters were not suitable. In both cases, the tensile strength was too low for the ambient conditions. The wires broke above the melt after a maximum resistance time in the molten slag of five minutes. The fracture was significantly thinner than the starting diameter. Oxidation was not a major failure mechanism. A high argon flow rate of 10 *l*/min provided a sufficiently oxygen-free atmosphere. A larger diameter was not used in order to avoid higher error rates due to increased inaccuracy. Using a Pt/Rh 70/30 wire in connection with the molybdenum cylinder was not successful because the wire had been broken because it was embrittled/corroded during the measurement at the slag/atmosphere interface. With the W5/Re wire a sufficient measurement of 30 to 60 minutes could be conducted. Different heavy molybdenum bobs were used with these wire for measurements.

The platinum sphere could only be combined successfully with the Pt/Rh wire for a very limited experiment time (between 1 and 15 minutes, depending on temperature). Then the connection failed due to increased weakness of the wire as an impact of chemical instability of the Pt/Rh-wire. A chemical impact of the slag compounds on the wire is assumed as well as a too high working condition for this wire type.

In literature[8] the density of pure CaO-CaF₂-systems varies between 2.58 and 2.62 g cm⁻³ (Figure 4) depending on temperature. At 1600°C a density of 2.62 g cm⁻³ with a CaO share of 30% is given. Thus a little higher density may be assumed for a ratio of 65/35 CaF₂ to CaO. However, measurements of the solid RE bearing CaO-CaF₂ slag at room temperature results in densities between 4.32 and 4.65 g cm⁻³. The results of IME experiments for the rare earth oxide containing slags give a density between 4.07 and 4.56 g cm⁻³ (Table IV). Obviously, the rare earth oxides have a significant influence on the slag density.

Table IV
Results of slag No. 7 density measurements at 1600°C, g cm⁻³

	ρ min	ρ max	Arithmetic mean	Standard deviation
Trial 1	4.072	4.556	4.309	0.142
Trial 2	4.073	4.550	4.315	0.139
Trial 3	4.082	4.550	4.307	0.150
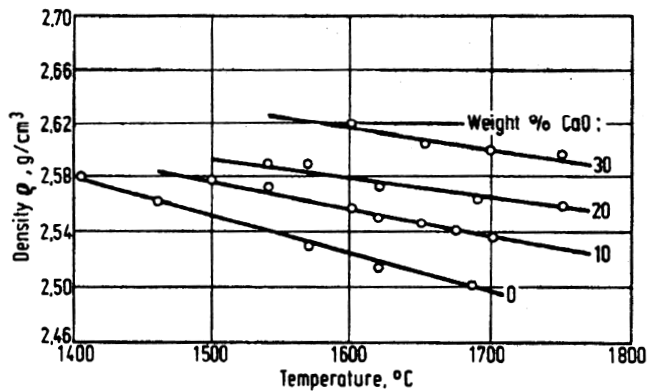
Figure 4. Temperature dependency of density of pure CaF₂-CaO melts

Figure 6. Gaussian distribution of conducted trials

In total, more than 360 successful measurements were conducted (Figure 5). All trials followed the Gaussian distribution (Figure 6). The standard deviation varies between 3.2 and 3.2 per cent. Nevertheless, the total variation of the obtained densities is 11 per cent. In order to improve the derived density values, more experiments will be conducted with different bob weights as well as at varying temperatures.

Conclusions

A suitable slag system for recycling process nickel-metalhydride batteries has been developed. In more than 50 lab-scale trials, different slag compositions (CaO-SiO₂, CaO-CaF₂, CaO-CaF₂-Al₂O₃) were investigated. Two suitable slag systems (CaO-SiO₂, CaO-CaF₂) were derived from the lab-scale trials and confirmed in pilot plant tests. For these slag systems, characterization of physical properties in comparison to common slag systems has been started by determination of the density. The influence of rare earth oxides on the density of a CaO-CaF₂-system with 35 weight per cent CaO was shown. The density was measured at 1600°C, resulting in 4.07 and 4.56 g cm⁻³. The slag density at room temperature was between 4.32 and 4.65 g cm⁻³. For validation of density, further experiments will be conducted at different temperatures. In addition, surface tension and viscosity will be determined.

Acknowledgements

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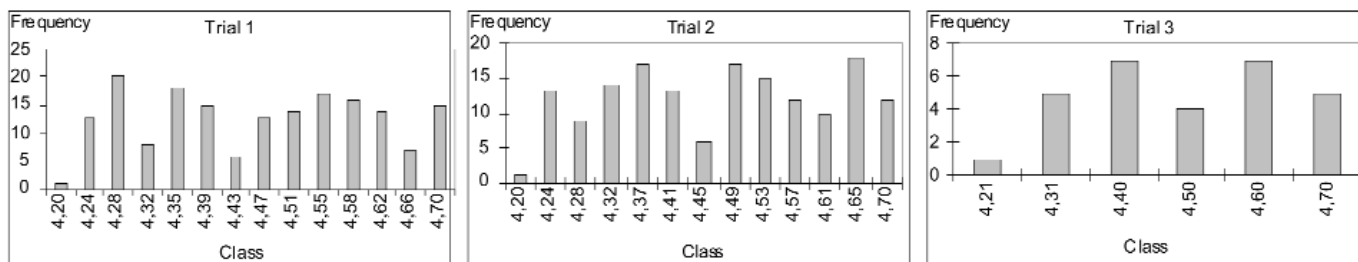8. MITCHELL, A. and JOSHI, S. The Densities of Melts in the Systems CaF₂ + CaO and CaF₂ + Al₂O₃. *Metallurgical Transactions*, vol. 3 1972, pp. 2306–07.

Figure 5. Histograms of conducted trials