Obtaining Nickel and Cobalt from Spent NiMH Batteries

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Abstract

Nickel metal hydride (NiMH) batteries represent a great metal value. Their recycling is therefore important not only for environmental, but also for economic reasons. NiMH batteries used in this study were provided by a Czech company, which is responsible for collecting this type of wastes in the Czech Republic. The batteries were processed in a cutting mill. From the resulting material, the fraction <0.5 mm was obtained by sieving. Electrode mass of NiMH batteries was treated hydrometallurgically in order to obtain metal values. A mixture of electrode mass originating from different types of batteries contained 51.0% Ni, 5.9% Co, 1.1% Zn, 0.7% Fe, 2.18% Mn, 9.2% La, 4.6% Ce, 0.7% Pr and 2.3% Nd. Leaching of the electrode mass was performed in 1 and 2 mol/L H_2SO_4 at liquid-to-solid ratios 10:1 or 20:1 and laboratory temperature as well as at 60 and 80°C. Extractions of 91.5% Ni, 92.6% Co and more than 97.5% rare earth metals (RE) were achieved. More than 99% RE were removed from the leach liquor using hydrolytic precipitation with NaOH up to pH = 1.2. Di-(2-ethylhexyl) phosphoric acid (D2EHPA) in low aromatic solvent was used as the extractant in the solvent extraction process for impurities removal from leach liquors after RE precipitation. Removal of 99.9% Fe, 94.5% Zn and 43.3% Mn was achieved when single-stage extraction was applied. When using two-stage extraction process, the achieved values of removed impurities were as follows: 99.9% Fe, almost 99% Zn and more than 60% Mn. in case of model solution. For leach liquor, the values for Fe and Zn were the same, but only slightly more than 50% Mn was removed. Nickel and Co losses did not exceed in the most cases 5%, in the best cases even less than 0.5%. The result of the proposed process is a solution of Ni and Co containing low level of other impurities. This solution is suitable intermediate for Ni and Co winning.

Keywords: NiMH batteries, nickel recovery, cobalt recovery, rare earth metals

Introduction

NiMH batteries still provide a price-efficient solution for many applications, especially for small electric and electronic devices. This is given by their lower price per kWh and performance characteristics in comparison with lithium based batteries. Therefore, recycling of this type of batteries is important topic not only because of the European legislation on this waste, but also for quite a big amount of valuable metals contained in the batteries.

The positive electrode of the NiMH battery is $Ni(OH)_2$. The electrode reaction during charging can be written as: $Ni(OH)_2 + OH^- \rightarrow \beta\text{-}NiOOH + H_2O + e^-$. The negative electrode's composition is more complex. The compounds forming the electrode are divided into groups classified by AxBy based on their composition and crystal structure. The A and B components can each consist of a number of different elements in varying ranges of stoichiometry. The most common, nevertheless, is the type AB_5, where A is mischmetal, La, Ce, Ti and B Ni, Co, Mn, Al. Negative electrode reaction (during charging): $M + H_2O + e^- \rightarrow MH + OH^-$, where M stands for A_xB_y. Solution of KOH is used as electrolyte in NiMH batteries.

Basically, there are three ways of recycling of NiMH batteries: mechanical, pyrometallurgical and hydrometallurgical. The mechanical way is not recycling in terms of recovery of particular metal values. However, it is often employed as the first step of pyro- or hydrometallurgical recycling. Pyrometallurgical recycling is based on melting the batteries and obtaining Ni-alloy and slag containing RE. Recovery of RE from the slag is, however, quite difficult. Hydrometallurgical recycling operates with leaching of electrode mass (the inner part of the battery) in suitable leaching medium, subsequent refining of leach liquors and winning of metals from the solution. Hydrometallurgy offers the possibility of recovery of all metals contained in the batteries.

Zhang et al. (1999) used 2 mol/L H_2SO_4 at 95°C for 4 h and achieved extraction efficiency of 97, 100 and 96% for Ni, Co and RE, respectively. RE were recovered by solvent extraction using 25% D2EHPA in kerosene. Extraction was effective not only for RE, but also for Fe, Zn, Al and partly for Mn. RE were obtained form the organic phase by stripping with 1 mol/L H_2SO_4 and subsequent precipitation with oxalic acid. The mixture of RE oxides containing 52.9% La_2O_3, 3.3% CeO_2, 10.3%

Tab. 1. Content of elements in the electrode material

Tab. 1. Zawartość pierwiastków w elektrodach

Element	Ni	Co	Fe	Zn	Mn	Al	Cu	Cd	La*	Ce*	Pr*	Nd*
Content [%]	51.0	5.92	0.72	1.12	2.18	0.70	1.40	0.08	9.23	4.56	0.71	2.30

*obtained by X-ray fluorescence analysis

Pr_6O_{11}, 32.5% Nd_2O_3 a 0.9% Sm_2O_3 was prepared by calcining resulted oxalates. Li et al. (2009) were able to extract 99% of all important metals except of RE by leaching electrode material in 3 mol/L H_2SO_4 at 95°C for 4 h. Resulting leach liquor was refined by solvent extraction under similar conditions as Zhang et al. Innocenzi and Veglio (2012a) utilized a leaching process with 2 mol/L, at 80°C for 3 h. Under these conditions, more than 94% Ni and Zn, 99% Co, 65% Al, 100% Mn a 35% RE were extracted. RE were removed form leach liquor by hydrolytic precipitation using NaOH up to pH = 2.

Leaching step with 2 mol/L H2SO4 at 90°C, L:S = 20:1 for 4 h was involved in a process of Ni and Co recovery from NiMH batteries (Bertuol et al., 2012). Leach liquor was neutralized with NaOH up to pH = 1.2 to obtain RE precipitate. It was possible to precipitate 97.2% La, 98.6% Ce, 97.8% Nd and 99.0% Pr. For impurities removal from leach liquors, Wu et al. (2009) employed solvent extraction. Leaching was performed in H_2SO_4; leaching efficiencies of Ni and Co were almost 99.5%. Partly neutralized 20% PC-88A in kerosene was used as extractant at pH = 3 – 3.5. For removal of all impurities, 8-stage extraction was required. Innocenzi and Veglio (2012b) used in their work 20% D2EHPA in n-dodecane as extractant. By organic-to-aqueous (O:A) phase ratio 1:1 at 40°C, 100% Zn and 95% Mn were extracted.

The aim of this work was to design and verify a process for obtaining a solution, which would contain only Ni and Co, from electrode mass of spent NiMH batteries.

Materials and methods

Batteries used in this work were provided by a company dealing with spent batteries system of collection. The batteries used were of two types: AA and from different mobile phones. The batteries were crushed to the particle size of maximum 4 mm in a cutting mill. Subsequently, the prepared material was sieved, the fraction –0.5 mm was separated and mixed with electrode materials prepared by the same way in the work (Neumannová, 2012). The resulting material was analyzed using X-ray diffraction (PANalytical X´Pert PRO), X-ray fluorescence (THERMO ARL 9400XP) and chemical analyses and then used for experiments. Element composition of the electrode material is given in table 1. Contents of Ni, Co, Fe, Zn, Mn, Al, Cu and Cd were determined by AAS analyses after decomposition of solid samples by standard methods, such as acid dissolution or alkali and acid fusion.

According to X-ray diffraction, electrode material consisted of $Ni(OH)_2$, Ni and $PrMnNi_4$.

Leaching experiments were carried out in a closed, thermostated, stirred 1L glass reaction vessel provided with temperature control and a water cooler. Mixing was accomplished by means of an impeller at agitation speed of 400 rpm. Leaching conditions were as follows: concentration of H_2SO_4 solution 1 or 2 mol/L, liquid-to-solid ratio (L:S) of 10:1 or 20:1, laboratory temperature, 60 and 80°C, reaction time 240 min. During leaching, samples were withdrawn at selected time intervals to determine the reaction rates of zinc and impurity dissolution, their concentrations in the filtrates were established using the AAS method (GBC 932plus) and ICP-OES (Optima 2000). After the completion of leaching tests, leach residues were filtered, water-washed and dried. Composition of leach residues was determined by X-ray diffraction and X-ray fluorescence analysis.

Rare earth metals were precipitated from leach liquors by adding 50% NaOH up to pH = 1.2. During NaOH adding, pH was continuously measured using pH electrode connected to a laboratory pH meter. Precipitation was performed in a beaker, at laboratory temperature, under mixing at agitation speed of 400 rpm. After completion of precipitation, the resulted precipitate was water-washed, dried and analyzed.

For impurities removal from leach liquors after RE precipitation, solvent extraction was applied.

For most of the solvent extraction experiments, model solution was used. It was prepared from chemicals of p.a. purity and its composition corresponded to the leach liquor from leaching the electrode mass in 1 mol/L H_2SO_4, L:S = 20:1 at laboratory temperature and from which subsequently RE were removed by

Tab. 2. Concentrations of metals in leach liquors

Tab. 2. Zawartość metali w roztworze po ługowaniu

H_2SO_4 concentration	L:S	Temperature (°C)	Metal concentration (mg/L)			
			Ni	Co	Fe	Zn
1 mol/L	10:1	laboratory	40.1	5.34	0.29	1.00
		60	41.6	5.80	0.36	1.03
		80	43.9	5.49	0.38	1.01
2 mol/L	10:1	laboratory	46.2	5.00	0.50	1.07
		60	53.0	5.74	0.59	1.04
		80	53.1	5.93	0.58	1.08
1 mol/L	20:1	laboratory	24.5	2.82	0.40	1.04
		60	24.4	2.89	0.41	0.95
		80	24.1	2.82	0.43	0.79

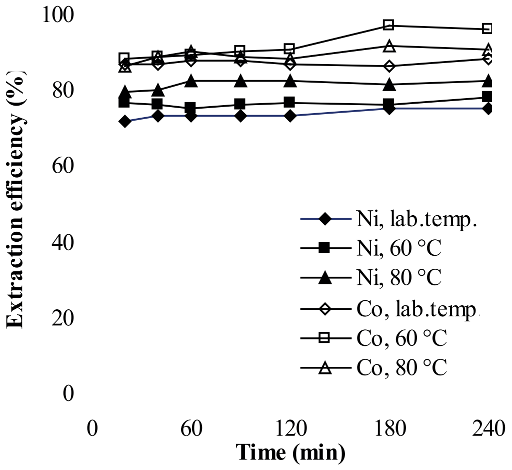

Fig. 1. Ni and Co extraction efficiency at different temperatures in 1 mol/L H_2SO_4, L:S=10:1

Rys. 1. Współczynnik wyługowania Ni i Co w różnych temperaturach przy stężeniu 1 mol/L H_2SO_4, L:S=10:1

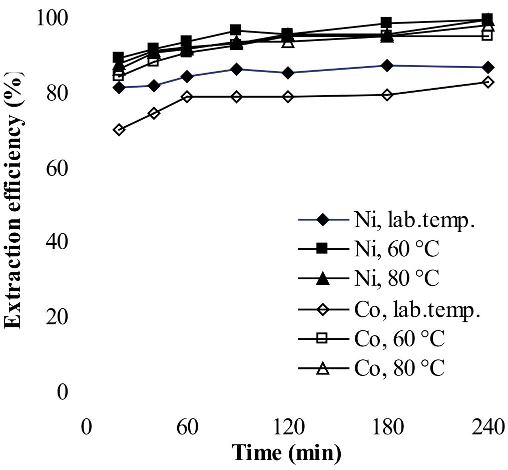

Fig. 2. Ni and Co extraction efficiency at different temperatures in 2 mol/L H_2SO_4, L:S=10:1

Rys. 2. Współczynnik wyługowania Ni i Co w różnych temperaturach przy stężeniu 2 mol/L H_2SO_4, L:S=10:1

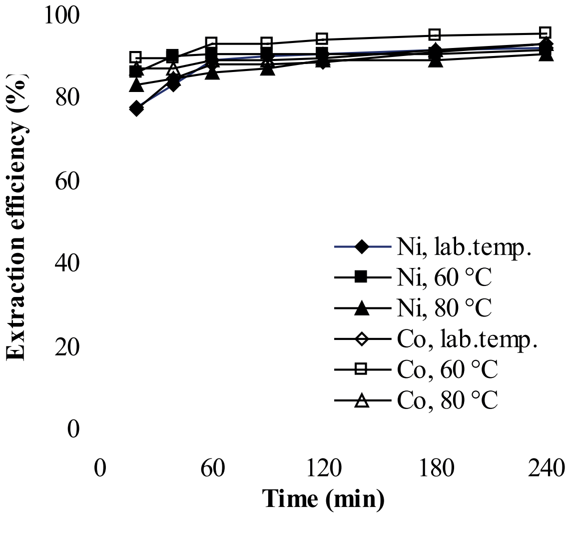

Fig. 3. Ni and Co extraction efficiency at different temperatures in 1 mol/L H_2SO_4, L:S=20:1

Rys. 3. Współczynnik wyługowania Ni i Co w różnych temperaturach przy stężeniu 1 mol/L H_2SO_4, L:S=20:1

Tab. 3. RE concentration in leach liquors and their extraction efficiencies

Tab. 3. Koncentracja REE w roztworze i efektywność ekstrakcji

H_2SO_4 concentration	L:S	Temperature (°C)	Metal concentration (mg/L)				Extraction efficiency (%)			
			La	Ce	Nd	Pr	La	Ce	Nd	Pr
1 mol/L	20:1	laboratory	4616	2223	1283	348	99.9	97.5	99.9	98.0
		60	4515	2178	1260	346	97.8	99.9	99.9	97.5
2 mol/L	10:1	60	6530	3110	1613	521	70.7	68.2	73.4	70.1

Tab. 4. Precipitation efficiency of RE

Tab. 4. Efektywność odsadzania REE

Original leach liquor	Precipitation efficiency (%)			
	La	Ce	Nd	Pr
1 mol/L H_2SO_4, L:S=20:1, lab. temperature	99.0	99.7	99.5	99.7
1 mol/L H_2SO_4, L:S=20:1, 60 °C	98.8	99.8	99.3	99.5

Tab. 5. Composition of leach liquors after RE precipitation

Tab. 5. Skład roztworu po osadzeniu REE

Original leach liquor	Element concentration												
	(g/L)									(mg/L)			
	Ni	Co	Fe	Zn	Mn	Al	Cu	Cd		La	Ce	Pr	Nd
1 mol/L H_2SO_4, L:S=20:1,lab.temp.	21.5	2.07	0.41	0.64	1.02	0.37	0.04	<0.01		45.6	7.3	6.3	1.1
1 mol/L H_2SO_4, L:S=20:1, 60 °C	22.9	2.22	0.42	0.67	1.03	0.39	0.04	<0.01		54.2	9.8	8.4	1.7

precipitation. 25% D2EHPA in low aromatic solvent SPIRDANE D-40 was used as the extractant. Extraction was performed in test tubes of 25 ml volume placed in the rotator drive (STR4). Various O:A phase ratios were tested. The extraction experiments were carried out at laboratory temperature and lasted 1 h. After completion of extraction, the aqueous phase was separated form organic phase and analyzed. Extraction efficiency was calculated from metal content in organic phase as the difference between concentration of metal in original solution and concentration of metal in aqueous phase.

Results and discussion

Results of leaching experiments in the form of time dependences of Ni and Co are illustrated in figures 1–3. Final metal content in acid liquors is in table 2.

The extraction efficiencies of rare earth metals and their concentrations in selected leach liquors after 240 min of leaching are given in table 3.

According to X-ray diffraction analysis, the leach residues contained Ni, Cu, $CuO_{0.94}$, $Ni(OH)_2$, $La_{0.33}Ce_{0.4}Nd_{0.27}Co_{0.7}Ni_{3.5}A_{l0.8}$, $Al(OH)_3$.

From the results of leaching tests, figures 1–2, it is obvious that extraction efficiency of Ni and Co increases with increasing temperature. By using 1 mol/L H_2SO_4, L:S = 10:1, at laboratory temperature, Ni and Co extraction efficiency did not exceeded 73 and 88%, respectively. At higher temperatures, these values rose to 82 and 95.5%. Extraction efficiencies of Ni and Co at 60 and 80°C by leaching in 2 mol/L H_2SO_4, L:S = 10:1, reached more than 95%. When using 1 mol/L H_2SO_4, L:S = 20:1, 91.5% Ni and 92.6% Co were extracted even at laboratory temperature. Increasing temperature did not improve these results significantly. In all experiments, extractions of Zn and Fe were very fast and almost complete. The best results of RE extraction were achieved by leaching in 1 mol/L H_2SO_4, L:S = 20:1 at laboratory temperature.

RE were precipitated from selected leach liquors by adding 50% NaOH up to pH 1.2. The initial pH of leach liquors was about 0.15. RE precipitation efficiency is given in table 4. Composition of selected liquors after rare earth metals precipitation is given in table 5.

Tab. 6. Composition of RE precipitates (established by XRF)

Tab. 6. Skład osadu REE (określone przez XRF)

Original leach liquor	Element content in precipitate (%)										
	Ni	Co	Fe	Zn	Mn	K	Na	La	Ce	Pr	Nd
1 mol/L H_2SO_4, L:S=20:1,lab.temp.	<0.01	<0.01	<0.01	<0.01	<0.01	3.2	9.9	36.1	16.9	2.4	7.9
1 mol/L H_2SO_4, L:S=20:1, 60 °C	<0.01	<0.01	<0.01	<0.01	<0.01	3.1	9.7	36.6	16.7	2.4	8.0

Tab. 7. Metal extraction efficiency in solvent extraction

Tab. 7. Efektywność ekstrakcji metali w ekstrakcji rozpuszczalnikowej

pH	O:A	Extraction efficiency (%)				
		Ni	Co	Fe	Zn	Mn
2.0	1:1	1.6	0.0	81.7	77.3	38.7
	2:1	0.1	4.9	97.8	88.5	30.8
2.5	1:1	4.5	7.7	96.5	84.0	19.0
	2:1	0.6	4.2	99.2	91.2	32.9
3.0	1:1	2.1	<0.1	98.0	89.7	25.3
	2:1	4.6	1.0	>99.9	94.5	43.3

Tab. 8. Metal extraction efficiency in solvent extraction (O:A = 2:1, pH = 2.5, leach liquor: from leaching in 1 mol/L H_2SO_4, L:S = 20:1, lab. temperature, after RE removal)

Tab. 8. Współczynnik ekstrakcji rozpuszczalnikowej metali (O:A = 2:1, pH = 2.5, roztwór ługujący: od 1 mol/L H_2SO_4, L:S = 20:1, temperatura pokojowa, po usunięciu REE)

	Metal extraction efficiency (%)				
	Ni	Co	Fe	Zn	Mn
model solution	<0.1	<0.1	>99.9	99.3	60.3
leach liquor	<0.1	<0.1	>99.9	98.9	51.3

According to X-ray diffraction analysis, the precipitates from rare earth metals precipitation contained $NaLa(SO_4)_2 \cdot H_2O$ and $NaCe(SO_4)_2 \cdot H_2O$. It is also possible that other rare earth metals are present in similar compounds as these can build solid solutions.

Increasing the pH value of leach liquors to 1.2 enabled precipitating of RE. The amount of precipitated RE exceeded 99% independently on leaching conditions of the original leach liquor.

For the majority of the solvent extraction tests, the model solution was used. Its pH was adjusted to desired values by 50% NaOH addition. The results of single-stage solvent extraction are showed in table 7. The results of two-stage extraction, where in the second stage fresh extractant was used, are showed in table 8.

By using single-stage solvent extraction, the amount of extracted impurities increases with increasing pH. The best results were achieved for pH = 3. Nickel and Co losses did not exceed 5%. Nevertheless, as the amount of removed Zn was not satisfactory, two-stage extraction was applied. It showed very good results, reaching the extraction efficiency more than 99.9% for Fe and about 99% for Zn. Moreover, more than 60% (model solution) and 51% (leach liquor) Mn was extracted.

Conclusion

Hydrometallurgical processing of the electrode mass from spent NiMH batteries was proposed and verified on a laboratory scale. Optimum leaching conditions are as follows: 1 mol/L H_2SO_4, L:S = 20:1, laboratory temperature, 240 min. Subsequent precipitation up to pH = 1.2 enabled almost complete removal of RE from leach liquors. The two-stage solvent extraction of the leach liquor makes it possible to remove the main impurities, either almost completely – Fe, Zn – or bigger part of it – Mn. The result of the proposed processing of the electrode mass is a solution containing Ni, Co and very low level of impurities, which is a suitable intermediate for Ni and Co recovery.

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Odzysk niklu i kobaltu ze zużytych baterii NiMH

Niklowo-metalowe akumulatory hybrydowe (skrót ang. NiMH) cechuje wysoka zawartość metalu. Zatem ich utylizacja jest ważna nie tylko ze względów środowiskowych, lecz również ekonomicznych. Akumulatory NiMH użyte w niniejszych badaniach otrzymano od czeskiego przedsiębiorstwa, które odpowiada za odbiór tego typu odpadów na terenie Republiki Czeskiej. Akumulatory rozdrobniono w młynie tnącym. Z uzyskanego w ten sposób materiału, przy pomocy odsiewu, uzyskano cząsteczki wielkości <0.5mm. Masa elektrodowa baterii NiMH została poddana procesom hydrometalurgicznym w celu otrzymania metalu. Mieszanka masy elektrodowej pochodzącej z różnego typu baterii zawierała 51.0% Ni, 5.9% Co, 1.1% Zn, 0.7% Fe, 2.18% Mn, 9.2% La, 4.6% Ce, 0.7% Pr oraz 2.3% Nd. Ługowanie masy elektrodowej zostało przeprowadzone w roztworze H_2SO_4 w ilości 1 i 2 mole /L, stosunek cieczy do ciała stałego wynosił 10:1 lub 20:1, natomiast temperatura procesu wynosiła odpowiednio 60 oraz 80°C. Uzyskano próbki o zawartości 91.5% Ni, 92.6% Co oraz ponad 97,5% metali ziem rzadkich (ang. skrót REE). Ponad 99% metali ziem rzadkich odseparowano z roztworu ługującego przy użyciu strącania hydrolitycznego za pomocą NaOH przy pH siegającym do 1.2 kwasu di - (2-etyloheksylowego) fosforowego (D2EHPA) w rozpuszczalniku aromatycznym użytym jako ekstrahent w procesie oczyszczania rozpuszczalnika, aby usunąć zanieczyszczenie z roztworów ługujących powstałych po procesie strącania hydrolitycznego metali ziem rzadkich. Po zastosowaniu jednofazowego procesu ekstrakcji udało się usunąć 99,9% Fe, 94,5% Zn oraz 43.3% Mn. Po zastosowaniu dwufazowego procesu ekstrakcji wyniki usunięcia zanieczyszczeń przedstawiały się następująco: 99,9% Fe, blisko 99% Zn oraz ponad 60% Mn w przypadku roztworu modelowego. W przypadku roztworu ługującego wartości dotyczące Fe oraz Zn były takie same, jednakże usunięto tylko trochę powyżej 50% Mn. Ubytki Niklu oraz Co w większości przypadków nie przekroczyły 5%, w najlepszym razie nie przekraczając nawet 0,5%. Wynikiem zastosowanego procesu jest roztwór Ni oraz Co o niskiej zawartości zanieczyszczeń. Roztwór ten może słuzych do odzysku Ni oraz Co.

Słowa kluczowe: akumulatory NiMH, odzysk niklu, odzysk kobaltu, metale ziem rzadkich