



Leaching of base metals from spent Ni–metal hydride batteries with emphasis on kinetics and characterization



Pratima Meshram^{a,*}, B.D. Pandey^a, T.R. Mankhand^b

^a Metal Extraction & Forming Division, CSIR-NML, Jamshedpur, India

^b Dept. of Metallurgical Engineering, IIT (BHU), Varanasi, India

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ABSTRACT

Nickel–metal hydride (Ni–MH) batteries which generally contain nearly 55–60% Ni and 4–6% Co along with a few other metals may be considered an important resource for recycling and supply of these metals. In this study, leaching kinetics of nickel and cobalt, and other base metals from the spent Ni–MH batteries in sulfuric acid solutions have been investigated with an emphasis on the process characterization at different stages of the treatment. The maximum dissolution of nickel, cobalt, iron, manganese and zinc was found to be 91.6, 97.8, 65.5, 93.5 and 99.2%, respectively in a single stage under the optimum conditions comprising of 2 M H₂SO₄, 100 g/L pulp density and 348 K temperature after 120 min of leaching. Kinetic data for the dissolution of all the metals including the rare earths (as a group) showed the best fit to the chemical control shrinking core model. The activation energy of 8.7, 6.8, 7.12, 6.7 and 7.9 kJ/mol was determined for the leaching of base metals viz., nickel, cobalt, iron, manganese and zinc, respectively in the temperature range 305–348 K. With the help of the XRD phase analysis and the change in morphological features along with the elemental mapping in the leach residues with time and the untreated electrode material by SEM-EDS, the leaching mechanism was established. The process characterization corroborated the kinetic model for the leaching of metals which progressed through the chemical reaction of the lixiviant on the surface of the spherical particles of electrode powder. The XRD analysis of the residue showed the presence of metallic nickel which required stringent conditions for improved recovery of this metal.

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1. Introduction

The nickel metal hydride (Ni–MH) batteries are widely used in portable electrical and electronic appliances, hybrid electric vehicles (HEV), etc. because of the associated advantages such as high energy density, fewer environmental problems and lesser resource concerns (Sakai et al., 1999). With the growing need of electronic devices, the consumption of batteries is expected to increase in the coming years (Meshram et al., 2014). Recycling of these batteries after use has thus become an important issue because of the stringent environmental regulations and resource conservation. Because of the economic worth of important strategic metals such as nickel and cobalt in the Indian context, development of an efficient recycling process is needed to achieve the goals of waste minimization and sustainability. It is expected that the recycling of such wastes could possibly justify the recovery of the strategic metals like nickel and cobalt, besides other values. The recycling at a certain scale may thus entail a fairly good supply of these metals, which may turn such a step profitable eventually while addressing the environmental concerns simultaneously.

Several studies have been carried out to recover valuable metals from the spent Ni–MH batteries by pyrometallurgical (Müller and Friedrich, 2006) and hydrometallurgical processes (Lyman and Palmer, 1995; Zhang et al., 1999; Luidold and Antrekowitsch, 2012; Kaindl et al., 2012). Because of the large amount of metals present in the spent Ni–MH batteries, a hydrometallurgical process seems more appropriate than the pyrometallurgical processing for the recycling. In general, leaching in HCl, H₂SO₄ and sometimes both acids in two steps in a sequence is applied which is followed by the use of a combination of separation techniques such as precipitation, solvent extraction, and ion exchange to recover different metals in the desired form. In this context, it is important to highlight the recovery of base and rare earth metals/alloys present in the spent Ni–MH batteries using different acids as the lixiviant.

Table 1 summarizes the relevant literature incorporating the significant findings of the leaching and separation of metals from such batteries. In most studies the conditions for leaching of Ni and Co, and rare earth metals as a group have generally been reported under varying conditions, and kinetic aspects have been often ignored. In a recent investigation, Yang et al. (2014) reported the leaching kinetics of total rare earth metals (REs) from the spent Ni–MH batteries in hydrochloric acid (20%). With a recovery of 95.2% REs at 10% pulp density and 70 °C in 100 min, the kinetic data showed best fit to the chemical control model

* Corresponding author.

E-mail address: pratima@nmlindia.org (P. Meshram).

Table 1
Summary of leaching conditions and results obtained in previous studies.

Material	Lixiviant Acid concentration	Conditions Temp., time, pulp density	Leaching (%)						Highlights
			Ni	Co	Fe	Mn	Zn	REs	
Spent Ni–MH batteries ^a	3 M HCl	368 K, 180 min, S/L = 1/9	96	100	–	–	–	99	REs extracted using 25% D2EHPA
Spent Ni–MH batteries ^b	2 M H ₂ SO ₄	363 K, 240 min, S/L = 1/20	82.6	92.3	53	91	95.7	83.4	REs separated by precipitation
Ni–MH battery residues ^c	2-Stage leaching, Stage-I: 6% (v/v) H ₂ SO ₄ + 3% (w/w) H ₂ O ₂ Stage-II: 2 M HCl	(I) RT, 60 min, S/L = 1/30 (II) RT, 120 min, S/L = 1/30	64.5	96.4	–	–	–	87.3	REs separated by precipitation and Ni & Co separated by SX
Ni–MH battery residues ^d	3 M H ₂ SO ₄ + 3% (w/w) H ₂ O ₂	343 K, 300 min, S/L = 1/10	99.9	99.4	–	–	–	98	HCl leaching not recommended; REs separated by precipitation, Ni & Co separated by SX
Spent Ni–MH batteries ^e	2-stage leaching, Stage-I: 3 M H ₂ SO ₄ Stage-II: 1 M H ₂ SO ₄	(I) 353 K, 180 min, S/L = 3/20 (II) RT, 60 min, S/L = 3/20	99	100	–	100	100	99	Precipitation used for REs extraction
Spent Ni–MH batteries ^f	20% HCl	343 K, 100 min, S/L = 1/10	–	–	–	–	–	95.2	Leaching followed chemical control model
Spent Ni–MH batteries ^g	2 M H ₂ SO ₄	348 K, 120 min, S/L = 1/10	91.6	97.8	65.5	93.5	99.2	90.2	Leaching kinetics studied

^a Zhang et al., 1999.

^b Bertuol et al., 2009.

^c Rodrigues and Mansur, 2010.

^d Aly et al., 2012.

^e Innocenzi and Vegliò, 2012.

^f Yang et al., 2014.

^g Present work.

yielding an activation energy of ~44 kJ/mol. Thus, the dissolution pattern and kinetics of leaching of most base metals present in these batteries have not been dealt with systematically. Besides, no adequate attempts were made to correlate the progress of the reaction with the leaching mechanism and the phase transformation during the process of metal dissolution.

In view of above, a process based on the sulfuric acid leaching has been investigated to recover nickel, cobalt, iron, manganese and zinc from the electrode material of the spent Ni–MH secondary batteries. The study encompasses the details of steps such as dismantling and physical–mechanical separation of the electrode material (a black powder), and optimizing the parameters for the leaching of base metals from the material. While evaluating the leaching kinetics of the base metals the process characterization has particularly been stressed upon with the aim of understanding the mechanism of metal dissolution at different stages.

2. Materials and methods

2.1. Material

The spent Ni–MH batteries (average wt. 57 g each) were collected from the local sources and used in this work. Batteries were dismantled and treated by physical beneficiation method to obtain the electrode material (both anodic and cathodic part). The chemical composition of the electrode powder was determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) after dissolution in the aqua-regia. All the solutions generated during the leaching experiments were analyzed by AAS (Atomic Absorption Spectrometer) and ICP-OES. Diluted solutions of 96% sulfuric acid (0.5–3 M) was used as the leaching agent. All the chemicals used were analytical grade reagents.

2.1.1. Dismantling of spent batteries and characterization of the electrode material

To obtain the battery material for leaching, the components of Ni–MH batteries were subjected to physical separation by crushing. The batteries consist of steel case, battery electrode as well as nylon separator and each material has different characteristics such as particle size

and specific gravity. The batteries were agitated and crushed by scutter crusher in water. Heavy particles mainly the steel case settled down and the nylon separator being lighter floated out, leaving the electrode material dispersed in the water. After scrubbing, floating material was first removed from water. The suspended fraction contained black powder which was separated by wet screening using a sieve of 20 µm size. Heavy materials which settled in the bottom layer, were also separated by the same method. After separation, the electrode powder was collected and dried at 353 K for 24 h, and was characterized for its composition by chemical analysis, phase identification by XRD (Bruker™ D8 Discover) and morphological features by SEM attached with EDS with gold coating (FEI-Quanta™). The particle size of the cathode powder was determined by a laser particle size analyzer (Malvern®, UK).

2.2. Leaching procedure

Leaching of metals from the electrode material of spent batteries was carried out in a 500 mL three necked round bottom flask with a magnetic stirrer, a sensor based temperature controller and a reflux condenser which was fitted to the flask to avoid the loss due to evaporation. Effect of concentration of sulfuric acid (0.5–3 M), pulp density (20–150 g/L), time of leaching (up to 5 h) and temperature (305–368 K) of the solution on the extent of dissolution of metals, was studied. A constant stirring speed of 500 rpm was maintained during the leaching experiments which was found to be sufficient to minimize the diffusion layer of lixiviant around the battery powder being leached out. In order to monitor the progress of leaching samples were taken out at different time intervals and analyzed. At the end of leaching, the residue was filtered through Whatman filter paper (No. 42) and washed with distilled water over a Büchner funnel. The filtered residue was then dried overnight at 353 K in an electric oven. The amount of the metals leached under a set of experimental conditions

Table 2
Chemical composition of Spent Ni–MH battery powder.

Element	Ni	Co	Mn	Fe	Zn	REs
% (w/w)	58.9	4.6	2.9	2.8	2.0	18.3

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