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Rare earth element recycling from waste nickel-metal hydride batteries

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HIGHLIGHTS

- Leaching kinetics of REEs has rarely been reported.
- A new method, including hydrochloric acid leaching and oxalic acid precipitation, was proposed.
- REEs recovery rate of 95.16% and pure rare earth oxides of 99% were obtained.
- Leaching process was controlled by chemical reaction.
- The kinetic equation was determined.

ARTICLE INFO

ABSTRACT

With an increase in number of waste nickel-metal hydride batteries, and because of the importance of rare earth elements, the recycling of rare earth elements is becoming increasingly important. In this paper, we investigate the effects of temperature, hydrochloric acid concentration, and leaching time to optimize leaching conditions and determine leach kinetics. The results indicate that an increase in temperature, hydrochloric acid concentration, and leaching time enhance the leaching rate of rare earth elements. A maximum rare earth elements recovery of 95.16% was achieved at optimal leaching conditions of 70 °C, solid/liquid ratio of 1:10, 20% hydrochloric acid concentration, −74 μm particle size, and 100 min leaching time. The experimental data were best fitted by a chemical reaction-controlled model. The activation energy was 43.98 kJ/mol and the reaction order for hydrochloric acid concentration was 0.64. The kinetic equation for the leaching process was found to be: $1 - (1 - x)^{1/3} = A/\rho r_0 [\text{HCl}]^{0.64} \exp\left(\frac{-439,800}{8.314T}\right) t$. After leaching and filtration, by adding saturated oxalic solution to the filtrate, rare earth element oxalates were obtained. After removing impurities by adding ammonia, filtering, washing with dilute hydrochloric acid, and calcining at 810 °C, a final product of 99% pure rare earth oxides was obtained.

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1. Introduction

China is one of the largest global producers of batteries at almost one third of the global output. The annual output of small nickel-metal hydride (Ni-MH) batteries alone reaches 0.16 billion per year. Generally, Ni-MH batteries have a useful life of two years [1], resulting in the wastage of a large quantity of these batteries every year. Eight to ten percent rare earth elements (REEs) exist in the anode of battery in the form of hydroxide, oxide, and pure metal.

The REEs include mainly lanthanum, cerium, praseodymium, and neodymium. To date, the recycling of REEs from waste Ni-MH batteries and the leaching kinetics of REEs have rarely been reported on. Pyro- and hydrometallurgical processes have been considered for REE recycling [2–6]. However, REEs in ashes cannot be recovered in the pyrometallurgy process, and serious pollution results. Compared with pyrometallurgy, the hydrometallurgical approach has more advantages, such as lower operating temperatures, lower energy, and harmless gas emissions. In 2006, Gerasimova et al. proposed sulfuric acid leaching and Na_2CO_3/NaOH precipitation for REE recycling from waste Ni-MH batteries [7]. However, because of the similar solubilities of REE carbonates and carbonate impurities in water and common acids, they are difficult to separate and the final REE product purity is reduced. In 2008, Mei et al. proposed

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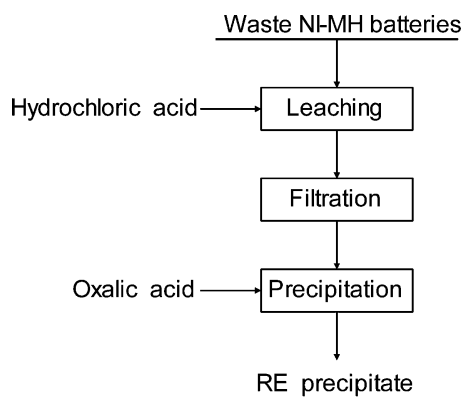E-mail address: yangxiuli21@126.com (X. Yang).

Fig. 1. Flow chart of REEs recycling from waste nickel-metal hydride batteries.

Table 1
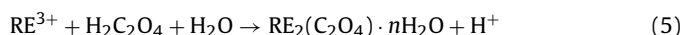Chemical composition of the anode material of waste nickel-metal hydride batteries (wt.%).

Ni	Cu	Co	Mn	K	Al	Ce	La	Nd	Pr
35.02	7.08	6.96	3.75	1.06	0.98	11.8	7.56	3.94	1.04

dilute sulfuric acid leaching and anhydrous sodium sulfate precipitation for REE recycling from waste Ni-MH batteries [8] with a reaction equation as follows:

$$RE_2(SO_4)_3 + Na_2SO_4 + xH_2O \rightarrow RE_2(SO_4) \cdot Na_2SO_4 \cdot xH_2O \qquad (1)$$

Eq. (1) shows that the introduction of sodium affects the recycled REE quality. Moreover, double salt formation between REE and nickel and/or alkali metals in the sulfuric acid leach decreases REE recovery.

Therefore, a new method was proposed, which includes hydrochloric acid leaching and oxalic acid precipitation. In this method, hydrochloric acid and oxalic acid replace sulfuric acid and sodium carbonate and sodium hydroxide or anhydrous sodium sulfate, respectively. The reaction equations are as follows:

$$RE + 6H^+ \rightarrow RE^{3+} + 3H_2 \qquad (2)$$

$$RE_2O_3 + 6H^+ \rightarrow 2RE^{3+} + 3H_2O \qquad (3)$$

$$RE(OH)_3 + 3H^+ \rightarrow RE^{3+} + 3H_2O \qquad (4)$$

$$RE^{3+} + H_2C_2O_4 + H_2O \rightarrow RE_2(C_2O_4) \cdot nH_2O + H^+ \qquad (5)$$

According to the above analysis, the processing flow to recover rare earths from waste nickel-metal hydride batteries is proposed, as shown in Fig. 1. Firstly, unwanted material in waste Ni-MH batteries is leached using hydrochloric acid. After filtration, oxalic acid is added to the filtrate, and rare earth oxalates, $RE_2(C_2O_4) \cdot nH_2O$, result. After roasting, pure anhydrous rare earth oxalate is obtained.

2. Materials and methods

2.1. Materials

We collected waste Ni-MH batteries from Jiangxi, China. The chemical composition of the unwanted material in the waste batteries as analyzed by inductively coupled plasma-atomic emission spectroscopy is shown in Table 1. Prior to analysis, samples were roasted and smelted with an appropriate amount of sodium carbonate and boric acid at 1000 °C for 20 min, and then dissolved using hydrochloric acid solution in a 1:1 (m/v) ratio. Lastly, the solution was diluted to a suitable concentration for analysis.

Hydrochloric and oxalic acids (both analytical reagent grade) were supplied by Ganzhou Chemical Reagent Company, Jiangxi, China. Distilled water was used in the experiments.

2.2. Procedure

The flow chart of the proposed method for recycling REEs from waste Ni-MH batteries is shown in Fig. 1. Firstly, the unwanted material, which had been separated manually from the waste Ni-MH batteries, was dried at 100 °C for 1 h. The dried and cut material was ground to −74 μm. The ground unwanted material (50 g) and hydrochloric acid (of different concentrations) was placed into a beaker at different solid/liquid (S/L) ratios, and then stirred constantly at 450 rpm. After reaction, the insoluble matter was filtered and oxalic acid was added to 100 ml of the filtrate. After oxalate precipitation and calcination, rare earth oxides were obtained.

The leaching efficiency was calculated from:

$$x\% = \left(1 - \frac{m \times x_{RE}}{m_o \times x_{oRE}}\right) \times 100 \qquad (6)$$

where x is the REE leaching efficiency, m_r the mass of leach residue (g), x_{RE} the fraction of REEs in the leaching residue, m_o the mass of unwanted material in the Ni-MH batteries (g), and x_{oRE} is the REE fraction in the unwanted material from the Ni-MH batteries.

2.3. Analysis

To examine phase changes of unreacted and reacted unwanted material in waste Ni-MH batteries, samples were analyzed by Philips X-ray diffractometry with Cu Kα radiation generated at 40 kV and 150 mA. X-ray diffraction spectra were obtained in the 5–90° range of 2θ and the diffraction patterns obtained were compared with the Joint Committee on Powder Diffraction Standards archives in the PDXL software program. Chemical composition was analyzed by inductively coupled plasma-atomic emission spectroscopy (Perkin Elmer Co., Ltd., OPTIMA 7000DV).

3. Results and discussion

3.1. Hydrochloric acid leaching

3.1.1. Effect of temperature on leaching rate of rare earth elements

The effect of temperature on REE leaching rate was tested for the −74 μm particle size fraction using a 20% hydrochloric acid solution and 450 rpm stirring speed from 50 to 70 °C. The results in Fig. 2 indicate that temperature has an appreciable effect on REE leaching. As temperature increases, the time required to extract maximum REEs decreases. This increase may be because of an increase in volatilization of hydrochloric acid with the increase in temperature.

To obtain the kinetic equation and apparent activation energy, experimental data were correlated to various kinetics models for liquid/solid reactions. For a liquid/solid reaction system, the reaction rate is generally controlled by diffusion through the liquid film, diffusion through the product layer, chemical reaction at the solid particle surface or a mixture of diffusion and chemical reactions [9–11]. The shrinking core model considers that the leaching process is controlled by one of these steps. When either diffusion or the surface chemical reaction is the slowest step, the shrinking core model equations can be expressed as follows [10]:

$$1 - 3(1-x)^{2/3} + 2(1-x) = k_d t \qquad (7)$$

$$1 - (1-x)^{1/3} = k_r t \qquad (8)$$