



All-metal recovery from spent Ni-MH batteries based on electrolysis of sodium sulfate solution

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Abstract: A sustainable strategy for all-metal recycling from spent nickel metal hydride (Ni-MH) batteries was proposed, where H₂SO₄ and NaOH solutions by the electrolysis of Na₂SO₄ solution were used as the leaching agent and precipitation agent, respectively. The leaching of electrode materials was performed in mild condition, and more than 99% of the rare earths were firstly precipitated at pH 1.0 in the form of double sulphates, which were converted to hydroxides by reacting with NaOH. In the following purification steps, Al³⁺ and Fe³⁺ were deposited at pH 5.5, and Zn²⁺ and Mn²⁺ were extracted by saponified D2EHPA–kerosene from the leaching solution, and two hydroxide byproducts with industrial application were obtained. Ni²⁺ and Co²⁺ were precipitated at pH 9.5 with a total recovery rate of 97.5%. The recovery efficiency of Na₂SO₄ was up to 97% in total. This metal recovery approach produces considerable economic profit, without solid or liquid waste in the closed-loop process.

Key words: spent Ni-MH batteries; metal recovery; electrolysis; sodium sulfate; closed-loop process

1 Introduction

Nickel metal hydride (Ni-MH) batteries have been widely used in various technical fields by replacing nickel–cadmium batteries due to the advantages of high-energy density, long life, non-cadmium pollution, etc [1,2]. Ni-MH batteries have occupied a considerable share of the battery market, including hybrid electric vehicles (HEVs) and high-tech electronic product power supplies, although new battery technologies are coming from laboratory to production [3–6]. Statistics shows that the number of HEVs worldwide reached about 5×10⁵ in 2021, with the consumption of Ni-MH batteries of 3.146×10⁶ kW·h [4]. As reported by

LARSSON et al [7], rare earth metals, nickel, cobalt and iron can account for 10 wt.%, 50 wt.%, 3.7 wt.% and 30 wt.% in the electrode materials of Ni-MH batteries, respectively. Therefore, several strategies have so far been developed for the recovery of valuable elements in spent Ni-MH batteries [8–11], including mechanical recycling, as well as pyrometallurgical, hydrometallurgical and biometallurgical methods [12,13], among which hydrometallurgical recovery combining with separation technology exhibits the significant advantages of low reaction temperature, low energy consumption and high recovery rate [14–16].

The metal elements in the electrode materials of spent Ni-MH batteries can be simply dissolved in hydrochloric acid, sulfuric acid (H₂SO₄) and nitric

acid, among which the low-cost H_2SO_4 is the most frequently used [17,18]. RABAH et al [19] utilized 3.0 mol/L H_2SO_4 to leach the electrode material of spent Ni-MH batteries, and the optimized leaching rates of nickel and cobalt reached as high as 99.9% and 99.4%, respectively. DHIMAN and GUPTA [20] studied cobalt and recycling of valuable metals from spent Li-ion batteries via solvent extraction and chemical precipitation MESHARAM et al [21] and BERTUOL et al [22] indicated that rare earth could be easily precipitated as double sulfate salts in the H_2SO_4 leaching solution, when the pH value was adjusted to 1.8 by sodium hydroxide (NaOH) solution, in which Ni^{2+} , Co^{2+} , Mn^{2+} and Zn^{2+} still remained in the solution. Other studies also reported that double sulfate precipitation was an effective method to separate rare earths [22–25]. After rare metals were precipitated, TANONG et al [17] employed NaOH to adjust the pH value of the leachate to 5–7, where Fe^{3+} , Zn^{2+} and Mn^{2+} were effectively removed, resulting in a purified solution for the recovery of Ni and Co. Although these technologies can effectively extract valuable metals, the waste water containing untreated acid and sodium salt after metal recovery brings the secondary pollution to the environment [26,27].

In order to avoid this secondary pollution, a mild hydrometallurgical strategy was proposed to realize all-metal recovery in spent Ni-MH batteries instead of only recycling valuable elements. Sodium sulfate (Na_2SO_4) solution was employed to produce H_2SO_4 and NaOH by electrolysis, which can avoid serious environmental impact and corrosion to equipment and tube lines caused by strong inorganic acids and alkalis. The metallic elements in the electrode materials were dissolved by the electrolyzed low-concentration H_2SO_4 solution enhanced by adding hydrogen peroxide (H_2O_2), and the NaOH was to neutralize the leaching solution and to prepare the hydroxide products, resulting in the regeneration of Na_2SO_4 available for recycling. The rare earths were firstly separated by double sulphates precipitation, followed by the purification of the leaching solution by the precipitation of Al^{3+} and Fe^{3+} and the extraction of Zn^{2+} and Mn^{2+} , leading to two hydroxide by-products after the neutralization of NaOH solution. Thereafter, nickel and cobalt hydroxides were precipitated by adjusting the pH value with the electrolyzed NaOH solution. As a

result, all the metal elements in the electrode materials were recovered in the form of hydroxides with high purities, and the overall recycled Na_2SO_4 in the process was up to 97%. The closed-loop process only needs Na_2SO_4 , H_2O_2 , electricity and water, which produces nearly zero solid waste and sewage, and hence a considerable economic profit could be expected due to the maximal output.

2 Experimental

2.1 Chemicals and materials

Sodium sulfate (Na_2SO_4 , GR, $\geq 99\%$), phenolphthalein, methyl red, potassium hydrogen phthalate (AR, $\geq 99.8\%$), hydrogen peroxide (H_2O_2 , 30%), nitric acid (AR, $\geq 99\%$), and hydrochloric acid (GR $\geq 99\%$) were purchased from Xilong Science Co., Ltd., and di-(2-ethylhexyl)phosphoric acid (D2EHPA, $\geq 95\%$) and sulfonated kerosene (aromatic hydrocarbons ≤ 50 mg/kg) were purchased from Shanghai Titan Technology Co., Ltd., and Zhengzhou Hecheng New Material Technology Co., Ltd., respectively. Homogeneous anion exchange membrane (HMED-0510-2) was bought from Hangzhou Huamo Technology Co., Ltd., and spent Ni-MH batteries (AAA750) were obtained from a local waste recycling station.

2.2 Electrolysis of Na_2SO_4 solution

A home-made electrolytic cell was used, where the anode was a titanium mesh coated with ruthenium, and the cathode was a titanium plate, which were separated by an anion exchange membrane with the anode–cathode distance of 2 mm. The geometric areas of the anode and cathode were 21.25 cm^2 . Two containers were both filled with 200 mL of 1.5 mol/L Na_2SO_4 electrolyte solutions, which were cycled between the electrolytic cell and the containers. H_2SO_4 and NaOH solutions were produced after electrolyzing at $55\text{ }^\circ\text{C}$ with a current density of 100 mA/cm^2 for 3 h, and Fig. S1 in the Supporting Information shows the structure and operation of the electrolytic cell.

2.3 Battery disassembly and metal recovery from electrode materials

Spent Ni-MH batteries were firstly discharged and then dismantled, where the metal shells, nickel

foams, membrane and other plastics were collected and weighed separately. The cathode and anode materials were mixed after drying at room temperature and ground into powders to pass through a screen with hole size of 0.85 mm. Scheme 1 is a brief description of the all-metal recovery from the electrode materials of spent Ni-MH batteries, where the employed H_2SO_4 and NaOH were produced by the electrolysis of Na_2SO_4 solution. The metal elements in the electrode materials were leached at the beginning, followed by the separation of the rare earths, the removal of Al^{3+} and Fe^{3+} and the extraction of Zn^{2+} and Mn^{2+} . Ni^{2+} and Co^{2+} remained in the purified leaching solution were finally recovered by precipitation. All the metals in the electrode materials of spent Ni-MH batteries were recovered in the form of hydroxides with high purities, and the overall recycled Na_2SO_4 in the process was up to 97%. There are nearly zero solid waste and sewage generated in the closed-loop process.

The leaching efficiency is calculated from the metal contents in the electrode materials and in the filter residue as follows:

$$R = \frac{m_1 w_1 - m_2 w_2}{m_1 w_1} \times 100\% \quad (1)$$

where R represents the leaching efficiency of the examined element, %; m_1 and m_2 are the masses of

the raw material and filter residue, respectively, g; w_1 and w_2 are the mass fractions of the examined element in the raw material and filter residue, respectively, %. Similarly, the purity of the product is estimated based on the mass fraction of the examined materials:

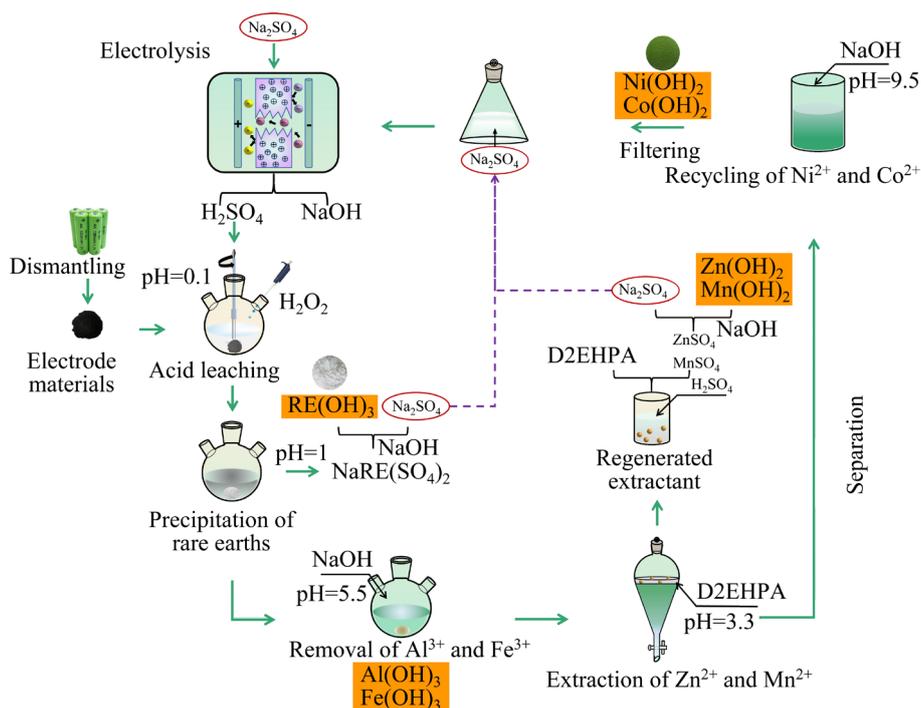
$$p = \frac{m_s}{m_t} \times 100\% \quad (2)$$

where p represents the purity of the product, %; m_s and m_t are the mass of the examined compound and the total mass of the product, g.

2.4 Characterization

Field emission scanning electron microscope (SEM, S-4800, Hitachi) and X-ray diffractometer (XRD, X'Pert PRO, PANalytical B.V., $\text{Cu K}\alpha = 0.15406 \text{ nm}$) were employed to characterize the morphology and structure of the raw materials and products in the recovery process. The concentrations of acid and alkali produced by electrolysis were determined by titration method, where the acidic solution was titrated with the standard NaOH titrant indicated with phenolphthalein, and the alkaline solution with the standard H_2SO_4 titrant indicated with methyl red.

Inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 8000, Perkin Elmer) was used to analyze the content of metal



Scheme 1 Diagram of all-metal recovery strategy for electrode materials of spent Ni-MH batteries

elements. 1.0 g of the specimen (the electrode materials or the filter residue after leaching) was dissolved in 15 mL of aqua regia, which was used for ICP-OES analysis.

3 Results and discussion

3.1 Electrolysis of Na_2SO_4 solution

The reaction agents used in the chemical recycling of spent Ni-MH batteries were prepared by the electrolysis of Na_2SO_4 solution in the home-made electrolytic cell and corresponding operating system (see Fig. S1), where H_2SO_4 was generated in the anode chamber with the evolution of oxygen, and NaOH was produced in the cathode chamber with the generation of hydrogen.

These gases are potentially applied in industry. Figure 1 displays the factors that influence the concentrations of acid (c_{H^+}) and alkali (c_{OH^-}) as well as current efficiency, including the concentration of Na_2SO_4 , electrolyte flow rate, current density, temperature, electrolytic time and volume of electrolyte. The optimized conditions were determined by these curves, where the Na_2SO_4 concentration was 1.5 mol/L, the electrolyte flow rate was 50–60 mL/min, the current density was 100 mA/cm², the electrolyte temperature was 55 °C, the electrolytic time was 3 h, and the volume of electrolyte was 200 mL. Under the optimized conditions, the c_{H^+} was determined as 0.82 mol/L with a current efficiency of 69.17%, and the c_{OH^-} was 0.87 mol/L with a current efficiency of 73.73%.

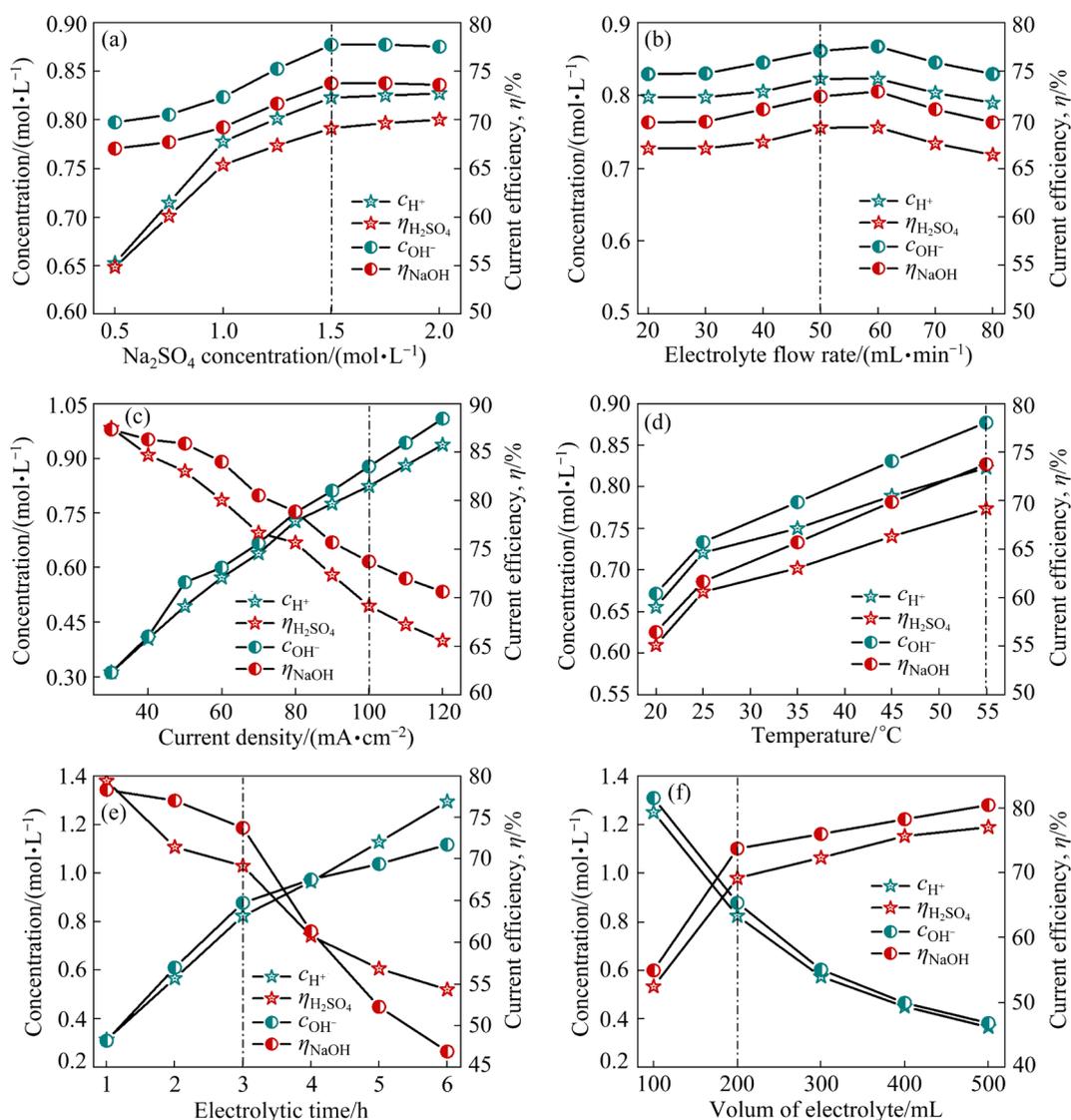


Fig. 1 Dependence of Na_2SO_4 concentration (a), electrolyte flow rate (b), current density (c), temperature (d), electrolytic time (e) and volume of electrolyte (f) on concentrations of acid (c_{H^+}) and alkali (c_{OH^-}) as well as current efficiency

3.2 Leaching of electrode materials

Table S1 shows the components in spent Ni-MH batteries, where the cathode and anode materials account for 28.78% and 34.22%, respectively. Table S2 further presents that the valuable elements of nickel, cobalt and rare earths occupy a mass fraction of up to 79.16% in the electrode material, highlighting the importance of resource recycling and economic gains of the process. Figure S2(a) illustrates the XRD analysis results of the electrode material, which is basically composed of $\text{Ni}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, MnAlO_4 , AlLaNi_4 , Ce_2Ni_7 , LaNi_5 , CeCo_3 , EuZn_5 and Co_2Eu , together with metallic Ni attributed to Ni foam fragments produced in battery disassembly.

In this study, a mild leaching condition ($\text{pH} \approx 0.1$) was adopted, where the electrolyzed H_2SO_4 solution ($c_{\text{H}^+} = 0.82 \text{ mol/L}$) was used with the addition of H_2O_2 solution. Considering the excellent solubility of rare earths and the tiny amount of Fe in the electrode materials (Table S2), the leaching efficiencies of Ni, Co, Zn, Al and Mn were

investigated at different values of H_2SO_4 dosage, temperature, leaching time and H_2O_2 dosage. The results are shown in Fig. 2. It is seen that the increase of H_2SO_4 dosage leads to the improvement of leaching efficiency (Fig. 2(a)). For example, the leaching efficiency of Ni increases from 72.7% to 94.82% as the H_2SO_4 dosage rises from 20 to 80 mL/g , and the leaching efficiency of Co simultaneously grows from 82.64% to 98.46%. Figure 2(b) illustrates that temperature plays an important role in leaching except for Zn, whose efficiency appears high enough at low temperature, in agreement with previous literature [28]. When the temperature reaches 90°C , the leaching efficiencies of Co, Al, Mn and Zn are all higher than 97%, but the efficiency of Ni is a bit low (about 92.1%). Figures 2(c) and (d) depict that the leaching efficiencies of Co, Al, Mn and Zn are all higher than 97% when the H_2O_2 dosage is higher than 4 mL/g and the leaching time is longer than 50 min. Thereby, the optimized conditions were settled, where the H_2SO_4 dosage was 60 mL/g , the

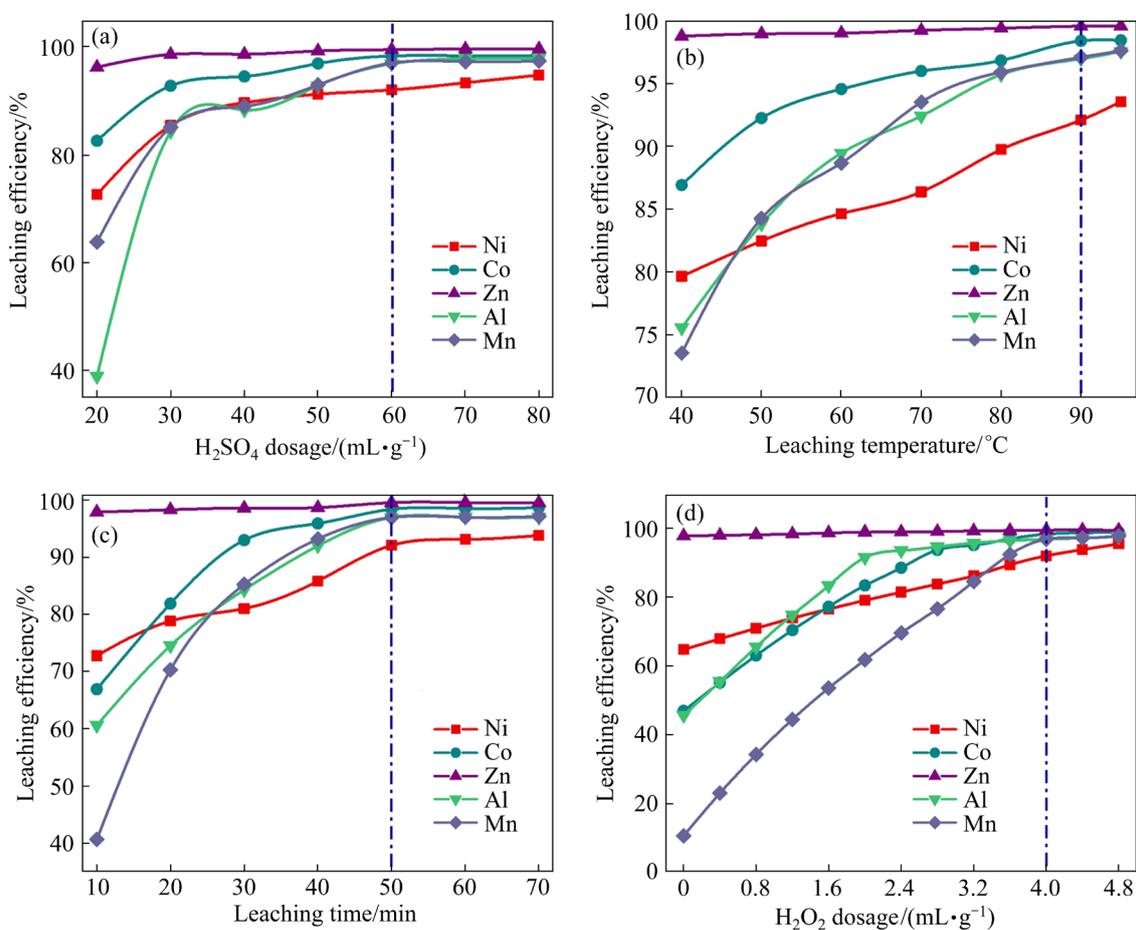


Fig. 2 Effects of H_2SO_4 dosage (a), leaching temperature (b), leaching time (c) and H_2O_2 dosage (d) on leaching efficiencies of Ni, Co, Zn, Al and Mn in electrode materials

H₂O₂ dosage was 4 mL/g, the temperature was 90 °C, and the leaching time was 50 min. The low leaching efficiency of Ni was caused by the partly dissolution of Ni foam fragments which were mixed with the electrode materials in battery dismantling, and the undissolved Ni was recovered with the separation of the rare earths.

3.3 Separation of rare earths

Rare earths could be precipitated as sodium double sulfate salts from the leaching solution at pH=1, which were neutralized with the electrolyzed NaOH and formed the RE(OH)₃ product. The corresponding reactions can be expressed as follows:

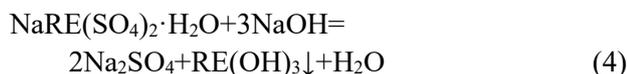
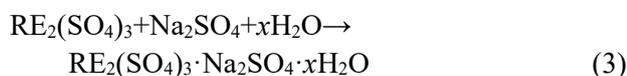


Figure 3(a) illustrates that temperature exerts little effect on the separation of La³⁺, Ce³⁺ and Eu³⁺. Therefore, the precipitation temperature remained the same as the leaching temperature at 90 °C, where more than 99% of La³⁺, Ce³⁺ and Eu³⁺ could be precipitated. Figure 3(b) illustrates that pH value has an important effect on the precipitation, where the recovery efficiencies decrease sharply when the pH is higher than 3. Figure 3(c) indicates that the precipitation of rare earths is a fast process. Therefore, the optimal conditions were set up according to the above results, where the electrolyte temperature was 90 °C, the pH value was 1.0, and the time of precipitation was 4 min. The recovery efficiencies of La, Ce and Eu elements were all over 99%.

It is worthy of mentioning that the undissolved Ni foam fragments mixed with the double sulfate salts of rare earths were successfully separated by magnetic selection. The inset of Fig. S2(b) displays the morphology of the separated Ni foam fragments, and the XRD pattern indicates that the solid is mainly Ni but with a small amount of Cu. When the part of recovered solid Ni is taken into account, the total recovery efficiency of Ni will also be higher than 97.5%.

Figure S3(a) displays the XRD pattern and SEM image (inset) of the double sulfate salts, which contain NaLa(SO₄)₂, NaCe(SO₄)₂ and NaEu(SO₄)₂ crystals. ICP-OES analysis results in

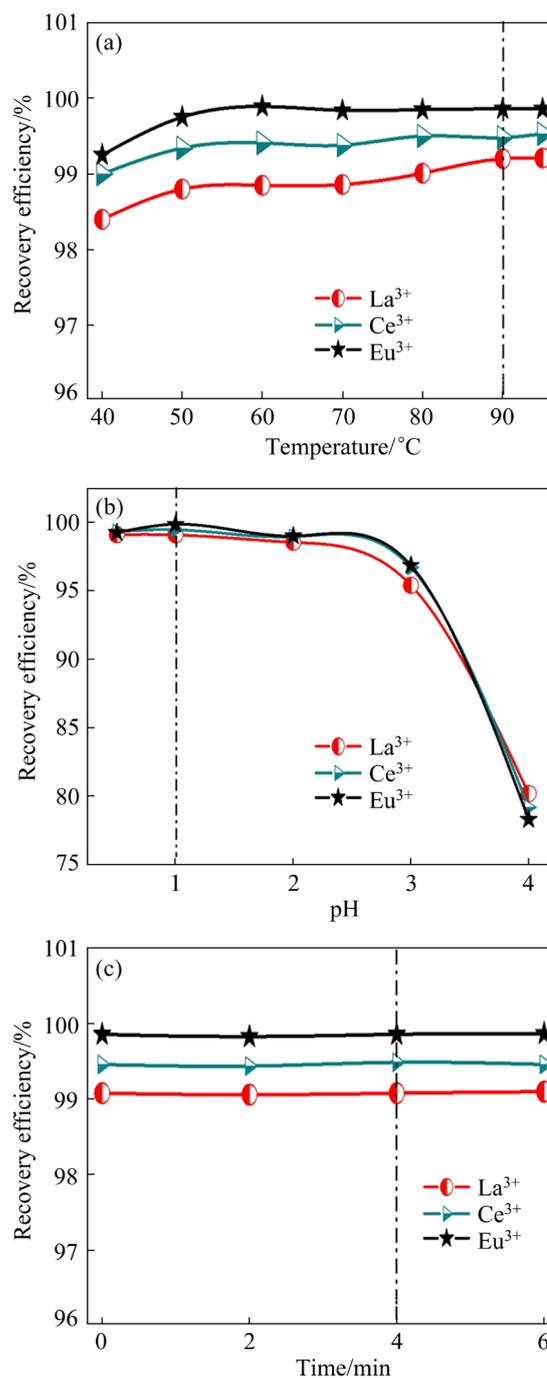


Fig. 3 Effects of temperature (a), pH value (b) and time (c) on recovery efficiency of rare earths

Table S3 further indicate that the recovered sodium sulfate double salts have a purity of 98.5%. The sodium sulfate double salts were then converted to yellowish rare earth hydroxides by reacting with the electrolyzed NaOH solution (0.87 mol/L), by which Na₂SO₄ was regenerated available for electrolysis. After rinsing with deionized water, XRD pattern and SEM image in Fig. S3(b) indicate that the RE(OH)₃ product contains La(OH)₃, Ce(OH)₃ and

La(OH)₃, with total content of La(OH)₃ and Ce(OH)₃ up to 99.4%.

3.4 Recovery of Ni and Co elements

The leaching solution was purified before the recovery of Ni and Co elements, in which Al³⁺, Fe³⁺, Zn²⁺ and Mn²⁺ were removed in sequence from the solution. The precipitation of Al³⁺ and Fe³⁺ was carried out by adjusting the pH value of the leaching solution. Figure 4(a) shows that the contents of Al³⁺ and Fe³⁺ in the leaching solution

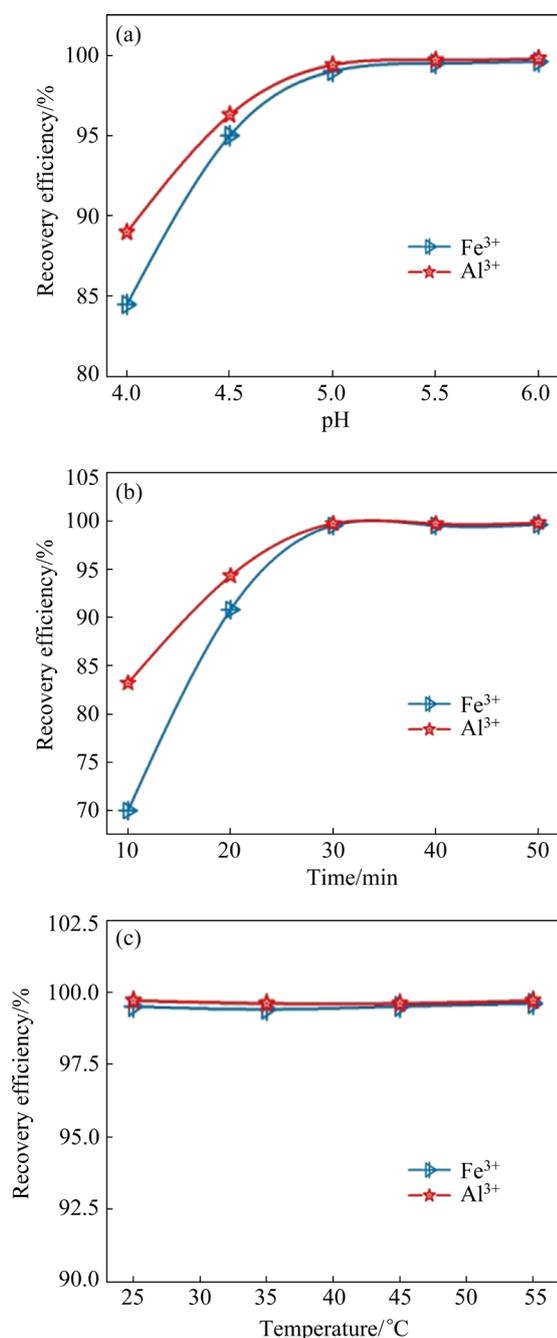


Fig. 4 Effects of pH (a), time (b) and temperature (c) on recovery efficiencies of Al³⁺ and Fe³⁺ from leachate

vary obvious from pH 4 to 5, where higher pH value is in favor of the precipitation. Figure 4(b) illustrates that the recovery efficiencies are also dependent on reaction time, which reach a plateau after 30 min. In comparison, Fig. 4(c) displays that the temperature has a weak influence on the precipitation of Al³⁺ and Fe³⁺. Therefore, the reaction was allowed to perform at 25 °C for 30 min with the pH value of 5.5, where more than 99% of Al³⁺ and Fe³⁺ were separated from the leaching solution. However, the ICP-OES analysis results in Table S4 indicate that the deposit not only has an Al and Fe hydroxides, but also contains a considerable amount of Ni, Co, Mn and Zn, and hence it has economic value for further treatment. Table S5 shows the concentrations of the leaching solution before and after removal of Al³⁺ and Fe³⁺, where the decrease of Ni²⁺, Co²⁺, Zn²⁺ and Mn²⁺ in the leaching solution also manifests the loss in the precipitation process.

Zn²⁺ and Mn²⁺ were extracted from the leaching solution with saponified D2EHPA-kerosene. The organic extractant was rinsed twice with 0.04 mol/L H₂SO₄ solution at an organic-to-aqueous (O/A) ratio of 5:1 (v/v), which was sent back to the raffinate solution to minimize the loss of Ni²⁺ and Co²⁺ in the extraction. Figure 5 illustrates the effects of pH value (Fig. 5(a)), D2EHPA concentration (Fig. 5(b)), saponification rate of extractant (Fig. 5(c)), O/A ratio v/v (Fig. 5(d)) and extraction time (Fig. 5(e)) on the separation of Zn²⁺ and Mn²⁺, from which the optimal extraction conditions were obtained as follows: 10% of D2EHPA, saponification rate of 65%, leaching solution pH value of 3.3, O/A ratio of 1:1 (v/v), and extraction time of 4 min. The extraction operation was repeated twice, and Table S6 demonstrated that nearly 100% of Zn²⁺ and 99.3% of Mn²⁺ were removed from the leaching solution (i.e. the raffinate solution), where the loss of Ni²⁺ and Co²⁺ in the extraction was only 0.3% and 2.5%, respectively. The extractant D2EHPA-kerosene was regenerated by rinsing with the electrolyzed H₂SO₄ solution ($c_{H^+}=0.82$ mol/L) at the O/A ratio of 5:1 (v/v), where Zn²⁺ and Mn²⁺ were transferred into the H₂SO₄ solution (Table S7) and were precipitated by neutralizing with the NaOH solution from electrolysis, leading to Zn and Mn hydroxides with a total content of 99% (Table S4). The resulted Na₂SO₄ in the process was returned for recycling.

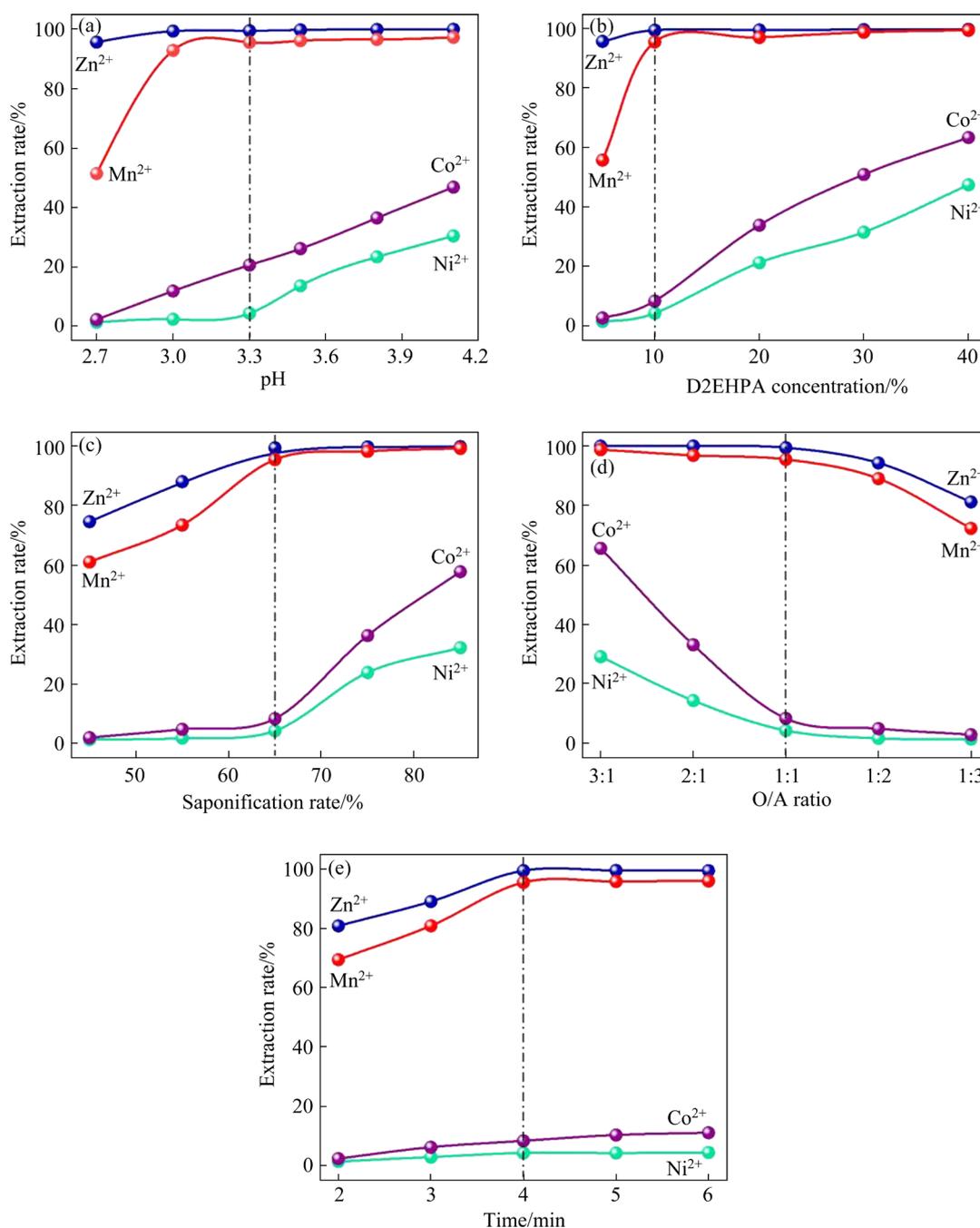


Fig. 5 Effects of pH value (a), D2EHPA concentration (b), saponification rate (c), O/A ratio (d) and time (e) on extraction rates of Zn²⁺, Mn²⁺, Co²⁺ and Ni²⁺

Cobalt and nickel hydroxides were then yielded in the form of a greenish-green precipitate by adjusting the purified leaching solution to pH 9.5 with NaOH. Figure S4(a) presents the EDS analysis data of the yielded precipitate, where the content of Ni is 29.25 at.%, and that of Co is just 1.43 at.%. Table S4 indicates that the nickel and cobalt hydroxides exhibit a total content of up to 99.9%, highlighting the effect of purification of the

leaching solution. XRD pattern (Fig. S4(b)) also indicates that the recovered precipitate contains Ni(OH)₂ and Co(OH)₂.

In this process, all the metals in the electrode materials of spent Ni-MH batteries were recovered. For the rare earth elements of La, Ce and Eu, the recovery efficiencies were 99.08%, 99.46% and 99.86%, respectively; for Ni and Co, the recovery efficiencies were 97.7% and 95.1%, respectively;

for Zn and Mn, the efficiencies were 96% and 97%, respectively; for Al and Fe, the efficiencies were 99.8% and 99.6%, respectively. Table S8 shows that the concentration of Na₂SO₄ is up to 206670 mg/L, followed by 95, 5 and 3.7 mg/L of Ni²⁺, Mn²⁺ and Co²⁺ in the recycled solution, respectively. It is estimated that about 97% of Na₂SO₄ was recycled for electrolysis when the volume of the recycled H₂SO₄ solution is considered. Therefore, the mild recovery strategy allows to recover all metal elements from the electrode materials of spent Ni-MH batteries in a closed-loop process at high recovery efficiencies, which only needs the chemicals of Na₂SO₄ and H₂O₂, and produces nearly zero solid waste and sewage with maximal output.

Table 1 lists the amounts and values of the recyclable materials from 1 t of spent Ni-MH batteries, including about 15.1 kg of plastics, 181 kg of steel, 364 kg of Ni, 18.9 kg of Co, 18.4 kg of Mn, 23 kg of Zn, 5.8 kg of Al, 80.4 kg of La, 17.5 kg of Ce and 5 kg of Eu. The metal prices came from CBC Metal Network, and the values of other materials were taken from China Reagent Network based on the exchange rate of RMB to USD on October 20, 2021. Recycling 1 t of spent Ni-MH batteries is estimated to make a value of US\$ 10933, in which the value of electrode materials accounts for about 98%, highlighting the importance of the recovery of electrode materials. On the other hand, Table 2 shows the consumptions and costs of power, chemicals and water in the recovery process, where 3340 kg of H₂O₂, 600 kg of sodium sulfate, 100 kg of extractant and 3000 kg of water are needed. In addition, the electricity for the entire Na₂SO₄ electrolysis and recycling process is calculated as 16535 kW·h. Therefore, the total cost of recycling 1 t of spent Ni-MH batteries is estimated to be US\$ 4674, where the cost of labor is not considered owing to the huge wage difference around the world. Therefore, recycling 1 t of spent Ni-MH batteries is expected to obtain an economic benefit of US\$ 6259. Besides, the closed-loop strategy avoids using strong acid and alkali with serious environmental impact, and saves the cost of wastewater treatment [29], and hence allows the green and sustainable process to be applied in the regions with strict environmental protection regulations.

Table 1 Estimated amounts and values of recycled materials in 1 t of spent Ni-MH batteries

Category	Plastic	Steel	Ni	Co	Mn
Amount/kg	15.1	181	364	18.9	18.4
Value/US\$	6.6	90	9093	1148	48
Category	Zn	Al	La	Ce	Eu
Amount/kg	23	5.8	80.4	17.5	5
Value/US\$	92	20	352	79	4.3

Table 2 Consumptions and costs for recycling 1 t of spent Ni-MH batteries

Consumption		Consumption amount/kg	Cost/US\$
Water		3000	188
Extractant		100	628
Power	Electrolysis	10675*	1216
	Others	5860*	782
Sodium sulfate		600	480
Hydrogen peroxide		3340	1380

* kW·h

4 Conclusions

(1) A novel strategy to recover all-metal elements from spent Ni-MH batteries was proposed based on the electrolysis of Na₂SO₄ solution, where 0.41 mol/L of H₂SO₄ and 0.87 mol/L of NaOH solutions were produced. Metal elements in the electrode materials were successfully leached by using the electrolyzed H₂SO₄ solution with the addition of H₂O₂, from which the rare earths of La, Ce and Eu were firstly precipitated at pH 1.0 in the form of sodium double sulfates, which were converted to hydroxides with a purity of 99.4%. The recovery efficiencies of La, Ce and Eu in the process were 99.08%, 99.46% and 99.86%, respectively.

(2) In the following purification steps, Al³⁺ and Fe³⁺ were removed at pH 5.5, leading to the byproduct of Al and Fe hydroxides together with considerable amounts of Ni, Co, Zn and Mn; Zn²⁺ and Mn²⁺ were extracted by sulfonated D2EHPA-kerosene, resulting in the byproduct of Zn and Mn hydroxides with a purity of 99.0% after the regeneration of the extractant. Ni²⁺ and Co²⁺ in the purified leaching solution were precipitated at pH 9.5, in the form of Co and Ni hydroxides with a

purity of 99.97%, and the total recovery rate in the process was 97.5%. It is estimated that the recycling can make an economic profit of US\$ 6259 with 1 t of spent Ni-MH batteries.

(3) Na₂SO₄ was recycled in the process and the recovery efficiency was accounted for up to 97%. The method allows to recover all-metal elements from the electrode materials of spent Ni-MH batteries in a mild and sustainable way at low cost, which brings about nearly zero solid waste and sewage.

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Supporting Information

Supporting Information in this paper can be found at: http://tnmsc.csu.edu.cn/download/21-p3860-2022-0634-Supporting_Information.pdf.

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基于硫酸钠溶液电解的废旧镍氢电池全金属回收

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摘 要: 提出废旧镍氢(Ni-MH)电池全金属可持续回收的方法, 分别用硫酸钠溶液电解获得的 H₂SO₄ 和 NaOH 溶液作为浸出剂和沉淀试剂。电极材料在温和条件下浸出, 超过 99% 的稀土元素在 pH 1.0 时以双硫酸盐的形式从溶液中沉淀, 进而通过与 NaOH 反应转化为氢氧化物。在后续浸出液的纯化过程中, Al³⁺和 Fe³⁺在 pH 5.5 时沉积, Zn²⁺和 Mn²⁺用皂化 D2EHPA-煤油从浸出液中萃取出来, 形成两种具有工业价值的氢氧化物副产品。Ni²⁺和 Co²⁺在 pH 9.5 时沉淀, 总回收率为 97.5%。Na₂SO₄ 的总回收率达 97%。这种金属回收方法可带来明显的经济效益, 且闭环处理过程中无固体或液体废弃物。

关键词: 废旧镍氢电池; 金属回收; 电解; 硫酸钠; 闭环过程

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