

Rare-Earth-Element Removal from Leaching Solution of Ni–MH Battery

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We developed a recycling process for spent Ni–MH batteries using hydrometallurgical treatment. In this process, impure rare-earth elements (REEs) are removed using sulfuric-acid double-salt precipitation and solvent extraction. In this paper, we describe the removal of yttrium among other REEs.

1. Introduction

Ni–MH batteries have been used in hybrid or electric vehicles. The electrode materials of Ni–MH batteries contain nickel, cobalt, and rare-earth elements (REEs). In the future, recovering these valuable metals will be necessary by recycling spent Ni–MH batteries. We developed a Ni–MH battery-recycling process. Electrode powder, which is a mixture of negative and positive electrodes, was leached using sulfuric acid. The leaching solution contained nickel, cobalt, and REEs. To obtain a pure nickel and cobalt aqueous solution, which is an intermediate product of nickel or cobalt, we need to remove the REEs. We developed the REE-removal process from a Ni–MH battery leaching solution using precipitation and solvent-extraction methods. In this process, light REEs (LREEs) such as cerium or lanthanum were removed from the leaching solution using double-sulfate precipitation. LREE sulfates form insoluble double sulfate with an alkali metal sulfate [1]. By taking advantage of this property, LREEs can be separated from the solution as a precipitate. A part of contained yttrium, which is one of the heavy REEs, was removed from the leaching solution by co-precipitation with the double sulfate of alkali metal and LREEs. The removal efficiency depended on the mixing conditions such as temperature, mixing time, concentration of alkali metal sulfate, and ratio of LREEs to yttrium [2]. The residual yttrium was removed via solvent extraction. We selected D2EHPA as the extractant of yttrium. D2EHPA has a high affinity with yttrium [3]. Therefore, extracting yttrium with high extraction efficiency under a low-pH condition was made possible. In this paper, we will mainly explain the yttrium-removal step.

2. Experimental

2.1 Leaching solution

A leaching solution of spent Ni–MH battery powder was prepared using atmospheric sulfuric-acid leaching. The initial slurry concentration during leaching was 100 g/L. The leaching temperature was 80 °C. The leaching pH was 1.0. Sulfuric acid was used to maintain the 1.0 pH during

leaching. The end point of the leaching process was determined by the increase in the oxidation-reduction potential. The vessel used in the laboratory test was a 1-L-size separable flask made of Pyrex. In the pilot-plant test, the vessel was a 500-L-size tank made of stainless steel coated with polytetrafluoroethylene (PTFE) inside. Impellers were used in both tests for stirring. The chemical compositions of the leaching solution were approximately 1.0 pH, 50 g-Ni/L, 5.5 g-Co/L, 0.7 g-Y/L, 5.0 g -Ce/L, and 10 g-La/L.

2.2 Reagents

The extractant used was D2EHPA (Lanxess Co., Ltd.). The diluent used was Teclean N20, which is a naphthenic solvent (JX Nippon Oil & Energy Co.). The used sulfuric acid, sodium hydroxide, and sodium sulfate were of reagent grade (Wako Pure Chemical Industries, Ltd.).

2.3 Precipitation

The precipitation test was carried out on a laboratory scale using beakers. The double-sulfate salt was precipitated by adding sodium sulfate powder to the leaching solution. Stirring was performed by the impeller made of PTFE. The temperature was controlled by a water bath in which a thermostat was installed. The solid and liquid were separated by a 5C filter made of cellulose fiber (Advantech Co., Ltd.). The metal concentrations of the test samples were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer Co., Ltd., Optima 3300 DV).

2.4 Solvent extraction

The aqueous phase for extraction was the solution obtained after the solid and liquid separation in the precipitation test. The aqueous phase for back extraction was prepared using sulfuric acid and pure water. The range of the sulfuric-acid concentration was 3–6 mol-H₂SO₄/L. The organic phase was D2EHPA diluted by Teclean N20. The D2EHPA concentrations were 20–50 vol%. The laboratory-scale batch tests of the extraction and back extraction were performed using beakers and separatory funnels. The continuous test was performed using 1-L small mixer settlers made of polypropylene. The metal concentrations of the test samples were analyzed by ICP-AES.

3. Results and Discussion

3.1 Precipitation

Most of the LREEs precipitated as insoluble double-sulfate salt under any condition. The lanthanum and cerium concentrations in the leaching solution were 0.02 g-La/L and 0.007 g-Ce/L, respectively, after the precipitation. The yttrium-removal efficiency depended on the mixing time, temperature, and concentration of the added Na₂SO₄. Figure 1 shows the relationship between the mixing time and residual yttrium concentration at each temperature when 90 g-Na₂SO₄/L was added. The yttrium concentration decreased as the mixing time increased. Under the same mixing time, the yttrium concentration decreased when the temperature was higher. Figure 2 shows the relationship between the Na₂SO₄ and residual yttrium concentrations. The yttrium concentration decreased as the Na₂SO₄ concentration increased. We selected the temperature of 80 °C, mixing time of 20 min or longer, and Na₂SO₄ concentration of 90 g-Na₂SO₄/L as the pilot-plant precipitation conditions. The yttrium concentrations were 0.011–0.015 g-Y/L in the laboratory test under these conditions. However, in the Ni–MH battery recycling pilot plant, the concentrations were 0.1–0.2 g-Y/L, which was

presumed to be caused by the different stirring and mixing conditions between the laboratory and pilot tests. We believe that this problem can be avoided by optimizing the stirring condition. However, because the high affinity between D2EHPA and yttrium is well known, we considered that removal of yttrium via solvent extraction using D2EHPA was more reliable than optimizing the stirring condition in the pilot plant. Therefore, we selected the solvent-extraction method using D2EHPA, which could reliably remove yttrium.

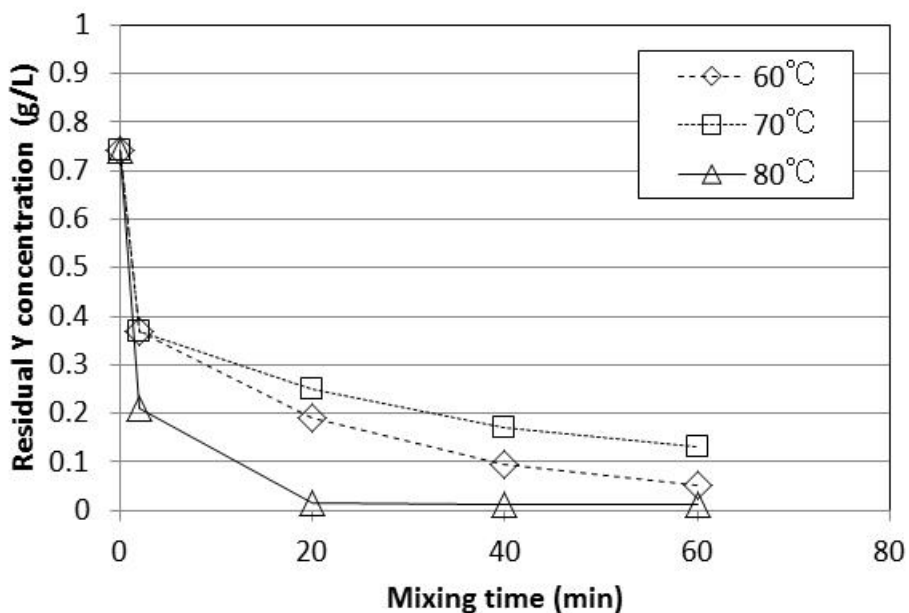


Figure 1. Relationship between the mixing time and residual yttrium concentration.

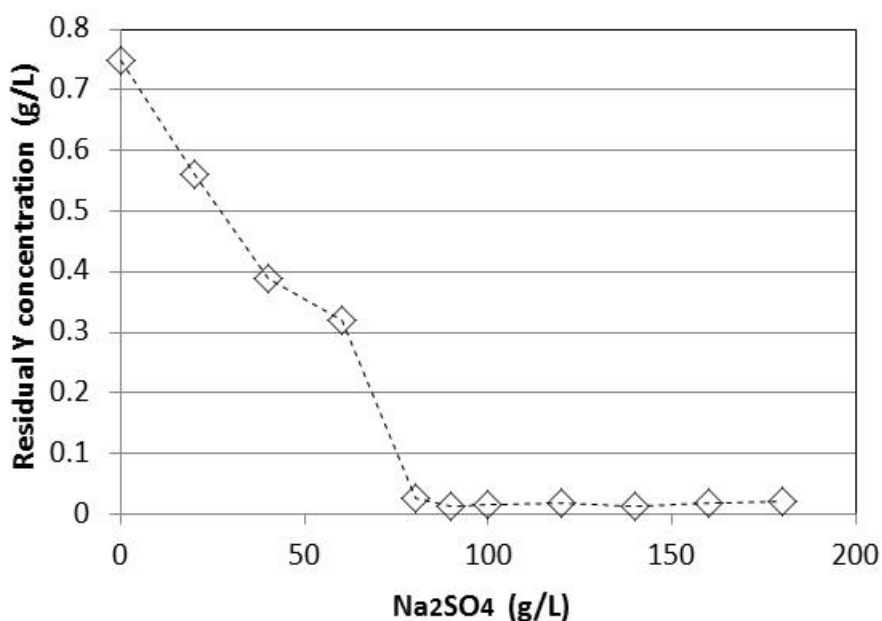


Figure 2. Relationship between the Na₂SO₄ and residual yttrium concentrations.

3.2 Solvent extraction

Figure 3 shows the yttrium-extraction isotherm. The D2EHPA concentration was 50 vol%, and the mixing time was 10 min. The pH was not adjusted in this test. The McCabe–Thiele diagram shows that if O/A is 0.013 or more, the yttrium concentration in the aqueous phase can be reduced from 0.2 to 0.01 g-Y/L or less via one-stage extraction. This result indicates that the D2EHPA has high affinity with yttrium. In the pilot-plant test, the D2EHPA concentration was set to 20 vol% to maintain lower viscosity in the organic phase. As a result of operating the mixer settler at O/A = 0.2, the yttrium concentration of the raffinate was reduced to 0.002 g-Y/L.

Figure 4 shows the relationship between the mixing time and back-extraction efficiency of Y. The D2EHPA concentration was 50 vol%, and the O/A was 0.03. The back-extraction efficiency of yttrium due to stirring and mixing for 15 min were 90% and 30% with 6 and 3 mol/L sulfuric acid, respectively. In the yttrium case, the equilibrium time of the back extraction was long. The back-extraction efficiency of yttrium increased with time in the 3 mol/L sulfuric acid. The higher the acid concentration was, the higher became the back-extraction efficiency. However, high acid concentration promotes extractant degradation and adversely affects the equipment. In the operation, we need to consider the optimization of sulfuric-acid concentration.

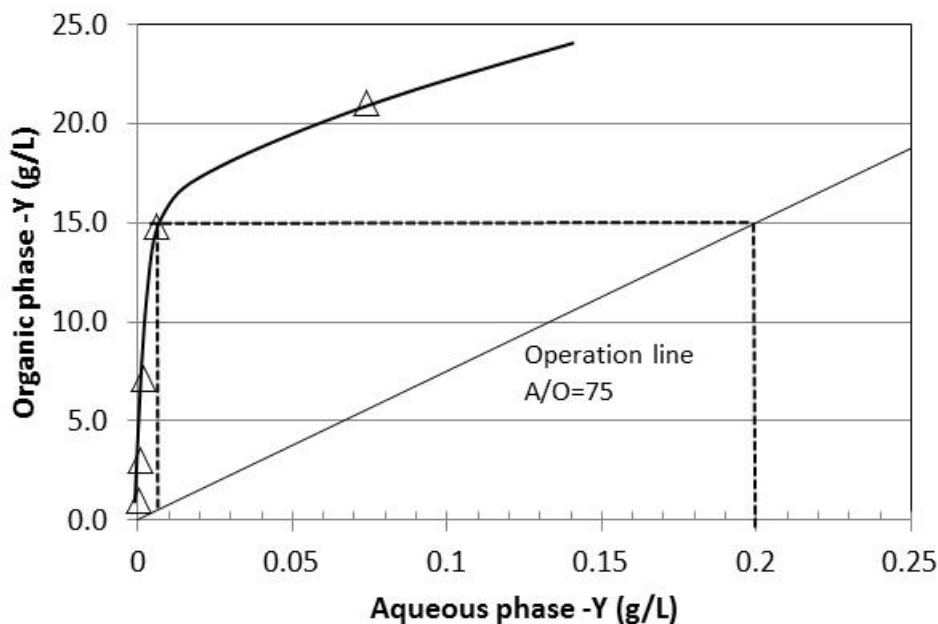


Figure 3. Yttrium-extraction isotherm.

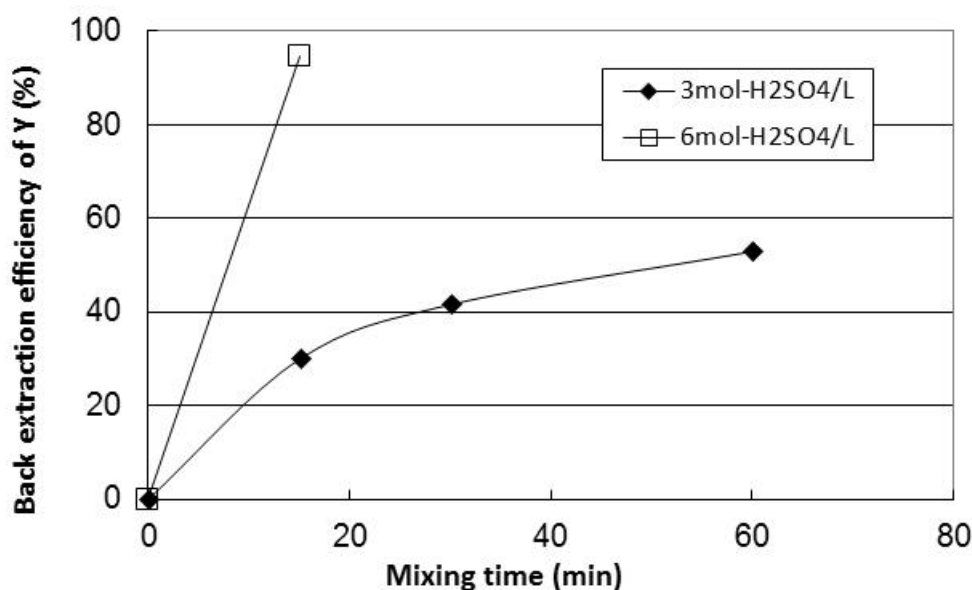


Figure 4. Relationship between mixing time and back-extraction efficiency of Y.

4. Conclusion

We have developed an REE-removal process from the leaching solution of Ni–MH battery electrode powder by combining double-sulfate precipitation and solvent extraction. LREEs such as cerium and lanthanum were removed from the leaching solution using double-sulfate precipitation. A part of yttrium was removed from the leaching solution by co-precipitation with double sulfate of alkali metal and LREEs. The residual yttrium was removed by solvent extraction using D2EHPA, which has high affinity with yttrium. Reducing yttrium in the leaching solution to 0.01 g-Y/L or less is possible. However, back extraction of yttrium from a loaded solvent is not easy. In the tests, we need to consider optimization of the sulfuric-acid concentration.

References

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