Preliminary Study on Separation of Dy and Nd by Multi-Step Extraction Using TDdDGA

Yuji SASAKI¹*, Yasutoshi BAN¹, Keisuke MORITA¹, Masahiko MATSUMIYA², Ryoma ONO³ and Hidenobu SHIROISHI³

¹Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan; ²Yokohama National University, 79-1 Tokiwadai, Yokohama 240-8501, Japan; ³National Institute of Technology, Tokyo College, Hachioji, Tokyo 193-0997, Japan

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Mutual separation technique of Dy and Nd in Nd magnets is studied. Dy is more valuable than Nd, and therefore, Dy should be isolated and reused. Lanthanide elements can be extracted thoroughly by using diglycolamide (DGA) extractants, and we use this reagent to recover and isolate Dy. N,N,N',N'-Tetradodecyl-DGA (TDdDGA) has a relatively high separation factor (SF) between Dy and Nd (SF: over 10) in the HNO₃ extraction system, so multi-step extraction using TDdDGA is applied to mutually separate them. In the present study, by using the condition, four extraction steps, organic phase: 0.1 M TDdDGA in n-dodecane, aqueous phase: 0.3 M HNO₃, 92 % Dy can be recovered with 0.7 % co-extraction of Nd.

1. Introduction

Neodymium-based permanent magnets (NdFeB) are used in various industrial products, such as hard-disks, hybrid cars, and cellular phones. To maintain the coercivity of such magnets, less than 10 % Dy is introduced into their components. Lanthanide elements are valuable, so a few methods to recover Nd and Dy from scrapped products have been proposed [1-4]. The amounts of Nd and Dy in the Earth’s crust are 20.8 and 3.94 ppm, respectively, Dy is rarer than Nd [5]. Therefore, it is desirable that Dy be recovered and recycled. To this end, we propose a hydrometallurgical technique for the mutual separation of Dy and Nd.

Lanthanide elements can be extracted easily by DGA compounds. This compound is widely available in the atomic energy field, because the gasification by heating after use and no production of the secondary waste can be expected. In addition, the separation factors between them are expected to be high [6-8]. Although TODGA has been applied to extract these metal ions thus far, this method co-extracts the ions, as opposed to separating them [9].

We intend to separate Dy from Nd by using multi-step extraction with a DGA compound. Multi-step extraction is used widely in the industry to treat huge volumes of aqueous solutions. The technique has an advantage to set-up different step numbers of organic phases from aqueous one, then various conditions of step numbers of extraction-reverse extraction can be prepared. We conduct a preliminary study on the multi-step extraction method using batch method for application to mutual separation of Dy and Nd.
2. Experimental

2.1 Reagents

TDdDGA ($N,N,N',N'$-Tetradodecyl-diglycolamide) was obtained from Wako Pure Chemical Industries. TDdDGA is known to have high lanthanide loading capacity [10]. Extractants with >98% purity were used for solvent extraction without further purification. Standard metal solutions with 1000 ppm concentration (Wako Pure Chemical Industries) were used for solvent extraction. Other reagents, for example, $n$-dodecane, nitric acid, Nd$_2$O$_3$, and Dy$_2$O$_3$ were of analytical grade.

2.2 Batch extraction method

TDdDGA was dissolved in $n$-dodecane, and Nd$_2$O$_3$ and Dy$_2$O$_3$ were dissolved in nitric acid at ambient temperature to the suitable concentrations. Each metal in the standard solution was evaporated, and the residues were dissolved in HNO$_3$ of a suitable concentration. The organic and aqueous phases were mixed and mechanically shaken at 1500 strokes/min for 30 min at 25 ± 0.1 °C. After centrifugation, the metal concentrations in the aliquots taken from the aqueous phases were measured by ICP-OES (SPS3100, Seiko Instruments Inc.) or ICP-MS (SPQ 9000, Seiko-EG&G). The metal concentrations in the organic phases were obtained by subtracting the aqueous concentration from the initial concentration. Alternatively, an aliquot of the organic phase was decomposed in HNO$_3$-HClO$_4$, and the residue was dissolved in 0.5 M HNO$_3$ prior to elemental analysis. The $D$ value was defined as the ratio of [M] in the organic phase to the [M] in the aqueous phase.

2.3 Multi-step extraction method

Three multi-step extraction methods were employed:

(1) One aqueous phase containing 28 mM Nd and 5 mM Dy was contacted sequentially with five samples of organic phases. The volumes of the aqueous and the organic phases were the same, and the condition, 28 mM Nd and 5 mM Dy, is employed for one of the references for sample solutions. After the first extraction, the organic phase was removed and a fresh sample of the organic phase was added to the aqueous phase, followed by shaking (second step). The sample of the organic phase was stored and subjected to elemental analysis. The procedure was repeated four times. The concentrations of Nd and Dy in aliquots of each phase were measured.

(2) One aqueous phase sample containing 28 mM Nd and 5 mM Dy and four other steps of the aqueous phase without metal, as well as an organic phase, were employed. After the aqueous phase containing 28 mM Nd and 5 mM Dy was mixed with the organic phase and shaken (first step). The aqueous phase was removed, and a fresh aqueous phase sample without metals was added to the organic phase, followed by shaking (second step). The used aqueous phase sample was stored and subject to elemental analysis. This procedure was repeated four times. The concentrations of Nd and Dy in the aqueous and organic phases were measured.

(3) An aqueous phase sample containing 28 mM Nd and 5 mM Dy and an organic phase sample were mixed and shaken (first step). The organic phase was removed and contacted into a fresh aqueous phase and shaken (second step). The procedures were repeated three times. This method can never simulate completely a continuous counter-current extraction process using mixer-settler equipment, because the organic phase can not attain the steady state of a flow-system, but nevertheless is a useful method to define the feasibility of separating two metals having the similar chemical behavior. Schematic diagrams of these methods are summarized in Figure 1.
3. Results and Discussion

3.1 Lanthanides extraction by TDdDGA

To establish suitable conditions for multi-step extraction, a batch experiment was performed using TDdDGA. With an organic phase consisting of 0.1 M TDdDGA/n-dodecane, experiments were conducted using various HNO$_3$ concentrations ranging from 0.3 M to 0.7 M. The results in Figure 2 indicate that $D$(Ln) increases gradually with the HNO$_3$ concentration. In terms of the condition of multi-step extraction, the $D$ values should be > 1 for Dy and < 1 for Nd. Figure 2 shows that for 0.1 M TDdDGA/n-dodecane and 0.3–0.4 M HNO$_3$ provides the best separation of Nd and Dy. In these experiments, the values of $D$ for Nd and Dy were set to 0.207 and 3.67 for 0.3 M HNO$_3$ and 0.257 and 10.4 for 0.4 M HNO$_3$.

3.2 Nd and Dy extractions using method (1) and (2)

Batch experiments based on extraction methods (1) and (2), shown in Figure 1, were conducted to obtain basic results of the multi-step extraction of Nd and Dy. These are plotted in Figure 3, where the x-axis represents the number of extraction steps and the y-axis represents integration of extraction (Figure 3(a)) and stripping (Figure 3(b)) percentages after each extraction step. From Figure 3(a), 99.8 % of Dy can be extracted in three extractions steps with 32 % co-extraction of Nd. All of the Nd can be stripped in four-steps with co-stripping of 61 % of Dy (Figure 3(b)). On this basis, it is predicted that at least four stages of extraction are required for high recovery of Dy and low co-extraction of Nd. In addition, it is clear that methods (1) and (2) can hardly separate Dy from Nd using solo extraction and back-extraction step.
3.3 Mutual separation of Dy from Nd by method (3)

Four-step extraction was performed under the same conditions as those in Figure 3. Figure 4 shows the experimental and calculated results for these extractions. Here, the Excel calculation was performed using $D(M)$ values, then substituting the metal concentrations in each aqueous and organic phase. Figure 4(a) and (b) represent the corresponding percentage of M concentration compared with the initial one for the

Figure 4. Multi-step extractions of Dy and Nd using 0.1 M TDDGA/ n-dodecane and 0.3 M HNO$_3$.
(a): Extraction (%) of Nd and Dy in organic phase at each step
(b): Rest (%) of Nd and Dy in aqueous phase at each step
Exp.: experimental results, Cal.: calculation
experimental and calculated values in the organic and aqueous phases at each extraction step. The experimental and calculated Nd and Dy concentrations in both phases show similar trends (Figure 4), which indicates that this calculation can be used to predict metal recovery using the multi-step extraction method. There are some differences between experimental and calculated values. In order to obtain more precise prediction, the experimental condition of method (3) should be re-investigated. The total recoveries in this work of Dy and Nd in the organic phase reach 92.0 and 0.7 %, and those in the aqueous phase 13.8 and 92.1 %. These results suggest that the best recovery of Dy and separation from Nd are obtained by method (3) rather than by methods (1) and (2).

4. Summary

This paper describes a preliminary study of the separation of Dy and Nd using multi-step extraction method. Our fundamental experiments indicate that four-step extraction leads to adequately high separation between Nd and Dy when using a DGA extractant. Using 0.1 M TDdDGA/n-dodecane in a four-step extraction gives a Dy recovery ratio of 92 % with 0.7 % co-extraction Nd from an aqueous feed containing 0.3 M HNO₃. This method has advantage to set up variable numbers of aqueous and organic phases. Better conditions for multi-step extraction could be determined by means of the calculation scheme proposed herein in order to achieve high Dy recovery with low levels of Nd contamination. In addition, the extraction behavior of these metals obtained by calculation using D values gives similar trends due to the experimental results, in order to reduce the difference between the two results, improvement of experimental method will be undertaken in the near future.

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