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Study on separation of Eu(II) from trivalent rare earths via electro-reduction and ion exchange

Ludek Jelinek*, Yuezhou Wei, Tsuyoshi Arai, Mikio Kumagai

Institute of Research and Innovation (IRI), 1201 Takada, Kashiwa 277-0861, Japan

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Abstract

Separation of Eu(II) from trivalent rare earths was carried out in 0.01 mol dm^{-3} hydrochloric acid medium. Eu(III) was selectively reduced to Eu(II) at glassy carbon cathode in flow type electrolyzer. For Eu(II) separation strong acid cation exchanger based on sulfonated polystyrene/DVB copolymer impregnated into porous silica beads was used. Breakthrough and chromatography curves were measured. Eu(II) exhibited lower affinity towards the sorbent than trivalent rare earths and therefore it was the first species to breakthrough the column. Excellent separation from middle rare earths was achieved while the separation from heavy rare earths was difficult. The back-oxidation of Eu(II) was a problem despite all the measures that were taken to prevent oxidation by dissolved oxygen and photo-oxidation.

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1. Introduction

Mutual separation of rare earths (RE) is complicated because of their similar chemical properties. They basically exist in aqueous solution in stable trivalent state. Separation of Eu(III) from middle RE fraction (Sm, Eu, Gd, Tb) by solvent extraction is complicated process [1]. However, in contrast to other rare earths, Eu(III) can be relatively easily reduced to divalent state ($E^0 = -0.43$ V). Chemical reduction of Eu(III) with zinc powder followed by Eu(II) sulfate precipitation [2] is preferred way of Eu separation at an industrial scale. However, the presence of zinc would complicate Eu(II) separation by means of ion exchange or solvent extraction. Also, the precipitation is generally inefficient separation process. In this case, electro-reduction in hydrochloric acid media is a better alternative. It has been thoroughly studied at different cathode materials including platinum [3], titanium [4] graphite [5–7] and glassy-carbon [8,9]. At carbon electrodes, Eu(III) reduction proceeds selectively [6] at potentials of −0.6 to −0.8 V (versus Ag/AgCl). Aquated monochloro Eu(III) species are involved in the rate determining step [10] in spite of their low stability [11]. The optimal conditions for reduction are limited not only by potential but also by pH. At pH 3 and above, precipitation of Eu(III) was observed. Therefore, it is necessary to maintain the proper pH of catholyte because pH can be shifted by hydrogen evolution reaction. Hydrogen evolution overpotential at glassy carbon fibers decreases with increasing acidity of solution [12]. Thus, at lower pH hydrogen evolution prevails over Eu(III) reduction.

The number of papers on Eu(II) separation by other processes than sulfate precipitation is so far very limited. Electro-reductive stripping of Eu(III) from loaded extractants (DP-18 and D2EHPE) and its recovery as Eu(II) sulfate was investigated [3]. Apart from solution chemistry, there is the method of Uda et al. [13] based on selective reduction and vacuum distillation of rare earths tri-halides/di-halides mixture. Though, this method has been originally applied to Sm and Nd.

In this work, separation of Eu(II) from RE(III) was investigated by means of electro-reduction of Eu(III) to Eu(II) at glassy carbon cathode in hydrochloric acid media and subsequent cation exchange separation.

2. Experimental

Electro-reduction of Eu(III) was carried out in a flow type electrolyzer, described previously in Ref. [14], at three-dimensional cathode made of glassy-carbon fibers in potentiostatic mode (−800 mV versus Ag/AgCl). Overall experimental setup is shown in Fig. 1. Potential was kept by potentio/galvanostat (HA-520G, Hokuto Denki). Concentration of Eu(II) was measured on-line by diode array UV–vis spectrophotometer (MD-2015 Plus, Jasco) equipped with a flow cell (path length = 1 cm). Flow rate in this branch was 7.5 cm^3 min^{-1}. In the studied concentration range 0.5–2.5 mmol dm^{-3} of Eu the wavelength 320 nm

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* Corresponding author. Tel.: +81 4 7144 8815; fax: +81 4 7144 7602.
E-mail address: ludek@iri.or.jp (L. Jelinek).

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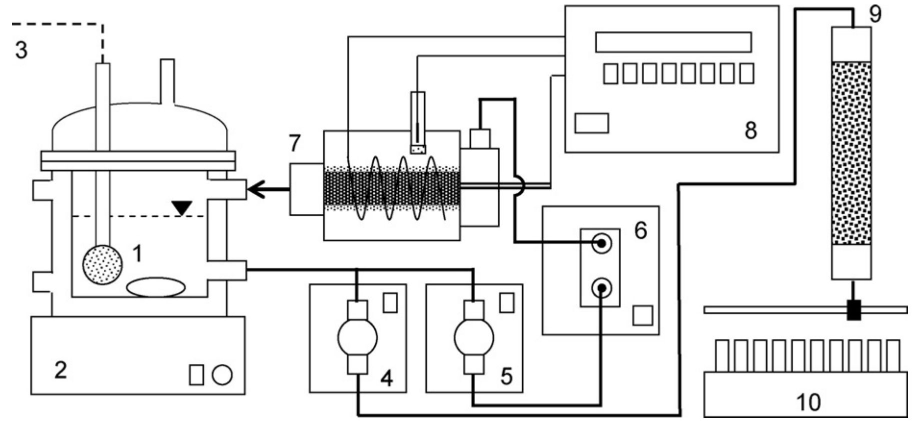

Fig. 1. Experimental setup: (1) catholyte storage, (2) magnetic stirrer, (3) argon supply, (4) column pump, (5) circulating pump, (6) UV–vis spectrometer, (7) flow-type electrolyzer, (8) potentiostat, (9) column and (10) fraction collector.

was selected, in accordance with our previous study [9], for the measurement of Eu(II) concentration. All experiments were carried out under protective Ar atmosphere to prevent back-oxidation of Eu(II) to Eu(III). Argon (Ar) gas was bubbled to the stirred stock solution container before and during the electrolysis at a flow rate of 250 cm^3 min^{-1}. For the ion exchange separation a special sorbent based on polystyrene/DVB copolymer (30 wt.%) impregnated into porous (porosity 0.69, pore diameter 600 nm) silica beads (70 wt.%) of uniform particle size (37–74 μm) was used. Strong acid cation exchanger (denoted as SiSCE) was previously prepared by its sulfonation (total capacity 4 mequiv. g^{-1}-resin). The silica support provides good mechanical strength, fast kinetics and small pressure drop across the column. Sorption was carried out in a closed system directly connected to the electro-reduction system. The column of inner diameter 8 mm and bed height 100 mm (bed volume 5.3 cm^3) was used. Flow rate was maintained at 1.1 cm^3 min^{-1} (12 BV h^{-1}). Concentration of metals was measured by ICP-OES.

3. Results and discussion

In preliminary experiments, electro-reduction of Eu(III) was carried out. At glassy carbon cathode, two-step reduction of dissolved oxygen ((1) and (2)) [15] proceeds preferably to the Eu reduction (3). The extent of hydrogen evolution reaction (4) depends on solution pH.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E^0 = 0.68\,V \tag{1}$$

$$H_2O_2 + 2H^+ 2e^- \rightarrow 2H_2O \quad E^0 = 1.77\,V \tag{2}$$

$$Eu^{3+} + e^- \rightarrow Eu^{2+} \quad E^0 = -0.43\,V \tag{3}$$

$$2H^+ + 2e^- \rightarrow H_2 \quad E^0 = 0.00\,V \tag{4}$$

It was found that at pH 2 (0.01 mol dm^{-3} HCl) and potential of glassy carbon cathode −800 mV versus Ag/AgCl, Eu(III) reduction proceeds steadily without any visible hydrogen evolution. In 0.1 mol dm^{-3} HCl, hydrogen evolution was clearly visible and current efficiency of Eu(III) reduction was greatly lowered. Also, with decreasing pH, UV absorbance of Eu(II) steeply decreased making its determination difficult [9]. There was no adverse effect of accompanying RE(III) on Eu(II) reduction. The typical course of electro-reduction for RE(III) solution is shown in Fig. 2. The current efficiency is relatively low because of the initial presence of dissolved oxygen and possible re-oxidation of Eu(II) during the process.

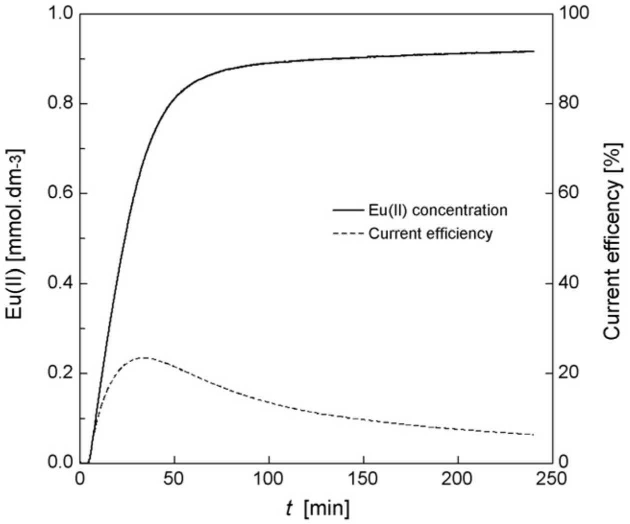

Fig. 2. The course of Eu(III) electro-reduction in the 1 mmol dm^{-3} rare earths mixture.

Breakthrough curves were measured at column packed with SiSCI for RE(III) mixture before and after electro-reduction (Fig. 3). It can be seen that the affinity of Eu(II) towards strong acid cation exchanger is lower than that of Re(III). Eu(II) was the first species to breakthrough the column. There was also visible Eu peak at the point where Eu(III) broke through in the case of solution before reduction. It was caused by re-oxidation of Eu(II). It can be probably suppressed by shortening the contact time by means of increasing the flow rate. Complete separation of Eu(II) from its adjacent middle RE (Sm, Gd) was achieved. Separation of Eu(II) from heavy RE should be improved by further optimization of ion exchange process. The separation of Eu(II)/RE(III) can be further improved by optimization of column geometry and flow rate.

Although the promising results of breakthrough tests, chromatographic separation was not successful. Despite all the measures taken to remove all the dissolved oxygen, it was impossible to keep Eu in the reduced form throughout the course of the experiment. Apart from oxidation by dissolved oxygen (5),

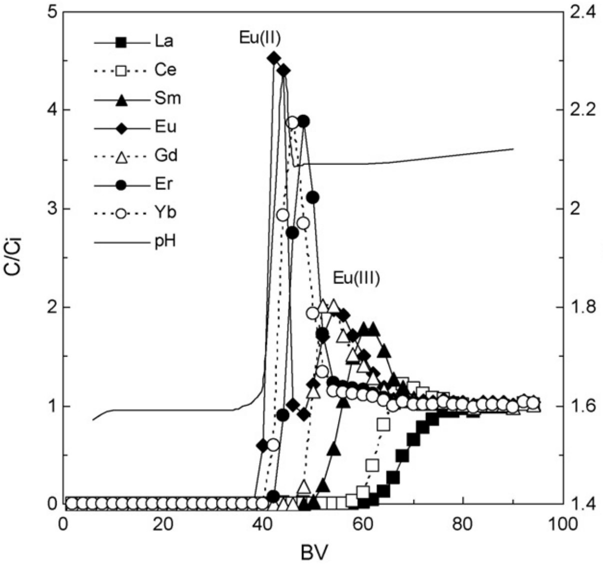

Fig. 3. Breakthrough curves during the sorption of reduced 1 mmol dm^{-3} rare earths mixture.

photo-oxidation (6) of Eu(II) may take place in aqueous solution.

$$Eu^{2+} + H^{+} + \frac{1}{4}O_2 \rightarrow Eu^{3+} + \frac{1}{2}H_2O \quad (5)$$

$$Eu^{2+} + H_2O \xrightarrow{h\nu} Eu^{3+} + H^{\bullet} + OH^{-} \quad (6)$$

Thus, in contrast to break through experiment, no Eu(II) peak was observed in chromatogram. Application of ascorbic acid as a stabilizing agent did not cause any visible effect. In further attempt the experiment was carried in darkness to suppress photo-oxidation (6) but no substantial improvement was achieved so far.

4. Conclusions

Eu(II) exhibited lower affinity towards the cation exchanger than trivalent rare earths. Complete separation of Eu(II) from its adjacent middle RE (Sm, Gd) was achieved. Separation of Eu(II) from heavy RE should be improved by further optimization of ion exchange process. The change of oxidation state in combination with ion exchange is a promising way for Eu separation from RE and especially middle RE for the applications where high Eu purity is needed. However, back-oxidation of Eu(II) is a problem that imposes serious limitations to the available separation techniques.

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