SEPARATION OF EUROPIUM FROM SAMARIUM AND GADOLINIUM BY COMBINATION OF PHOTOCHEMICAL REDUCTION AND SOLVENT EXTRACTION

TAKAYUKI HIRAI*, NAOHISA ONOE
AND ISAO KOMASAWA

Department of Chemical Engineering, Osaka University, Toyonaka, Osaka 560

The separation of Eu from Sm and Gd by a combination of photochemical reduction and solvent extraction was investigated. A low-pressure mercury lamp having emission peaks of 184.9 nm and 253.7 nm was used as a light source. The trivalent Eu was reduced to the divalent state by photoreduction in $(NH_4)_2SO_4$ aqueous solution containing $SmCl_3$, $EuCl_3$, $GdCl_3$ and scavenger (2-propanol or isopropyl formate) to make $EuSO_4$ precipitate selectively. The purity of Eu in the precipitate was more than 97%. The photoreductive stripping of Eu was studied by using a two-compartment cell separated by a sintered glass filter. In a two-phase system consisting of bis(2-ethylhexyl)phosphoric acid (D2EHPA)/xylene containing the three elements and $(NH_4)_2SO_4$ aqueous solution, Eu^{3+} was reduced in the aqueous phase using isopropyl formate as scavenger, and $EuSO_4$ precipitated selectively. The recovery of Eu as $EuSO_4$ from the organic solution containing equal amounts of the three elements was dependent on the aqueous-phase pH and reached 68% at pH 0.4. The purity of Eu in the precipitate was more than 95%.

Introduction

In the previous work[10], the separation of Eu from Sm and Gd by using electrochemical reduction was investigated. Trivalent Eu was reduced to the divalent state by using a titanium plate electrode on which $EuSO_4$ precipitated selectively. In the two-phase system, Eu^{3+} was reduced at the aqueous phase/electrode interface and $EuSO_4$ precipitated selectively in the aqueous phase.

Photochemical reduction of lanthanide and actinide has been studied by several investigators. Donohue reported that the trivalent Eu was reduced to the divalent state by using a low-pressure mercury lamp or an ArF excimer laser in aqueous solutions, and the reduced Eu was precipitated as $EuSO_4$[4-6]. The scheme of photoreduction of Eu and the photochemical separation factors for Eu in lanthanide mixtures were shown, but fundamental information such as the effect of irradiation time on the precipitation was not given. In alcoholic media, γ-ray[11] or high-pressure mercury lamp[14] were also usable for the photoreduction of Eu^{3+}. Purification of the rare-earth elements using lasers as light source was summarized by Donohue[5]. Photoreduction of uranyl nitrate[3, 15], plutonium[2] and neptunium[7, 8, 16] was also investigated with aim of applying the techniques in nuclear fuel reprocessing[1, 9]. In the case of pentavalent vanadium, photochemical reduction to the tetravalent state was possible by using an argon laser in aqueous perchloric acid solutions[12]. These photoreduction methods need no reduction agent and are therefore free from contamina-

tion. They are also easy to operate and may show high selectivity for the reduction if an appropriate wavelength is chosen.

In this work, the separation of Eu from Sm and Gd by a combination of photochemical reduction and solvent extraction has been investigated. The separation of one of these three elements from the others is known to be difficult by traditional solvent extraction processes. A low-pressure mercury lamp was used as a light source. Photochemical reduction of Eu^{3+} to Eu^{2+} in $(NH_4)_2SO_4$ aqueous solution to make $EuSO_4$ precipitate was studied, using two types of scavengers such as 2-propanol and isopropyl formate. Photoreductive stripping of Eu in a two-phase system consisting of bis(2-ethylhexyl)phosphoric acid (D2EHPA)/xylene and $(NH_4)_2SO_4$ aqueous solutions was also studied, using a two-compartment photochemical cell separated by a sintered glass filter.

1. Experimental

The preparation of $SmCl_3$, $EuCl_3$ and $GdCl_3$ and extraction of the metals by 0.2 mol/*l* D2EHPA diluted with xylene were carried out as described in the previous paper[10]. The concentrations of Sm, Eu and Gd in the resulting organic phase were ca. 4.3×10^{-3} mol/*l*.

The photochemical reduction of Eu was carried out by using a 20 W low-pressure mercury lamp (Eikohsha), which had emission peaks of 184.9 nm and 253.7 nm. When only the 253.7 nm line was required, the 184.9 nm line was cut off with a filter. To determine the elements
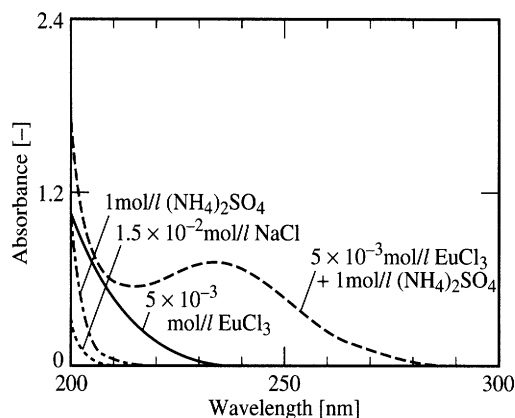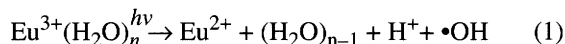
Fig. 1 Absorption spectra of aqueous solutions

remaining in the organic phase after photoreductive stripping, the organic solution was stripped with 6 mol/l HCl solution. The concentration of the elements in the aqueous solution was determined by use of an inductively coupled argon plasma emission spectrophotometer (Nippon Jarrell-Ash ICAP-575 Mark II). The absorption spectra of the aqueous and organic solutions containing Eu^{3+} were measured with an UV-vis spectrophotometer (Shimadzu UV-265FW).
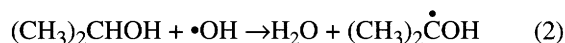
2. Results and Discussion

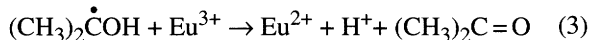### 2.1 Photochemical reduction of Eu in aqueous solution

The photochemical reduction of Eu^{3+} in aqueous solution is reported to proceed as shown in Eq. (1), where (H_2O) is a coordinated water[4-6].

$$Eu^{3+}(H_2O)_n \xrightarrow{h\nu} Eu^{2+} + (H_2O)_{n-1} + H^+ + \bullet OH \quad (1)$$

The radical ($\bullet OH$) must be scavenged to prevent the reverse reaction, i.e., the oxidation of Eu^{2+}. An alcohol such as 2-propanol or an ester such as isopropyl formate scavenges the radical effectively[4].

$$(CH_3)_2CHOH + \bullet OH \rightarrow H_2O + (CH_3)_2\overset{\bullet}{C}OH \quad (2)$$

The organic radical formed can reduce Eu^{3+}.

$$(CH_3)_2\overset{\bullet}{C}OH + Eu^{3+} \rightarrow Eu^{2+} + H^+ + (CH_3)_2C=O \quad (3)$$

In this study, isopropyl formate or 2-propanol was used as the scavenger. Since Eu^{2+} is not stable in aqueous solution, it must be removed as precipitate immediately. Ammonium sulfate was used as a precipitation agent to make $EuSO_4$, as in the case of electroreduction[10].

Figure 1 shows the absorption spectra of aqueous solutions containing $EuCl_3$. It is known that the charge-transfer band from H_2O to Eu^{3+} appears at 188 nm.[4, 13] In the solution containing Eu^{3+} and SO_4^{2-}, an absorption band around the wavelength of 235 nm also appeared, and corresponded to the charge-transfer band from SO_4^{2-} to Eu^{3+}[4, 6]. This suggests that a longer-wavelength light as well as a shorter-wavelength light may be employed for the photoreduction. The solutions containing SO_4^{2-} and Cl^- also show absorption bands in the deep UV
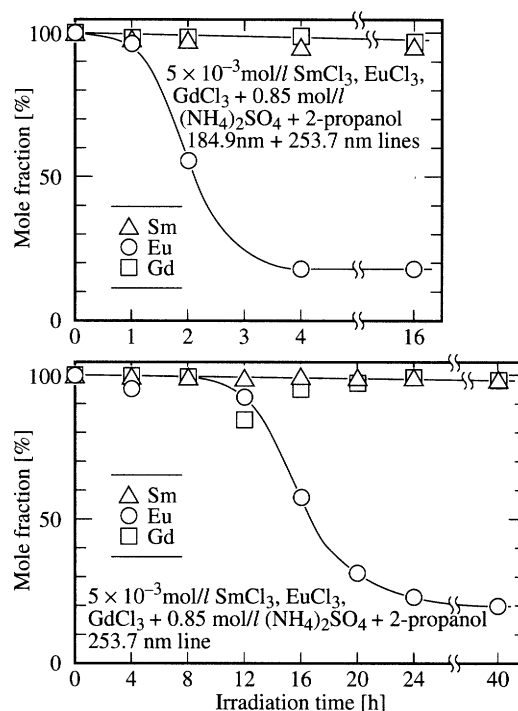

Fig. 2 Relationship between irradiation time and mole fractions of rare-earth elements in $(NH_4)_2SO_4$ aqueous solution using 2-propanol as scavenger
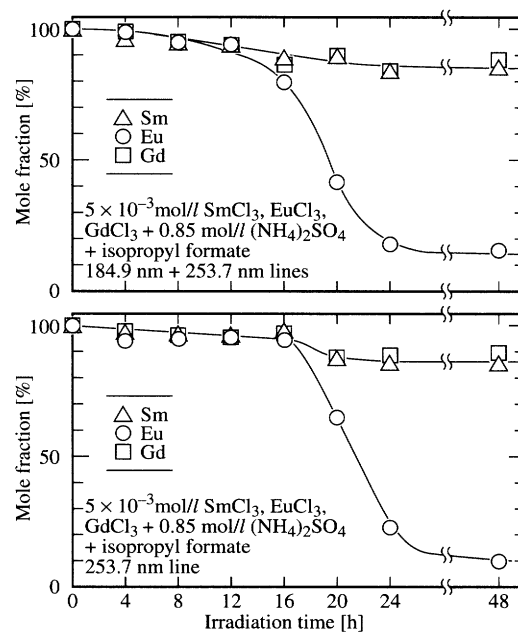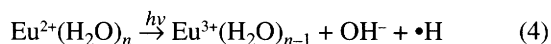

Fig. 3 Relationship between irradiation time and mole fractions of rare-earth elements in $(NH_4)_2SO_4$ aqueous solution using isopropyl formate as scavenger

region. These anions may be reduced by the 184.9 nm line ($SO_4^{2-} \rightarrow SO_4^- + e^-$, $2Cl^- \rightarrow Cl_2^- + e^-$) and the electron may reduce Eu^{3+}.

The photochemical reduction of Eu in aqueous solution was carried out in a beaker-type glass bottle with agitation at 800 minutes^{-1} by a magnetic stirrer. The relationships between irradiation time and mole fractions

of Sm, Eu and Gd in 0.85 mol/l $(NH_4)_2SO_4$ aqueous solution are shown in **Figs. 2 and 3** for the cases using 2-propanol and isopropyl formate respectively as the scavenger. The feed amounts of the elements are set as 100%. The aqueous solution and scavenger were 15 ml and 3 ml, respectively. The concentration of Eu decreased by photolysis, while those of Sm and Gd were almost constant, indicating that Eu precipitated selectively as $EuSO_4$. Precipitation did not occur when no scavenger was added. The recovery of Eu as $EuSO_4$ precipitate reached 80 to 90%. Complete precipitation was not achieved, since the photooxidation of Eu^{2+} shown in Eq. (4) might occur under the present condition. Actually, the reduced Eu^{2+} solution is reported to have a strong absorption at around 250 nm, which corresponds to the f–d band[5, 6].

$$Eu^{2+}(H_2O)_n \xrightarrow{h\nu} Eu^{3+}(H_2O)_{n-1} + OH^- + \bullet H \qquad (4)$$

The white precipitate obtained was separated by centrifuge and was dissolved in concentrated HNO_3 to measure the metal concentrations. The purity of Eu in the precipitate was more than 97% in all cases, which was comparable to that obtained by the electroreduction method.[10] In the case where 2-propanol was employed, the precipitation occurred in a shorter time (80% of the feed Eu precipitated in 4 hours) than in the case of isopropyl formate, since 2-propanol is water-soluble and scavenges the OH radical effectively. When the 184.9 nm line was cut off, a longer irradiation time was needed for the photoreduction of Eu^{3+}. Induction periods of ca. 1 and 10 hours, seen in Fig. 2, may be caused by the slow precipitation rate. On the other hand, when isopropyl formate was used as the scavenger, precipitation of $EuSO_4$ hardly occurred in the first 12 hours since the solubility of isopropyl formate in the aqueous phase was small. Almost no difference was seen between the case of using both the 184.9 nm and 253.7 nm lines and that where the 253.7 nm line alone was used, when isopropyl formate was employed. In the case where the concentration of the rare-earth chlorides was 1×10^{-2} mol/l, precipitation of $EuSO_4$ took a longer time than in the case of 5×10^{-3} mol/l. In this case, 70% of the feed Eu precipitated in 28 hours.

2.2 Photo-reductive stripping of Eu

Figure 4 shows the absorption spectra of the metal-loaded and non-loaded D2EHPA/xylene solutions. No absorption band corresponding to the charge-transfer is seen. The photoreduction of Eu seems to occur only when the coordinated water and scavenger are located near the Eu^{3+} ion, and it does not occur in the organic phase. Therefore, Eu^{3+} must be reduced in the aqueous phase after the mass transfer of Eu from the organic phase into the aqueous phase. An aqueous solution of pH < 2.5 must be used as in the case of electro-reductive stripping in the D2EHPA system[10]. When water-soluble scavengers such as ethanol, 1-butanol, 2-propanol, 3-pentanol, ammonium sulfite and formic acid were used, an undesirable white precipitate containing Sm, Eu and Gd was obtained when the organic and aqueous solu-
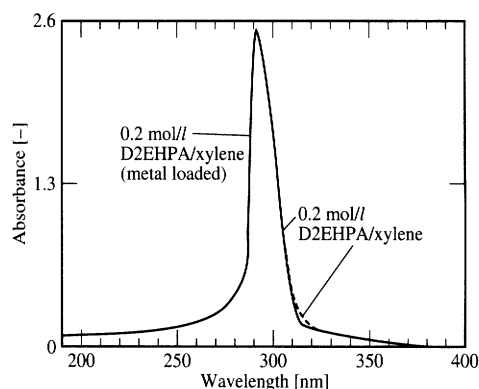

Fig. 4 Absorption spectra of metal-loaded and non-loaded D2EHPA/xylene solutions
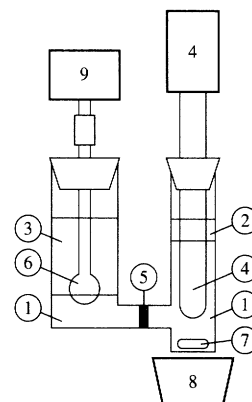

Fig. 5 Two-compartment photochemical cell for reductive stripping of Eu. 1: Aqueous solution (22 ml); 2: Isopropyl formate (3 ml); 3: Organic phase (25 ml); 4: Low-pressure mercury lamp; 5: Sintered glass filter; 6: Agitator; 7: Stirring bar; 8: Magnetic stirrer; 9: Stirring motor
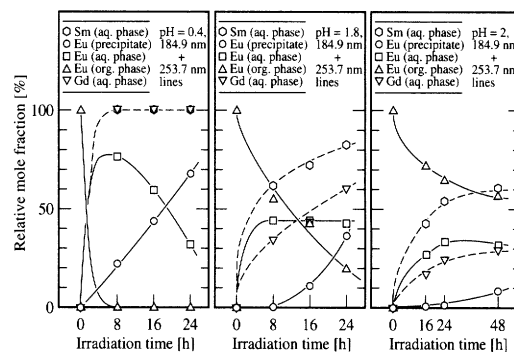

Fig. 6 Effect of irradiation time on stripping yield of Sm and Gd and precipitation of $EuSO_4$ at various final pH values

tions were mixed. When isopropyl formate was employed, no such undesirable precipitates were observed. However, when the two phases were mixed in a beaker-type glass bottle, isopropyl formate hardly worked as a scavenger, since the solubility was much oriented to the organic phase. This indicates that isopropyl formate must be separated from the organic phase.

Figure 5 shows a two-compartment photochemical cell separated by a sintered glass filter (#3, 1 mm thick) used for the photoreductive stripping. The metal-loaded organic solution (25 ml), aqueous solution (1 mol/l H$_2$SO$_4$–(NH$_4$)$_2$SO$_4$, 22 ml) and scavenger (isopropyl formate, 3 ml) were agitated and photolyzed at room temperature. The agitation speed of both the agitator and the magnetic stirrer was 800 minutes^{-1}.

The effect of irradiation time on the stripping yields of Sm and Gd and on the precipitation of EuSO$_4$ is shown in **Fig. 6**, where the feed amounts of the elements in the organic phase are taken as 100%. The pH values in the figure are the aqueous-phase final pH. The fraction of Eu in the precipitate was calculated by mass balance. The purity of Eu in the precipitate was more than 95% in all cases. The separation factors (= ([Eu]$_p$/[Ln]$_p$)/([Eu]$_f$/[Ln]$_f$) where Ln is Sm or Gd), ß$_{Eu/Sm}$ and ß$_{Eu/Gd}$, were 27.3 and 95.5 respectively. These are comparable to those obtained by the electroreduction method.[10] The recovery of Eu as EuSO$_4$ reached 68% at pH 0.4.

In the case of 24 hours irradiation at pH 1.8, the fractions of EuSO$_4$ and Eu^{3+} in the aqueous phase were 42.7% and 36.7% respectively, and the stripping percentage was the sum of them, 79.4%. This is greater than the stripping percentage obtained without irradiation (72.9%). This indicates that photoreduction can enhance the stripping of Eu. A better result is expected from use of a more powerful light source or by improvement of the equipment. The stripping of Sm and Gd decreases with increasing pH. The selective recovery of Eu as the EuSO$_4$ precipitate is therefore plausible, leaving Sm and Gd in the organic phase. However, it seems to be difficult to retain all of the Sm and Gd in the organic phase because of the very similar stripping performances of the three elements, as encountered previously with electroreductive stripping[10].

Conclusion

The separation of Eu from Sm and Gd by a combination of photochemical reduction and solvent extraction techniques was investigated, with the following results.

1) The trivalent Eu was reduced to the divalent state by UV light irradiation with a low-pressure mercury lamp. In (NH$_4$)$_2$SO$_4$ aqueous solution containing equal amounts of SmCl$_3$, EuCl$_3$, GdCl$_3$ and scavenger (2-propanol or isopropyl formate), EuSO$_4$ precipitated selectively by photoreduction. The purity of Eu in the precipitate was more than 97%.

2) In the two-phase system consisting of bis(2-eth-ylhexyl)phosphoric acid (D2EHPA)/xylene containing the three elements and (NH$_4$)$_2$SO$_4$ aqueous solution containing isopropyl formate as scavenger, Eu^{3+} was reduced in the aqueous phase, resulting in selective precipitation of EuSO$_4$. The recovery of Eu as EuSO$_4$ from an organic solution containing equal amounts of the three elements was dependent on the aqueous-phase pH, and reached 68% at pH 0.4. The purity of Eu in the precipitate was more than 95%.

Nomenclature

Ln	= rare-earth element	
ß	= separation factor	[–]
[ ]	= concentration of species in brackets	[mol/l]

<Subscripts>

f	= feed (input) value
p	= precipitate

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