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A Study on the Photo-reductive Precipitation Rate of Europium Sulfate from Rare Earth Mixture by Addition of Hydrogen Peroxide

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Abstract–The influence of H_2O_2 on the photo-reductive precipitation of Eu^{3+} from a solution containing Sm^{3+}, Eu^{3+} and Gd^{3+} was investigated. The solution contains isopropanol as a reduction agent, ammonium sulfate as a precipitation agent, and hydrogen peroxide as an acceleration agent of precipitation rate. A mercury lamp emitting a wavelength of 254 nm was used as a light source. Adding a small amount of H_2O_2 considerably increased the photo-reductive precipitation rate of Eu^{3+}. OH radicals obtained from the photodecomposition of H_2O_2 oxidized isopropanol into the radical $(CH_3)_2C^{\cdot}OH$ and the resulting radicals reduced Eu^{3+} rapidly. It was found that the organic radical has the ability to reduce only Eu^{3+} in the solution containing Sm^{3+}, Eu^{3+} and Gd^{3+}. The precipitation yields of Eu, Sm and Gd were about 99%, 10% and 4%, respectively. It was also found that the Sm and Gd were not photo-reduced and co-precipitated with Eu.

Key words: H_2O_2, Photodecomposition, Isopropanol, Eu, Radical

INTRODUCTION

Rare earth elements have been widely used in various industrial fields such as optics, metallurgy, electronic and magnetic areas, catalysts and nuclear energy [Kirk and Othmer, 1980]. Due to such importance, many efforts for the individual separation of the rare earth elements have been also carried out.

Recently, in the nuclear field, the minor actinides (Am, Cm, Np), classified to be long-lived nuclides, were partitioned from HLLW (high-level radioactive liquid waste) either by solvent extraction [Lee et al., 2001; Oh et al., 1985] or by precipitation [Kim et al., 1995] to be transmuted in transmutation systems such as an accelerated driven reactor or a fast reactor [OECD/NEA Room Document, 1999]. At this time, the rare earth elements (La, Eu, Sm, Gd, Nd, etc.) were extracted together and some middle rare earths (Sm, Eu, Gd) were finally co-stripped into the aqueous solution [Morita et al., 1995]. Middle rare earth elements, having a large cross section area on neutrons, should be removed from the solution for the effective transmutation of minor actinides.

Since the separation factor of Eu is lowest in rare earth elements during solvent extraction and stripping, it is important to ultimately remove Eu in aspects of neutron economics. Trivalent Eu^{3+} is known to be the most reducible to the divalent form in the rare earth elements. Since the reduced Eu^{2+} is different from Eu^{3+} in chemical behavior, Eu^{2+} can be easily separated from the trivalent rare earth elements either by solvent extraction or by ion exchange.

Several methods [Peppard et al., 1962; Hirai and Konasawa, 1992] were introduced for the reduction of Eu: electrolysis, reduction with zinc powder, etc. Although they have been applied to commercial plants, these methods have some problems such as the use of large amounts of chemicals and difficulty in operation. Another method, the photochemical method, is also available [Donohue, 1977; Qiu et al., 1991; Hirai et al., 1993; Hirai and Komasawa, 1995; Selin et al., 1989]. The photochemical method has some advantages; for example, photons can be used as chemical reagents and this method may also show high selectivity for the reduction if an appropriate wavelength is chosen. Donohue [1977] first reported the possibility of separating some elements of the lanthanide and the actinide by photochemical reaction. Qiu et al. [1991] studied the photoreduction of Eu from the Sm, Eu and Gd concentrate in a mixed alcohol (ethanol and isopropanol) system by using a high-pressure mercury lamp as a light source. Hirai et al. [1993, 1995] presented the photoreduction of Eu^{3+} from a mixture containing Sm, Eu and Gd in the aqueous phase including chloride ions and the organic phase using bi (2-ethylhexyl) phosphoric acid/xylene. Selin et al. [1989] reported that γ-irradiation with ^{60}Co could be applied to reduce Eu^{3+} to Eu^{2+} in an aqueous solution of a mixture of rare earth elements. Through these studies, fundamental information such as the effect of irradiation type, time, the light wavelength and the reduction agent on the photoreduction of Eu were revealed. However, information on the photoreduction rate of Eu was not available yet.

In this work, the effect of H_2O_2 on the reductive precipitation rate of Eu and its behavior were examined, when separating Eu^{3+} as $EuSO_4$ from Sm^{3+} and Gd^{3+} by photoreductive precipitation. This study was focused on the separation of Eu from the rare earths mixture to acquire basic data for the further purification of a solution containing minor actinides.

EXPERIMENTAL

A mixed solution including Eu, Sm and Gd was used for photoreductive precipitation of Eu. Isopropanol, ammonium sulfate and hydrogen peroxide were used as a reductive agent, a precipitation agent and a precipitation rate agent, respectively. Eu, Sm and Gd were used in the form of chloride salts supplied from Aldrich Co. Other chemicals such as isopropanol, ammonium sulfate and hydrogen peroxide were supplied from Merck Co. In all experiments, the

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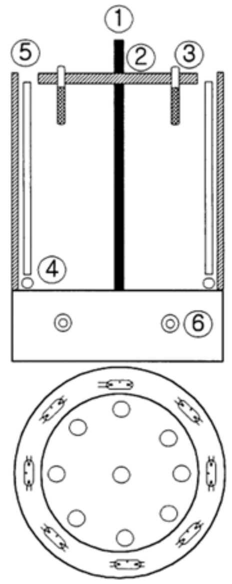

Fig. 1. Schematic diagram of the photoreactor.
1. Vertical supporter
2. Horizontal acrylic supporter
3. Sample tube
4. Aeration port
5. Hg-Lamp
6. Power generator

concentrations of Eu, Sm and Gd were fixed as 0.01 M, respectively. The concentrations of ammonium sulfate and isopropanol were 0.1 M and 2 M, each. The concentration of hydrogen peroxide ranged from 0 M to 2 M.

The equipment used for the photo reductive precipitation of Eu was supplied from Rayonet Co (Model: RPR-208). It consists of an Hg-lamp with 120 W, emitting a wavelength of 254 nm. A schematic diagram of the experimental equipment is shown in Fig. 1. The photo reactor is a cylinder-type 40 cm in diameter and 60 cm in height. Eight mercury lamps are located at the circumference of the reactor, from which UV light travels in the direction of the core of the reactor. The material of the reaction tube is quartz and its capacity is 15 ml. As seen in Fig. 1, the reaction tubes are located on the circumference of the circular-type horizontal supporter, which is made of acrylic resin and is designed so that the eight reaction tubes can run simultaneously. In order to control the temperature of the reaction tubes during irradiation of UV on the reacting solution, air-circulation ports are installed at the bottom of the reactor for air-cooling. However, during UV irradiation, the temperature of the working solution was increased from room temperature (19±2 °C) to 41±2 °C within 30 min and then was kept stable at all times during the photolysis. Since it was not easy to cool the photo reactor to room temperature, all the experiments were carried out at approximately 41 °C. When the temperature of the solution approached about 41 °C and became stable, the tubes containing the working solutions were placed into the photoreactor. The amount of working volume used in all experiments was 10 ml. A sample of 100 μl was taken to determine the precipitation yield of Eu in the solution during photolysis.

The concentration of the elements (Eu, Sm and Gd) in the aqueous solution was determined by an inductively coupled plasma atomic emission spectrophotometer (ISA Jobin-Yvon JY 50P). The absorption spectra of the aqueous solutions containing Eu, Sm and Gd were measured with a UV-vis spectrophotometer (Shimadzu UV-160 A). The hydrogen peroxide concentration was measured by reflectometry (Reflectoquant, Merck).

RESULTS AND DISCUSSION

Fig. 2 shows the result of the photo-reductive precipitation of Eu, Sm and Gd in the solution. As seen in Fig. 2, the precipitation yield of europium increased during photolysis and reached about 95% after a photolysis time of 8 hours, while both Sm and Gd were hardly precipitated. This can be easily understood from the fact that

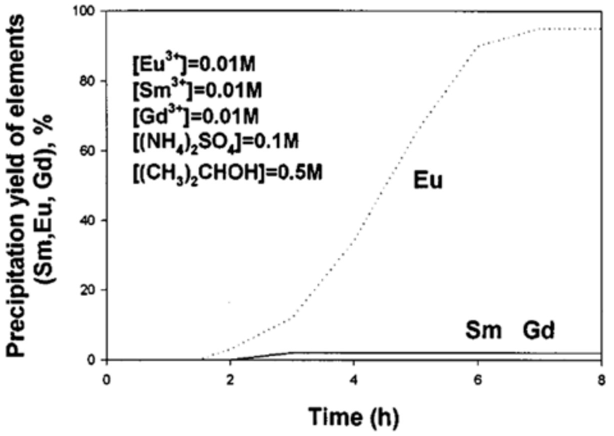

Fig. 2. Photoreductive precipitation of Eu, Sm and Gd elements.

Table 1. Redox potential values E°(III/II) of the lanthanides calculated by Nugent et al.

Element	Value [V]	Element	Value [V]
La	−3.1±0.2	Gd	−3.9±0.2
Ce	−3.2±0.2	Tb	−3.7±0.2
Pr	−2.7±0.2	Dy	−2.6±0.2
Nd	−2.6±0.2	Ho	−2.9±0.2
Pm	−2.6±0.2	Er	−3.1±0.2
Sm	−1.6±0.2	Tm	−2.3±0.2
Eu	−0.3±0.2	Yb	−1.1±0.2

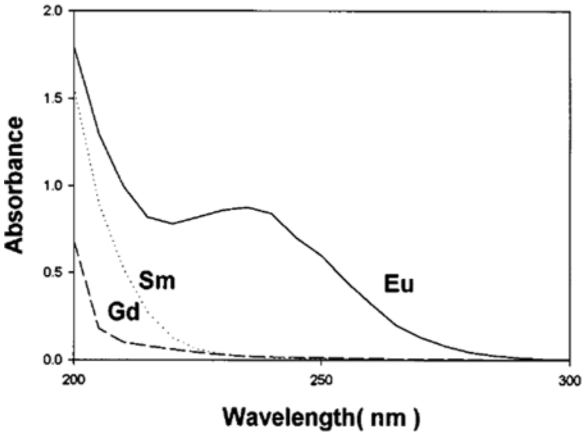

Fig. 3. UV spectrums of Eu, Sm and Gd chlorides in an ammonium sulfate solution.

the reductive potential of Eu^{3+} is the highest of the rare earth elements as shown in Table 1 [Nugent et al., 1973], and also from the results of the absorption spectra of each single element (Eu, Sm, Gd)-containing solutions as shown in Fig. 3. It was observed that Eu^{3+} ions absorbed light of around 250 nm, whereas both Sm^{3+} and Gd^{3+} ions did not absorb that of around 250 nm at all. Since the light source used in this work emits light around 254 nm, only Eu^{3+} can be excited. Therefore, Eu could be selectively separated from both Sm and Gd.

Generally, the photo-reductive mechanism of Eu^{3+} into Eu^{2+} was known as follows [Donohue, 1977; Qiu et al., 1991; Hirai et al., 1993; Hirai and Komasawa, 1995]:

$$Eu^{3+}+H_2O+hv=Eu^{2+}+H^{+}+OH \qquad (1)$$

$$(CH_3)_2CHOH+OH=H_2O+(CH_3)_2C^{\cdot}OH \qquad (2)$$

$$(CH_3)_2C^{\cdot}OH+Eu^{3+}=Eu^{2+}+H^{+}+(CH_3)_2C=O \qquad (3)$$

$$Eu^{2+}+SO_4^{2-}=EuSO_4 \qquad (4)$$

Donohus [1977] reported that the charge transfer band from H_2O to Eu^{3+} appears at 188 nm and that from SO_4^{2-} to Eu^{3+} appears at 235 nm in the solution containing Eu^{3+} and SO_4^{2-}. This agrees with this work as seen in Fig. 3. Donohus [1977] also reported that the radicals (OH) formed in the primary process (1) should be scavenged with isopropanol to prevent the reverse reaction, i.e., the oxidation of Eu^{2+}. The resulting organic radicals $(CH_3)_2C^{\cdot}OH$ can cause further reduction of Eu^{3+}, and then Eu^{2+} combines with SO_4^{2-} to be removed from the solution as a precipitate.

From the above mechanism, we can enhance the precipitation rate of Eu. This mechanism indicates that if the concentration of OH radicals increases during photolysis, the reduction rate of Eu^{3+} will also increase. In order to verify this, a small amount of H_2O_2 was added to the solution before photolysis was begun. It is well known that H_2O_2 is dissociated into OH radicals under the irradiation of light with a wavelength of less than 300 nm. The experimental result is given in Fig. 4. As expected, the precipitation rate of europium ions considerably increased as compared to those in the solution without H_2O_2. The precipitation was initiated in 10 min and almost terminated within 1 hour after irradiation of UV. It was considered that the reductive precipitation rate was accelerated by the formation of relatively large amounts of organic radicals $(CH_3)_2C^{\cdot}OH$ which are produced through Eq. (2) by adding small amounts of H_2O_2. Fig. 5 shows the relation of the added amounts of H_2O_2 and the initial precipitation time of the reduced Eu^{2+}. Surprisingly, it was confirmed that the initial precipitation time was longer as the added amounts of H_2O_2 increased. With the experimental condition in this work, the minimal initial precipitation time was found at an H_2O_2 concentration of 0.05 M in the solution. This implies that an excess of H_2O_2 can oxidize the reduced Eu^{2+} and subsequently prevent the formation of the reduced Eu^{2+}. In fact, H_2O_2 and OH radicals have high oxidation potentials. The values are known to be 1.77 V [Kotrly and Sucha, 1985] and 2.72 V [Sawyer, 1989], respectively. These potential values can sufficiently oxidize Eu^{2+} into Eu^{3+}. Based on this fact, the oxidation mechanism of Eu^{2+} in the presence of H_2O_2 and OH radicals can be proposed. In the case of OH radicals, the possibility of oxidation through Eq. (1) was already given. In other words, the OH radicals produced during photolysis of H_2O_2 react not only with isopropanol but with Eu^{2+} as seen in Eqs. (1) and (2). Therefore, the increased OH radicals during photolysis sufficiently oxidized Eu^{2+}. In the case of H_2O_2, an oxidation of Eu^{2+} can be expressed as follows:

Potential (V)

$$2Eu^{2+}+H_2O_2+2H^{+}=2Eu^{3+}+2H_2O \qquad +2.12 \qquad (5)$$

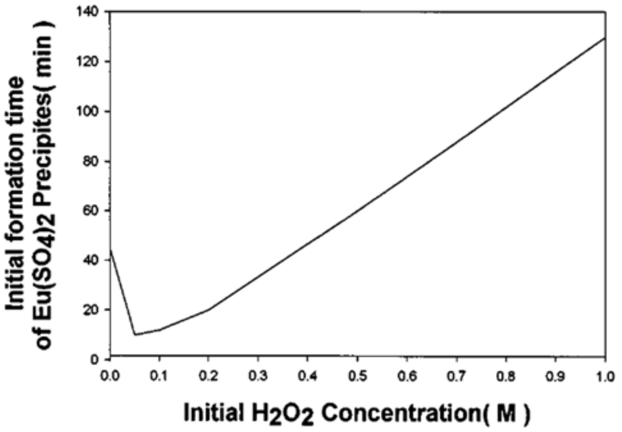

Fig. 5. Variation of initial formation time of $EuSO_4$ with initial H_2O_2 concentration.

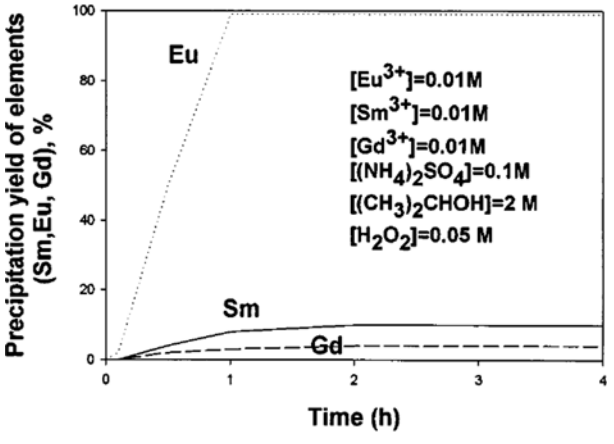

Fig. 4. Photoreductive precipitation of Eu, Sm and Gd elements in the presence of H_2O_2.

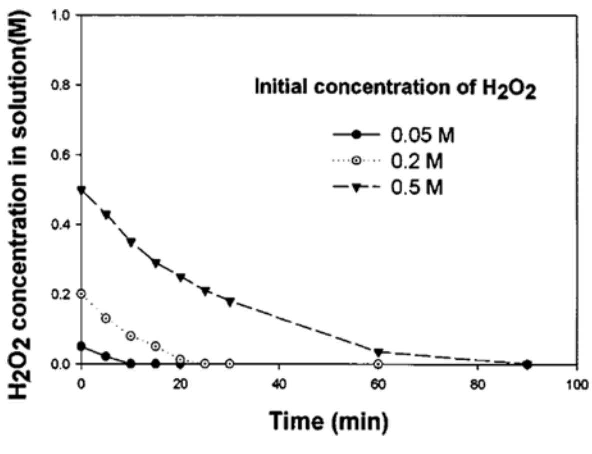

Fig. 6. Photodecomposition rate of H_2O_2.

Eq. (5) indicates that when a large amount of H_2O_2 exists in the solution, the Eu^{2+} produced by photolysis can be rapidly oxidized. Accordingly, the photo reduction of Eu^{3+} cannot occur until H_2O_2 nearly disappears in the solution. Fig. 6 shows the result of photodecomposition of H_2O_2. The complete photodecomposition time of H_2O_2 became much longer with an increase in the H_2O_2 concentration. We can find from these results that at a given H_2O_2 concentration the complete photodecomposition time of H_2O_2 is almost identical to initial precipitation time of $EuSO_4$. Accordingly, small amounts of H_2O_2 should be used for the effective photo-reductive precipitation of Eu.

Precipitation yields of Eu reached 99% when H_2O_2 was added. Such an increase of the reduction yield of Eu^{3+} is considered to be due to the production of large amounts of reducing agent $(CH_3)_2C^{\cdot}$ OH. The reduction potential of the organic radicals is known to be 1.3 V in water [Schwarz and Dodson, 1989]. This value can sufficiently reduce Eu^{3+}, but is insufficient to reduce Sm^{3+} or Gd^{3+}. Accordingly, although large amounts of organic radicals are produced during photolysis, both Sm^{3+} and Gd^{3+} are not reducible. This indicates that Eu can be selectively and rapidly separated from a rare earth mixture including Sm and Gd. Nevertheless, when H_2O_2 was added the precipitation yields of Sm and Gd increased slightly to 10% and 4%, respectively. This is attributed to the fast precipitation of Eu causing the co-precipitation of both Sm and Gd. This could be confirmed from the fact that when the solutions containing single elements (Sm, Eu and Gd) were irradiated in the presence of H_2O_2, both Sm and Gd were not precipitated at all although this result was not given in this work. On the other hand, the results are expected to be usable for the solution with minor actinides. The reduction potential value of trivalent americium (E°(III/II)=2.4 V) is the lowest of the minor actinides. In other words, the present system cannot reduce trivalent americium to divalent americium and furthermore, cannot reduce Np and Cm.

CONCLUSIONS

The following results were obtained from the study on the photoreductive precipitation of Eu from the solution containing Sm^{3+}, Eu^{3+} and Gd^{3+}.

1. The trivalent Eu was reduced to the divalent state by UV light irradiation with the mercury lamp emitting 254 nm, and was precipitated in the form of $EuSO_4$.
2. The fast precipitation rate of Eu could be obtained by the addition of small amounts of H_2O_2. This was attributed to the OH radicals, produced by photolysis of H_2O_2, radicalized isopropanol and the resulting organic radicals rapidly reduced Eu^{3+} into Eu^{2+}. The addition of H_2O_2 results in a higher Eu precipitation yield of 99%.
3. The precipitation yield of Sm and Gd was 10% and 4%, respectively.

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