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Separation Science and Technology
Publication details, including instructions for authors and subscription information:
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Online publication date: 10 September 2002

To cite this Article de Morais, Carlos Antônio and Ciminelli, Virginia S. T.(2002) 'EUROPIUM RECOVERY BY PHOTOCHEMICAL REDUCTION FROM Eu AND Eu-Gd CHLORIDE SOLUTIONS', Separation Science and Technology, 37: 14, 3305 — 3321

To link to this Article: DOI: 10.1081/SS-120006163

URL: http://dx.doi.org/10.1081/SS-120006163

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SEPARATION SCIENCE AND TECHNOLOGY, 37(14), 3305–3321 (2002)

EUROPIUM RECOVERY BY PHOTOCHEMICAL REDUCTION FROM Eu AND Eu–Gd CHLORIDE SOLUTIONS

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ABSTRACT

The recovery of europium in aqueous chloride solution by photochemical reduction/precipitation was evaluated in the presence of sulfate ions and a radical scavenger. A commercial low-pressure mercury lamp with an emission peak at 253.7 nm was used as an irradiation source. The influencing factors were investigated in detail with a pure europium (III) chloride solution and then applied to a solution containing a Gd/Eu molar ratio of 27. Europium recovery was shown to increase with an increase in SO_4^{2-}/Eu molar ratio up to 7, which corresponds to a stoichiometric excess of 600%. Similarly, high scavenger requirements

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(formic acid/Eu ratio of 500) were needed to achieve high yields. Faster reaction rate in the presence of formic acid, as compared with 2-propanol (2 and 15 hr, respectively, at 99% Eu recovery), used as scavengers, was observed. This was related to the photoactivation of formic acid, demonstrated by a strong absorption in the near-UV region, not observed with 2-propanol, and a ready drop of the solution Eh. Measurements of redox potential indicated the reducing character in the formic acid system. This reducing character, that was not observed with 2-propanol, increases with the irradiation at 253.7 nm. The increase in rare earth concentration led to either Eu(III) precipitation prior to irradiation, in pure Eu solutions, or Eu–Gd coprecipitation, in multicomponent solutions. Europium recovery reached 99% when the experiments were carried out with pure, dilute europium chloride solutions. High yields could not be achieved in the presence of high gadolinium concentration, owing to the Eu–Gd coprecipitation.

Key Words: Europium; Europium reduction; Photochemical reduction

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INTRODUCTION

In recent years, the interest in the commercial utilization of lanthanide compounds, such as those of europium, has significantly increased. With high purity degree, europium oxide shows a high market value as a result of important applications, such as red phosphors in color TV tubes and computer monitors, laser materials, high-intensity mercury vapor lamps, X-ray screens, etc.

In an aqueous phase, the rare earth elements are stable as trivalent species; among these elements, europium is the most easily reduced to the divalent form. On the basis of this feature, the separation of europium from rare earth concentrates is usually carried out by reduction of Eu(III) to Eu(II), followed by its precipitation as $EuSO_4$. The reduction can be accomplished by (i) cementation using Zn or Zn–Hg amalgams,[1–5] (ii) electrochemical reduction, using titanium or graphite as cathode[6–10] or (iii) photochemical reduction, using a low-pressure mercury lamp (LPML), high-pressure mercury lamp (HPML) or excimer lasers.[11–22]

The basic differences among the sources of irradiation mentioned in the previous paragraph are the power and the region of wavelength emission. The LPML is characterized by a lower power and higher energy photon emission,

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i.e., lower wavelength (for instance 184.9/253.7 nm) as compared to the HPML source (310/365 nm).[14,20,21] The excimer (a notation based on the contraction of the words *excited* and *dimer*) lasers are generally of high power and use electronic transitions between an excited and the ground-state of a gas molecule. The region of emission depends on the composition of the materials. Most ultraviolet molecular gas lasers involve, in fact, a combination of two different atoms, frequently a noble gas and a halogen: ArF (193 nm); KrCl (222 nm); KrF (248 nm). These molecules, which are not dimers, should be called exciplex (a contraction of *excited* with *complex*) lasers.[23]

The photoreduction of Eu(III) to Eu(II) takes place in the charge transfer band (CT band), corresponding to the transfer of an electron from a complexing ligand to the metal ion.[17,18,24] The reduction should be carried out in the presence of a radical scavenger to avoid the reverse reaction of oxidation. The radical scavenger, an alcohol, an ester, or an organic acid, may also participate in the reduction of Eu(III), as it will be shown in this paper. The europium photoreduction can be carried out in aqueous or organic phases, the source of irradiation being dependent on the nature of the solvent. In aqueous solution, LPML or excimer lasers have been tested.[18–21]

The chemical reduction of a Sm–Eu–Gd mixture was previously investigated by our group.[5] In that work, purity was no higher than 99.4% Eu_2O_3, this value being too low for more noble applications. As an attempt to improve recovery and grades in less reduction/precipitation stages, samarium was removed by solvent extraction. The combination of a more concentrated solution in europium (Gd/Eu molar ratio of 27), less concentration of total rare-earths with processing adjustments, resulted in grades higher than 99.99% Eu_2O_3, in two steps of reduction and precipitation.[25] Despite the good results, the environmental problems related to the disposal of Zn–Hg residues were a matter of concern. The photochemical reduction appears as an attractive option from the environmental point of view, since, in this case, the disposal of Hg-containing residues can be avoided. The photoreduction of europium in aqueous solutions has been previously studied in dilute, pure, or equimolar mixtures (binary or ternary) of lanthanides[19–22] and, therefore, under experimental conditions that may not reflect the actual composition of industrial solutions, such as the one previously mentioned.[25] In addition, some important information, such as the influence of the redox potential, scavenger/europium and sulfate/europium molar ratios on europium recovery, is not yet available.

In the present work, the photochemical reduction of europium is analyzed with the objective of europium recovery from a commercial mixture of Eu–Gd. As in the study of chemical reduction,[25] discussed above, samarium was previously removed by solvent extraction. The effect of europium concentration and other variables such as nature and amount of the radical scavenger and sulfate salt, redox potential, total rare earth concentration, and irradiation time have been

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at first evaluated in detail with a pure europium solution and then with a solution containing high gadolinium concentrations (Gd/Eu molar ratio of 27).

EXPERIMENTAL

Reagents

Europium chloride solutions were prepared by dissolving the oxide (99.5% Eu_2O_3 supplied by Rhone-Poulenc) in a small volume of concentrated hydrochloric acid, and these solutions were further diluted with distilled water to a final concentration of $10.0\,g\,L^{-1}$ Eu_2O_3 and acidity of $0.003\,mol\,L^{-1}$ (pH 2.5).

The europium/gadolinium chloride solutions were prepared by dissolving the respective carbonates (1.90% Eu_2O_3 and 52.4% Gd_2O_3) supplied by "Indústrias Nucleares do Brasil S.A.—INB" (RJ, Brazil) in an aqueous hydrochloric acid solution ($3.0\,mol\,L^{-1}$). The concentration of Eu_2O_3 and Gd_2O_3 in the commercial stock solution was 5.0 and $138.2\,g\,L^{-1}$, respectively, with $0.003\,mol\,L^{-1}$ of acidity. The chemical composition of the Eu/Gd mixture is shown in Table 1. All other chemicals were of analytical reagent grade; distilled water was used throughout the experiments.

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Experimental Procedure

The europium photoreduction and precipitation were carried out in a beaker-type glass bottle with diameter 65 mm and height 70 mm, standing on a magnetic stirrer and under an ultraviolet source, at 25°C. Two commercial LPML of 15 W (germicidal Lamp), supplied by General Electric—GE (USA), with emission peak at 253.7 nm were used as source of irradiation. The distance from the lamps to the europium solution surface was maintained at 80 mm. The solution bed was 20 mm high and the irradiation area was $33\,cm^2$. During irradiation, the solution temperature was observed to increase by approximately 3°C.

The pure $EuCl_3$ stock solution ($10\,g\,L^{-1}$ Eu_2O_3) was diluted to the desired experimental level and the sulfate (H_2SO_4 or $(NH_4)_2SO_4$) was added to a final

Table 1. Chemical Composition of the Solid Europium and Gadolinium Carbonate Mixture

Species	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	CO_3^{2-}	Cl^-	Fe^{3+}	H_2O
Content (%wt.)	<0.005	1.64	45.4	<0.005	43.3	2.30	0.060	7.28

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volume 50 mL, used in all the experiments. The radical scavengers were introduced immediately before the beginning of the experiments in order to avoid possible losses by degradation before europium reduction.

After precipitation, $EuSO_4$ was filtered in a Gooch-type crucible and washed with 0.002 $mol\,L^{-1}$ ammonium sulfate solution. The precipitate was then dissolved in a HCl solution (6 $mol\,L^{-1}$) with drops of hydrogen peroxide (H_2O_2), reprecipitated as a carbonate salt through the addition of sodium carbonate and finally submitted to calcination at 800°C to produce the oxide. The recovery was calculated by measuring europium concentration in the feed and in the filtrate solutions. The measurements were made in an energy-dispersive X-ray spectrometer (Kevex system, Kevex, CA, USA), with a detection limit of 0.01 $g\,L^{-1}$.

The Kevex system has a radioactive source of americium (Am^{241}) with 100 mCi of activity for the X-ray generation. The complete setup is built around a Si(Li) detector X-ray spectrometer, with an energy resolution of 220 eV at 5.94 keV. The peaks observed in the X-ray fluorescence spectra are fitted with a multicomponent spectrum analysis and the intensities of the characteristic X-ray lines are extracted, for calculating the elemental concentrations. Analytical sensitivities of the order of a few μg/g can be obtained for elements with atomic numbers (Z) in the range $40 \leq Z \leq 68$.[26–28] The analytical sensitivity was shown to depend on the counting time. In the present work, it was adjusted to 400 sec. A good performance of this method was shown in solid and liquid samples. The experimental error including the analytical error was 3 at 95% of confidence level.

The absorption spectra of aqueous solutions of the species involved in the process were investigated using an UV-vis Perkin Elmer spectrophotometer model Lambda 20, (Perkin Elmer, USA). The redox potential was measured with a Pt electrode (Digimed pH-meter model DM 20, Digimed, SP, Brazil) under mild stirring, using a saturated Ag–AgCl as the reference electrode.

RESULTS AND DISCUSSION

Among the lanthanides, Eu(III) is the most easily reduced to the divalent state. The photoreduction (Eq. (1)) takes place in the charge transfer band (CT band), corresponding to the transference of an electron from a complexing ligand to the metal ion.[17,18,24] In europium (III) aqueous solution, a CT band from H_2O to Eu(III) occurs at 188 nm. In solutions containing sulfate, another CT band appears around 240 nm, corresponding to the charge-transfer transition from SO_4^{2-} to Eu(III). The hydroxyl radical ($^{\cdot}OH$) formed during europium reduction (Eq. (1)) is removed by a scavenger, such as formic acid and 2-propanol, through a reaction that produces an organic radical (Eqs. (2) and (3)). It has been suggested that this radical may reduce a second molecule of Eu(III) ion to its

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divalent state:[19–21]

$$Eu^{3+}(H_2O)_n + h\nu = Eu^{2+}(H_2O)_{(n-1)} + {}^{\cdot}OH + H^+ \tag{1}$$

$$HCOOH + {}^{\cdot}OH = H_2O + {}^{\cdot}COOH \tag{2}$$

$$(CH_3)_2CHOH + {}^{\cdot}OH = H_2O + (CH_3)_2^{\cdot}COH \tag{3}$$

As the Eu(II) ions are formed they are precipitated as $EuSO_4$ according to the equation:

$$Eu^{2+} + HSO_4^- = EuSO_4 + H^+ \tag{4}$$

The effect of process parameters on the reduction and precipitation of europium was first studied with pure europium solutions. Figure 1 compares the influence of formic acid and 2-propanol on europium reduction. It is important to emphasize that recovery of europium as $EuSO_4$ by photochemical process does not occur in the absence of a radical scavenger, which is added to avoid the reverse reaction (Eu(II) oxidation).[18,20–22] As shown by Fig. 1, relatively longer irradiation time is needed with 2-propanol, as a result of significantly slower reaction rates. In the presence of formic acid, 2 hr of irradiation were adequate to achieve approximately 100% europium recovery, while for the 2-propanol 15 hr of irradiation were required to achieve comparable conversion. Similar trend was reported by Hirai and Komasawa,[21] who explained their results in terms of the

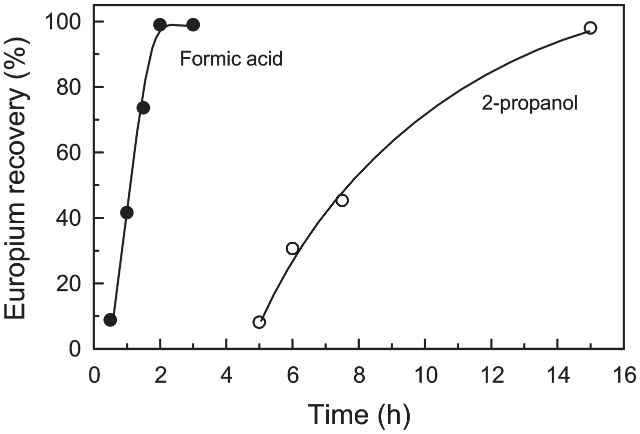

Figure 1. Influence of the radical scavenger on europium recovery: 7×10^{-3} mol L^{-1} Eu^{3+} (1.25 g L^{-1} Eu_2O_3), molar ratios: $SO_4^{2-}/Eu = 35$; $HCOOH/Eu = 600$; $CH_3CH(OH)CH_3/Eu = 730$.

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formation of a $^{\cdot}$COOH radical through the photodecomposition of formic acid, these species also being capable of reducing Eu(III):

$$Eu^{3+} + {}^{\cdot}COOH = Eu^{2+} + CO_2 + H^+ \tag{5}$$

The authors reported that 4 hr were needed to attain equilibrium with formic acid and 24 hr with 2-propanol (irradiation wavelength at 253.7 nm). The Sm–Gd coprecipitation was reported.

In order to investigate the differences depicted in Fig. 1, the absorption and the redox potentials of both systems were measured. The absorption spectra of the solutions containing 2-propanol and formic acid are shown in Fig. 2. In pure europium chloride solution (line A), only the charge-transfer band from H_2O to Eu(III) at 188 nm is observed. When SO_4^{2-} is introduced, a transition band at approximately 240 nm, corresponding to the charge-transfer from SO_4^{2-} to Eu(III),[19–21] is identified (line B). Now, the europium/sulfate system in the presence of 2-propanol and formic acid will be analyzed. The addition of 2-propanol to the solution containing $EuCl_3$ and H_2SO_4 (line C) does not modify the behavior depicted by the $EuCl_3/H_2SO_4$ solution (line B). The slightly lower absorbance level observed in the presence of 2-propanol is related to the

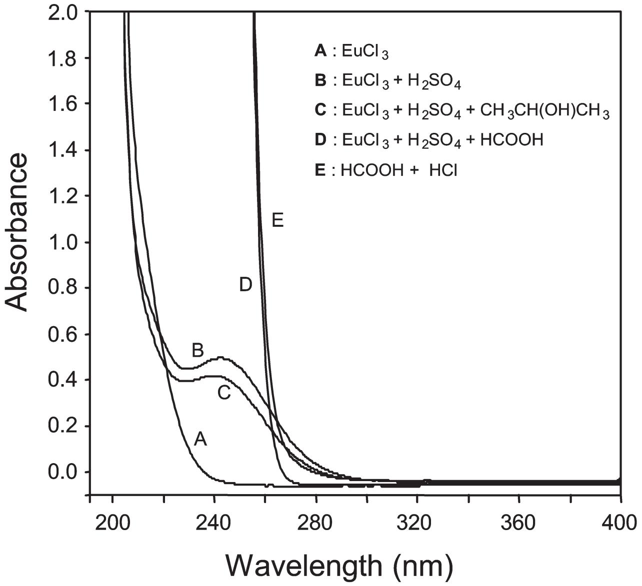

Figure 2. Absorption spectra of aqueous solutions (reference: air, $EuCl_3$: 0.005 mol L^{-1}, H_2SO_4: 0.25 mol L^{-1}, HCl: 0.005 mol L^{-1}, $CH_3CH(OH)CH_3$: 2 mol L^{-1}, HCOOH: 2 mol L^{-1}).

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relatively lower europium concentration caused by the addition of the scavenger. Conversely, the presence of formic acid (line D) creates a broad absorption band at around 260 nm. This band remains even in the absence of $EuCl_3$ (line E), thus indicating that the absorption is not related to an interaction (charge-transfer) involving this compound and europium. The excited electronic state of formic acid created by the absorption at 260 nm, not observed with the 2-propanol, may indirectly enhance Eu(III) reduction, thus justifying the high reactivity in the presence of the formic acid, as indicated by Eqs. (6)–(8).

$$HCOOH + h\nu = {}^{\cdot}COOH + H^{\cdot} \tag{6}$$

$$H^{\cdot} + H^{\cdot} = H_2 \tag{7}$$

$$H^{\cdot} + {}^{\cdot}OH = H_2O \tag{8}$$

Equations (6) and (7), discussed by Allmand and Reeve[29] and Hirai,[21] explain the photoactivation of formic acid at 260 nm, shown in Fig. 2. The reaction depicted by Eq. (6) creates an additional source of formic radical to that of the reaction of a hydroxyl radical with formic acid (Eq. (2)), favoring europium reduction. On the other hand, it is shown by Eq. (8) that the formation of an $H^{\cdot}$ radical creates another pathway for scavenging the $OH^{\cdot}$ generated by Eq. (1), which in turn also favors Eu(III) reduction. Summarizing, the enhanced europium reduction in the presence of formic acid is related to its photoactivation, shown in Fig. 2, which increases the reducing agent (${}^{\cdot}COOH$) concentration and provides an additional scavenger ($H^{\cdot}$) to remove the hydroxyl radical (${}^{\cdot}OH$) formed by Eq. (1).

The redox potential of the aqueous solutions containing formic acid and 2-propanol was measured, before and after UV light irradiation. The potentials as a function of the irradiation time are shown in Fig. 3. Line A represents the behavior of an aqueous europium chloride solution containing both sulfuric and formic acids. Line B represents the aqueous solution without europium ($H_2O + HCl + H_2SO_4 + HCOOH$) and line C is the aqueous europium chloride solution plus sulfuric acid and 2-propanol. The concentrations of the species were maintained at the experimental levels shown in Fig. 1 (7×10^{-3} mol L^{-1} Eu^{3+}, molar ratios: $SO_4^{2-}/Eu = 35$; $HCOOH/Eu = 600$; $CH_3CH(OH)CH_3/Eu = 730$). Before light irradiation, the potential ($Eh_{298\,K}$) was approximately 0.30 V in the presence of formic acid, while 0.55 V in the 2-propanol system. The stronger reducing nature of pure formic acid solutions is magnified by the presence of the irradiation source (Fig. 3, line B). With 5 min of irradiation, the potential reached an $Eh_{298\,K}$ of -0.05 V in the formic acid-Eu system (line A), while more than 4 hr were needed for the potential to reach similar value with the 2-propanol-Eu solution (line C).

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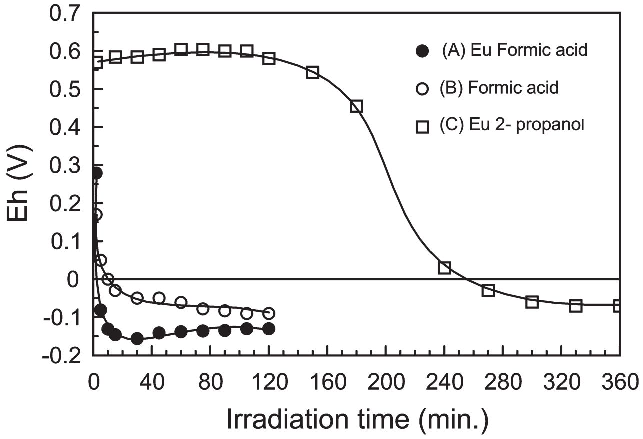

Figure 3. Variation of $Eh_{298\,K}$ with the irradiation time for the aqueous systems ($EuCl_3$, H_2SO_4, HCOOH), (HCl, H_2SO_4, HCOOH), and ($EuCl_3$, H_2SO_4, $(CH_3)_2CHOH$).

On the basis of its better performance, the study was continued with formic acid. The important role of the HCOOH/Eu molar ratio on europium recovery, not clearly addressed in previous studies, is depicted in Fig. 4. The recovery increases slightly with the HCOOH/Eu ratio up to a level of approximately 500. At this point, a sharp increase in recovery takes place, reaching levels of approximately 100%.

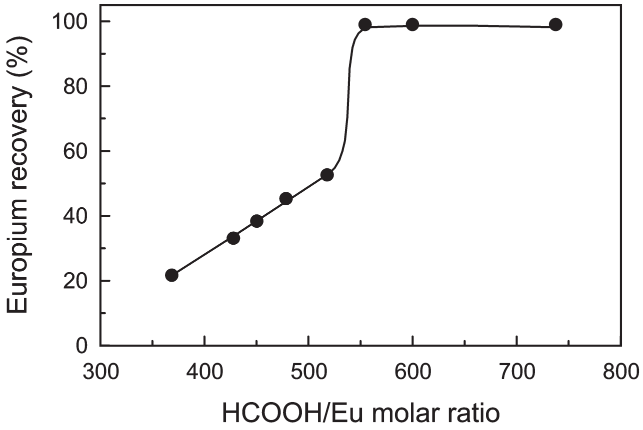

Figure 4. Influence of the molar ratio HCOOH/Eu on europium recovery: $8 \times 10^{-3}\,mol\,L^{-1}$ ($1.25\,g\,L^{-1}$) Eu_2O_3, SO_4^{2-}/Eu molar ratio of 35, 2 hr of irradiation.

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Variations in HCOOH/Eu molar ratios from 370 to 600 did not affect the redox potential; in both cases, the Eh followed the same trend depicted in Fig. 3, stabilizing at $-0.13\,\mathrm{V}$.

In the recovery of europium by photochemical reduction, sulfate ions have two important roles. The primary role of SO_4^{2-} is the removal of Eu(II) as insoluble europium(II) sulfate ($EuSO_4$), avoiding its reoxidation. In addition, the sulfate ion is also important to create a charge-transfer band around 240 nm that corresponds to the C-T from SO_4^{2-} to Eu^{3+}. This band enables the use of the commercial LPML with an emission peak of 253.7 nm. In the absence of sulfate, the absorption takes place near 190 nm, in the C-T band from H_2O to Eu^{3+}.[19–21] Nevertheless, the reduced Eu^{2+} will be photooxidized in its f–d transition, which occurs in the same wavelength of the charge-transfer transition of Eu(III) to SO_4^{2-}, the photoactivation acting as a catalyst in the oxidation reaction.[12,18,21,22,30,31]

$$Eu^{2+} + H_2O + h\nu = Eu^{3+} + OH^- + H^{\cdot} \tag{9}$$

$(NH_4)_2SO_4$ and H_2SO_4 were investigated as sulfate sources and led to similar europium recoveries. Sulfuric acid was selected based on the comparatively higher grade Eu_2O_3 obtained in experiments of chemical reduction of solution containing high gadolinium concentration.[25] The better results were explained by the lower pH of the medium as compared to the $(NH_4)_2SO_4$ solution, which helped to prevent gadolinium coprecipitation. The sulfate amount was then varied from SO_4^{2-}/Eu molar ratio of 1.5–35 (0.01–$0.25\,\mathrm{mol\,L^{-1}}$ SO_4^{2-}). Europium recovery was shown to increase with an increase in SO_4^{2-}/Eu molar ratio up to 7, which corresponds to a stoichiometric excess of 600% (Fig. 5).

The pH dependence on the Eu(III) photoreduction was investigated by Haas et al.,[22] who reported a maximum reduction between pH 1 and 1.5. Nevertheless, in that study, europium reduction was studied in terms of H_2 evolution and the authors did not make clear how the effects of pH on H_2 evolution and europium reduction were separated. In the present study, the pH varied from 0.8 to 0.3 as a result of varying sulfuric acid concentration. When ammonium sulfate was used as SO_4^{2-} source, the pH was maintained at 1.5. In this relatively large interval (pH 0.3–1.5), no effect of pH on europium recovery was detected.

When aiming at industrial applications, concentration becomes a key factor, affecting product recovery, grade, and the overall process economics. Haas et al.[22] studied the effect of concentration in the interval of 10^{-4}–$10^{-1}\,\mathrm{mol\,L^{-1}}$ Eu^{3+}. The results indicated that europium reduction yields increased with concentration up to about $10^{-2}\,\mathrm{mol\,L^{-1}}$ Eu^{3+} and then remained constant. Nevertheless, rather than being associated with concentration, the plateau may result from insufficient irradiation time and scavenger amount,

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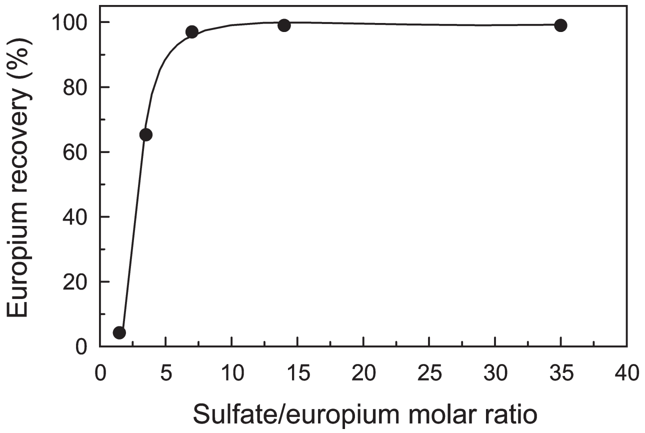

Figure 5. Influence of the SO_4^{2-}/Eu molar ratio on europium recovery: 8×10^{-3} mol L^{-1} (1.25 g L^{-1}) Eu_2O_3, molar ratio HCOOH/Eu = 600, 2 hr of irradiation.

which were maintained constant when europium concentration was increased. In other studies,[13,19–21] europium concentrations were kept at 10^{-2} or 10^{-3} mol L^{-1}. In the present work, concentrations were varied from 6×10^{-3} to 5.7×10^{-2} mol L^{-1} Eu^{3+}. As expected, the irradiation time needed for a given europium recovery increases with concentration. Two hours of irradiation were sufficient to achieve approximately 99% europium recovery from a solution containing 1.25 g L^{-1} Eu_2O_3 (7×10^{-3} mol L^{-1} Eu^{3+}). When concentration was doubled, 4 hr were required to achieve the same recovery (Fig. 6). The relative amount of formic acid should also be considered. For a fixed 1.5 hr of irradiation, europium recovery attained 99% with a HCOOH/Eu molar ratio of 750, dropping to 74% with a HCOOH/Eu molar ratio of 600.

When europium concentration was increased to 10.0 g L^{-1}, the precipitation of $Eu_2(SO_4)_3$ took place prior to irradiation. Considering the high solubility of trivalent rare earth sulfate salts in water, the phenomenon can be ascribed to the anti-solvent effect caused by the high concentration of scavenger required to maintain an adequate HCOOH/Eu ratio. High concentrations of organic compounds, such as formic acid and 2-propanol, decrease the dielectric constant of the medium, thus increasing the electrostatic attraction between the oppositely charged species ($Eu^{3+}-SO_4^{2-}$) and decreasing $Eu_2(SO_4)_3$ solubility. The effect also depends on sulfate concentration, which again, in order to maintain the ratio SO_4^{2-}/Eu, should increase with europium concentration. The previous results indicate difficulties in applying photochemical reduction to more concentrated solutions. This conclusion will be supported by the results shown in the following paragraphs.

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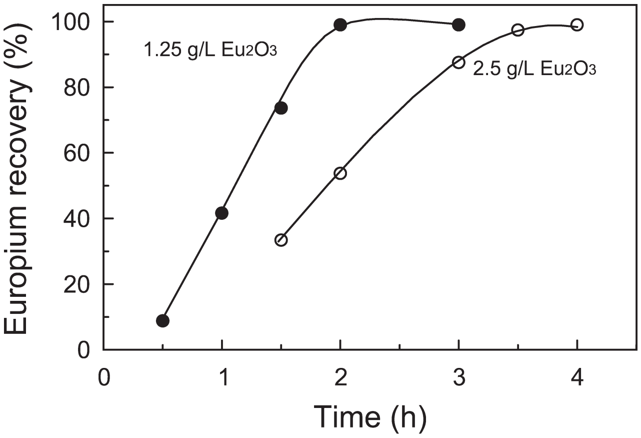

Figure 6. Effect of feed concentration on europium recovery. $8 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ ($1.25\,\mathrm{g\,L^{-1}}$) Eu_2O_3, molar ratios: HCOOH/Eu = 600; $SO_4^{2-}/Eu = 10$.

The main goal of this work was to investigate the recovery of europium from an Eu/Gd solution. Most of the previous studies were carried out with equimolar, binary, or ternary lanthanide mixtures, which do not properly represent the conditions found in many actual systems such as in ours. Now europium reduction from a solution with a Gd/Eu molar ratio of 27 is investigated. Tests were carried out varying sulfate, europium, and HCOOH concentrations (Table 2). The irradiation time was fixed at 3 hr. Results with the pure europium solution with HCOOH/Eu molar ratio of 560 and SO_4^{2-}/Eu of 7 and europium concentration of $1.25\,\mathrm{g\,L^{-1}}$ Eu_2O_3 indicated that over 98% europium can be recovered as $EuSO_4$ in 2 hr of irradiation. Under similar conditions (HCOOH/Eu molar ratio of 600 and SO_4^{2-}/Eu molar ratio of 10) no precipitation took place with the Eu/Gd mixture. When SO_4^{2-}/Eu was varied from 10 to 120 and HCOOH/Eu was maintained at 600, solids were formed for SO_4^{2-}/Eu ratios above 60, but with no selectivity. In other series of experiments, the SO_4^{2-}/Eu molar ratio was fixed at 30 (four times the one needed for maximum recovery with pure europium solutions) while the HCOOH/Eu ratio was varied from 800 to 1400. Precipitation took place for HCOOH/Eu ratios above 1200, but again with no selectivity. As an attempt to achieve selectivity, europium and gadolinium concentrations were reduced to half and 1/4, respectively, of the previous ones, whereas SO_4^{2-}/Eu and HCOOH/Eu molar ratios were chosen above the threshold for europium precipitation (Table 2). No precipitation was observed.

Measurements of the redox potentials indicated a final $Eh_{298\,K}$ similar to that of the pure europium solution (-0.13 V), thus suggesting that the difficulties were not related to this variable. Aimed at favoring nucleation, further

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Table 2. Experiments Carried Out with Europium and Gadolinium Chloride Solution

	Feed Solution		Reagents and Quantities		Recovery	
Test #	Eu_2O_3 ($g\,L^{-1}$)	Gd_2O_3 ($g\,L^{-1}$)	SO_4^{2-}/Eu (mol/mol)	HCOOH/Eu (mol/mol)	Eu_2O_3 (%)	Gd_2O_3 (%)
1	1.0	27.6	10	600	0	0
2	1.0	27.6	20	600	0	0
3	1.0	27.6	30	600	0	0
4	1.0	27.6	60	600	8.7	6.3
5	1.0	27.6	100	600	15.3	11.7
6	1.0	27.6	120	600	75.5	68.5
7	1.0	27.6	30	800	0	0
8	1.0	27.6	30	1000	0	0
9	1.0	27.6	30	1200	7.0	7.2
10	1.0	27.6	30	1400	29.3	28.4
11	0.5	13.8	60	1400	0	0
12	0.25	6.9	120	2800	0	0
13[a]	1.0	27.6	10	600	21.6	14.1
14[a]	1.0	27.6	30	600	20.5	20.2
15[a]	1.0	27.6	10	1000	35.6	33.0
16[a]	1.0	27.6	30	1000	44.4	38.6

[a] 0.01 g of $EuSO_4$ added as seeds.

experiments were carried out using $EuSO_4$ seeds. The other variables were maintained at HCOOH/Eu molar ratio of 600 and 1000, and SO_4^{2-}/Eu of 10 and 30. A comparison of the tests 1/13, 3/14, and 8/16 clearly indicates the role of the sulfate seeds in favoring precipitation, but again with no selectivity.

In conclusion, the experiments with a europium solution with high gadolinium concentrations led to two undesirable situations. In one, europium precipitation did not occur at all and in the other, europium and gadolinium were both precipitated.

These results suggest that the use of photochemical reduction in aqueous phase is limited to dilute and relatively pure solutions, conditions not usually present in industrial application. The separation of Eu from a Sm/Eu/Gd mixture was investigated by Hirai et al.[20,21] with solutions containing equimolar ($0.005\,mol\,L^{-1}$) concentrations of $SmCl_3$, $EuCl_3$, and $GdCl_3$, which correspond to only $2.66\,g\,L^{-1}$ total rare earth oxide (approximately 10% of that indicated in Table 2). For this very dilute system with formic acid, the coprecipitation of Sm–Gd limited the purity of europium precipitates to 90%. Donohue[19] also worked with equimolar mixture ($0.01\,mol\,L^{-1}$) of binary or ternary lanthanide

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combinations. The separation factor, β, ([Eu/Ln](precipitated)/[Eu/Ln](initial)), was less than 5 for the light rare earths, and less than 300 for the heavy rare earths, thus showing the same lack of selectivity observed in the present work. A comparison of these separation factors may indicate that the anti-solvent effect caused by the presence of the scavenger is more accentuated for the light rare earths. Turning to the lack of precipitation, a possible lowering of free sulfate concentration, owing to its complexation with Gd is a possibility to be explored in order to explain the results obtained here. It is clear that a better understanding of the failure of photochemical reduction in Gd rich solutions should rely on a better comprehension of the solution chemistry of the system under consideration. Thermodynamic calculations together with activity coefficient determinations to estimate speciation and stability in the medium of interest may help to understand the cause of the failed separation.

The good results with dilute, relatively pure europium chloride solutions found in this and other works indicate the possibility of some niche applications for the photochemical reduction process in aqueous solution, such as the treatment of dilute rare earth solution or the removal of europium radionuclides from radioactive waste solutions. On the other hand, from the environmental point of view, one has to consider the large consumption (and further disposal) of organic compounds (scavengers) involved in the photochemical reduction of Eu(III) solutions. This aspect minimizes potential advantages with respect to the conventional process of europium reduction with zinc amalgam.

CONCLUSIONS

The factors influencing europium photoreduction/$EuSO_4$ precipitation were investigated by using a LPML (germicidal lamp) with photon emissions at 253.7 nm as the light source. The main factors affecting europium recovery by photochemical reduction/precipitation were shown to be the total rare earth concentration, the sulfate/Eu molar ratio and the nature and the radical scavenger/Eu molar ratio. Europium recovery was shown to increase with an increase in SO_4^{2-}/Eu molar ratio up to 7. Similarly, high scavenger requirements (Formic acid/Eu ratio of 500) were needed to achieve high yields. A comparison between formic acid and 2-propanol used as scavengers indicated a faster kinetic reaction of the former (2 and 15 hr, respectively). This was explained by photodecomposition of the formic acid, and the consequent increase in the reducing agent concentration and a fast decrease in Eh. The increase in europium concentration in the feed solution is limited by the anti-solvent effect caused by the presence of the scavenger, which in turn results in precipitation of this element as trivalent europium sulfate or the co-precipitation of gadolinium.

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ACKNOWLEDGMENTS

The authors would like to thank “INB—Industrias Nucleares do Brasil S.A.” for supplying the sample and the technical support of the CDTN chemical laboratory, specially Eugênio M. Oliveira, José dos Santos J. Pereira, Liliane P. Tavares, Luiz Carlos da Silva, and Marcos A. Evangelista. V. Ciminelli thanks the sponsorship of the Brazilian Research Council-CNPq.

REFERENCES

1. McCoy, H.N. Contribution to the Chemistry of Europium. J. Am. Chem. Soc. **1936**, *58*, 1577–1580.
2. Krumholz, P.; Bril, K.; Bril, S.; Behmoiras, J.; Gottdenker, F.; Lima, F.W. Brazilian Practice in the Separation of Rare Earths. In Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958. Proceedings. Geneva, United Nations, Vol. 28, 184–195.
3. Geschneidner, K.A., Jr. Rare Earth Speciality Inorganic Chemicals. In *Symposium on Speciality Inorganic Chemicals*; Thompson, R., Ed.; The Royal Society of Chemistry: London, 1980; 403–443.
4. Preston, J.S.; du Preez, A.C. The Separation of Europium from a Middle Rare Earth Concentrate by Combined Chemical Reduction, Precipitation and Solvent Extraction Methods. J. Chem. Technol. Biotechnol. **1996**, *65*, 93–101.
5. Morais, C.A.; Ciminelli, V.S.T. Recovery of Europium from a Rare Earth Chloride Solution. Hydrometallurgy **1998**, *49*, 167–177.
6. Lu, D.; Horng, J.-S.; Tung, C.-P. Reduction of Europium in a Redox Flow Cell. J. Metals **1988**, 32–34.
7. Dumousseau, J.-Y.; Rollat, A. Sabot, J.-L. Recovery of Europium (II) Values by Electrolysis. U.S. Patent 4,938,852, July 3, 1990.
8. Hirai, T.; Komasawa, I. Separation of Europium from Samarium and Gadolinium by Combination of Electrochemical Reduction and Solvent Extraction. J. Chem. Eng. Jpn **1992**, *25* (6), 644–648.
9. Hirato, T.; Kajiyama, H.; Majima, H.; Awakura, Y. Electrolytic Reduction of Eu(III) to Eu(II) in Acidic Chloride Solutions with Titanium Cathode. Metal. Mat. Trans. B **1995**, *26B*, 1175–1181.
10. Atanasyants, A.G.; Seryogin, A.N. The Reaction of the Electrochemical Reduction $Eu(III) + e^- \rightarrow Eu(II)$ in Hydrochloric Solution. Hydrometallurgy **1995**, *37*, 367–374.
11. Pinch, H.L. The Photochemical Reduction of Rare Earth Ions in Fused Halides. J. Am. Chem. Soc. **1964**, *86*, 3167–3168.

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12. Donohue, T. Photochemical Separation of Metals in Solution by Precipitation Following Reduction or Oxidation. U.S. Patent, 4,172,775, Oct. 30, 1979.
13. Donohue, T. Lanthanide Photochemistry Initiated in f–f Transitions. Am. Chem. Soc. **1978**, 7411–7413.
14. Qui, L.-F.; Kang, X.-H.; Wang, T.-S. A Study on Photochemical Separation of Rare Earths: The Separation of Europium from an Industrial Concentrate Material of Samarium, Europium and Gadolinium. Sep. Sci. Technol. **1991**, *26* (2), 199–221.
15. Kusaba, M.; Nakashima, N.; Kawamura, W.; Izawa, Y.; Yamanaka, C. Higher Yield of Photoreduction from Eu^{3+} to Eu^{2+} with Shorter Wavelength Irradiation. Chem. Phys. Lett. **1992**, *197*, 136–140.
16. Kusaba, M.; Nakashima, N.; Kawamura, W.; Izawa, Y.; Yamanaka, C. High Photoreduction Yield of Eu^{3+} to Eu^{2+} in Alcoholic Solutions and its Wavelength Dependence. J. Alloys Comp. **1993**, *192*, 284–286.
17. Haas, Y.; Stein, G.; Tomkiewicz, M. Fluorescence and Photochemistry of the Charge-Transfer Band in Aqueous Europium (III) Solutions. J. Phys. Chem. **1970**, *74* (12), 2558–2562.
18. Donohue, T. Laser Purification of the Rare Earths. Optical Eng. **1979**, *18* (2), 181–186.
19. Donohue, T. Photochemical Separation of Europium from Lanthanide Mixtures in Aqueous Solution. J. Chem. Phys. **1977**, *67* (11), 5402–5404.
20. Hirai, T.; Onoe, N.; Komasawa, I. Separation of Europium from Samarium and Gadolinium by Combination of Photochemical Reduction and Solvent Extraction. J. Chem. Eng. Jpn **1993**, *26* (1), 64–67.
21. Hirai, T.; Komasava, I. Separation of Eu from Sm/Eu/Gd Mixture by Photoreductive Stripping in Solvent Extraction Process. Ind. Eng. Chem. Res. **1995**, *34* (1), 237–243.
22. Haas, Y.; Stein, G.; Tenne, R. The Photochemistry of Solutions of Eu(III) and Eu(II). Israel J. Chem. **1972**, *10*, 529–536.
23. Woldseth, R., (Ed.) Molecular Gas Lasers II. *Lasers and Electro-Optics, Fundamentals and Engineering*, 1st Ed.; Cambridge University Press: UK, 1996; 225–247.
24. Barnes, J.C.; Day, P. Charge-Transfer Spectra of Some Inorganic Complexes in Solution. J. Chem. Soc. **1964**, 3886–3892.
25. Morais, C.A.; Ciminelli, V.S.T. Recovery of Europium by Chemical Reduction of a Commercial Solution of Europium and Gadolinium Chlorides. Hydrometallurgy **2001**, *60*, 247–253.
26. Woldseth, R., (Ed.) *X-Ray Energy Spectrometry*, 1st Ed.; Kevex Corp: Burlingame, CA, 1993; 150 p.
27. Leroux, J.; Mahmud, M. X-Ray Quantitative Analysis by an Emission–Transmission Method. Anal. Chem. **1966**, *38* (1), 76–82.

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28. Blackburn, J.A. Computer Program for Multicomponent Spectrum Analysis using Least-Squares Method. Anal. Chem. **1965**, *37* (8), 1000–1003.
29. Allmand, A.J.; Reeve, L. The Photochemical Decomposition of Aqueous Formic Acid Solutions. J. Chem. Soc. **1926**, 2852–2863.
30. Davis, D.D.; Stevenson, K.L.; King, G.K. Photolysis of Europium (II) Perchlorate in Aqueous Acid Solution. Inorg. Chem. **1977**, *16*, 670–673.
31. Brandys, M.; Stein, G. Photochemical Evolution of Hydrogen from Aqueous Solutions of Europium ions at $\lambda > 310$ nm. The Role of Europium (II). J. Phys. Chem. **1978**, *82* (8), 852–854.

Received November 2001
Revised March 2002

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