ORNL/TM-10284

ornl

OAK RIDGE NATIONAL LABORATORY

MARTIN MARIETTA

# The Application of Electroreduction of Europium in the Production of Gadolinium-153

T. C. Quinby
D. W. Ramey
M. Petek



MASTER



OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A03 Microfiche A01

---

ORNL/TM--10284

DE87 005281

# THE APPLICATION OF ELECTROREDUCTION OF EUROPIUM IN THE PRODUCTION OF GADOLINIUM-153

Operations Division

T. C. Quinby, D. W. Ramey, and M. Petek



Date Published - January 1987



Prepared by the
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
operated by
Martin Marietta Energy Systems, Inc.
for the
U.S. DEPARTMENT OF ENERGY
under Contract No. DE-AC05-84OR21400

TABLE OF CONTENTS

# THE APPLICATION OF ELECTROREDUCTION OF EUROPIUM IN THE PRODUCTION OF GADOLINIUM-153

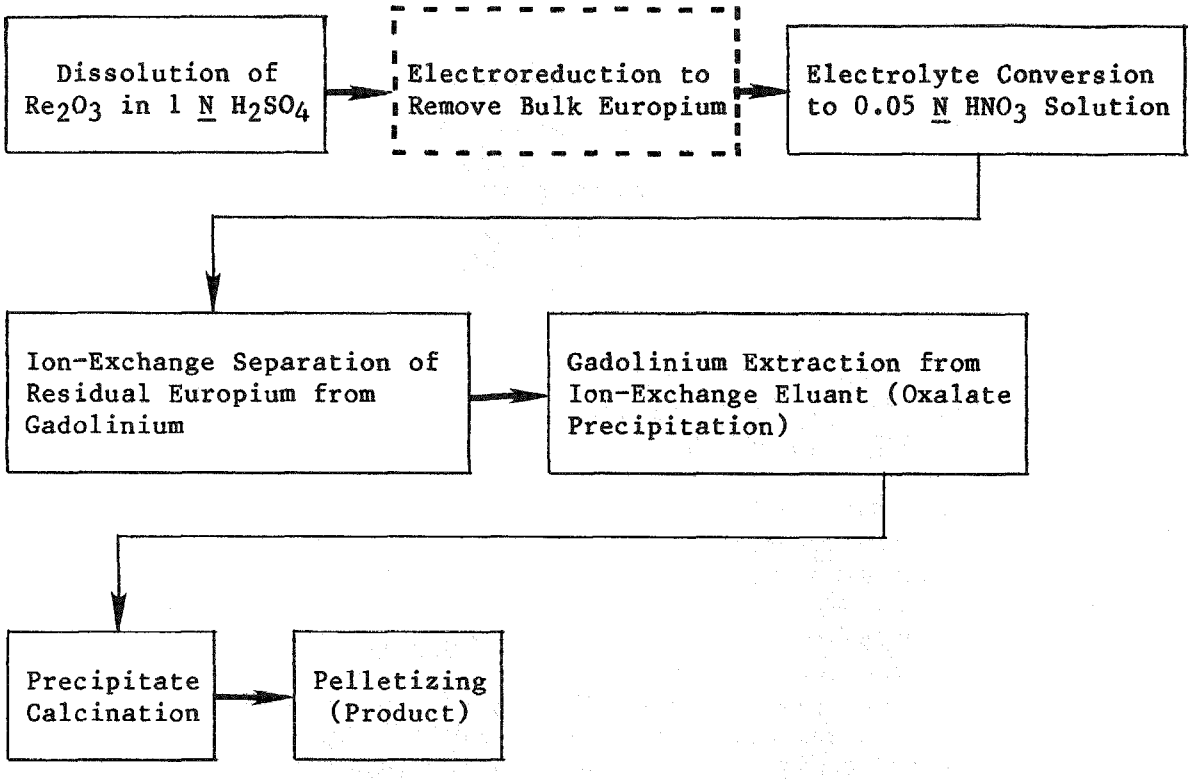
T. C. Quinby, D. W. Ramey, and M. Petek


## ABSTRACT

The Oak Ridge National Laboratory (ORNL) is presently producing $^{153}Gd$ by the neutron irradiation of normal europium in the form of $Eu_2O_3$. The resulting europium-to-gadolinium weight ratio produced after a one-cycle (approximately 21 days) irradiation of normal europium in the High Flux Isotope Reactor (HFIR) approaches 17. To achieve the required $\geq$99.99% radiochemical purity of the $^{153}Gd$ product and to achieve a respectable yield, the gadolinium must be quantitatively separated from the europium. This is achieved in a two-step process. First, the bulk (90 to 95%) of the europium is removed by the selective electroreduction of Eu(III) to Eu(II) using zinc electrodes in an electrolytic cell that contains $H_2SO_4$. Efficient europium removal is achieved in 4 h at a current density of 14.9 $mA/cm^2$. The remaining europium is separated from the gadolinium in a second step that involves the use of high-pressure ion exchange. The introduction of the electrolytic step in the $^{153}Gd$ production process increased the process capacity by a factor of four and increased the $^{153}Gd$ yield by $\geq$70%.


## 1. Introduction

In the present ORNL $^{153}Gd$ production process, normal europium, which is composed of 47.8% $^{157}Eu$ and 52.2% $^{153}Eu$ in the form of europium oxide encapsulated in glass ampoules, is bombarded with neutrons to produce $^{153}Gd$ from the beta decay of $^{152m}Eu$ and $^{152}Eu$. After a steady-state concentration of $^{153}Gd$ in europium oxide is reached, the material is processed to obtain pure $^{153}Gd$. The separation of gadolinium from europium and the preparation of $Gd_2O_3$ powder for $^{153}Gd$ pellet preparation consist of the following steps.




In the past[1,2], high-pressure ion exchange was the only separation process used. Because of the substantially higher content of europium over gadolinium in the ion-exchange column feed material (europium/gadolinium ratio of approximately 17 by weight), the ion-exchange process was often repeated once and sometimes twice before the desired purity of $^{153}Gd$ ($\geq$0.9999 Ci $^{153}Gd$/Ci total active rare earths) was obtained. Aside from the time-consuming reprocess, smaller yields were obtained with each successive recycle. High concentrations of energetic $^{152}Eu$, $^{154}Eu$, and $^{156}Eu$ caused considerable radiation damage to the ion-exchange resin, which needed to be replaced frequently. A separation process for removing bulk amounts of europium prior to the ion-exchange step was needed to shorten the process time, to avoid the radiation damage to the ion-exchange resin, and to increase the overall ion-exchange efficiency and $^{153}Gd$ yield.

Several reduction processes for separating europium from gadolinium have been reported, all of which are based on the fact that europium (III)

can be reduced to a lower oxidation state at potentials at which gadolinium (III) remains unaffected. However, in each case, mercury is used as the cathode[2,3] or in the form of lithium[2], sodium[4], or zinc amalgams[5]. Since relatively large quantities of material need to be handled in a hot cell which required using remotely operated equipment and also for environmental concerns, mercury was considered impractical. Zinc was chosen as a possible replacement for mercury. The aim was to reduce europium (III) electrolytically to the bivalent state and precipitate it simultaneously as the europium (II) sulfate while leaving behind an europium-depleted solution of $^{153}Gd$.

When the rare-earth mixture is electrolyzed in 1 $\underline{N}$ $H_2SO_4$ in a cell with two identical zinc electrodes, the following electrode reactions are considered at the cathode.

$$Eu^{3+} + SO_4^{2-} + e \longrightarrow EuSO_4 \downarrow \quad (1)$$

$$H^+ + e \longrightarrow 1/2H_2 \uparrow \quad (2)$$

$$Zn^{2+} + 2e \longrightarrow Zn \quad (3)$$

All of these reactions can take place in parallel at the cathode since their reduction potentials are quite close. Although initially there is no zinc present in the solution, it is gradually generated by dissolution of the anode material.

$$Zn \longrightarrow Zn^{2+} + 2e \quad (4)$$

$$Zn^{2+} + SO_4^{2-} \rightleftharpoons ZnSO_4 \quad (4a)$$

After all sulfuric acid is removed from the solution by reactions (1), (2), and (4a), the formation of ZnO or $Zn(OH)_2$ can take place at the anode.

$$Zn + H_2O \longrightarrow ZnO + 2\,H^+ + 2e \quad (5)$$

## 2. Experimental

In the preliminary experiments, a mixture of normal $Eu_2O_3$ (6.796 g) and $Gd_2O_3$ (0.404 g), which is representative of the amounts of material used in the $^{153}Gd$ production, was dissolved in 250 mL of 1 N $H_2SO_4$, mixed with 750 mL of $H_2O$, and placed in the electrolytic cell shown in Fig. 1. Two zinc rods served as the electrodes (1.56 cm diam by 8.57 cm wetted length immersed in 1-L solution, the electrolytic surface area being 42 $cm^2$ per electrode). A gas-dispersion tube was inserted through the center of the cell. The end of the tube was immersed in a small well atthe bottom of the vessel. The function of this device was twofold: (1) to supply argon purge gas to the cell to keep the electrolyzed solution oxygen free and mixed and (2) to serve as a filter-siphon for transferring the solution for further treatment after electroreduction. A water jacket kept the temperature constant at 23 $\pm$ 1°C. A Lambda power supply (Model LK 350 FM) was used as a controlled-current or controlled-voltage source. During the electrolysis, the polarity of the electrodes was switched periodically to avoid passivation of the electrode surface and to ensure a parallel degradation of both electrodes, thus prolonging their useful lifetimes over several electroreductions.

## 3. Results and Discussion

Constant Voltage. Two runs were performed by keeping the cell voltage constant at 13.5 V and 18 V, respectively. Polarity of the electrodes was switched every 15 min. A 15-mL sample was withdrawn every 30 min and analyzed for the europium, gadolinium, and zinc content. The acidity was determined either by titration or by measuring the pH of the sample solution.

The results are shown in Fig. 2 (a and b) for the 18-V run. The results for the 13.5-V run are very similar to the results at 18 V. The concentration of europium in the solution decreases exponentially approaching the zero value after about 5 h of electrolysis at 18 V and 7 h at 13.5 V. The concentration of $Zn^{2+}$ increases with time and reaches a steady-state value after approximately 3 h (approximately 5 mg/mL for 18 V and approximately 4.5 mg/mL for 13.5 V), and the pH increases from approximately 1.5 to approximately 6 in 4 h and then

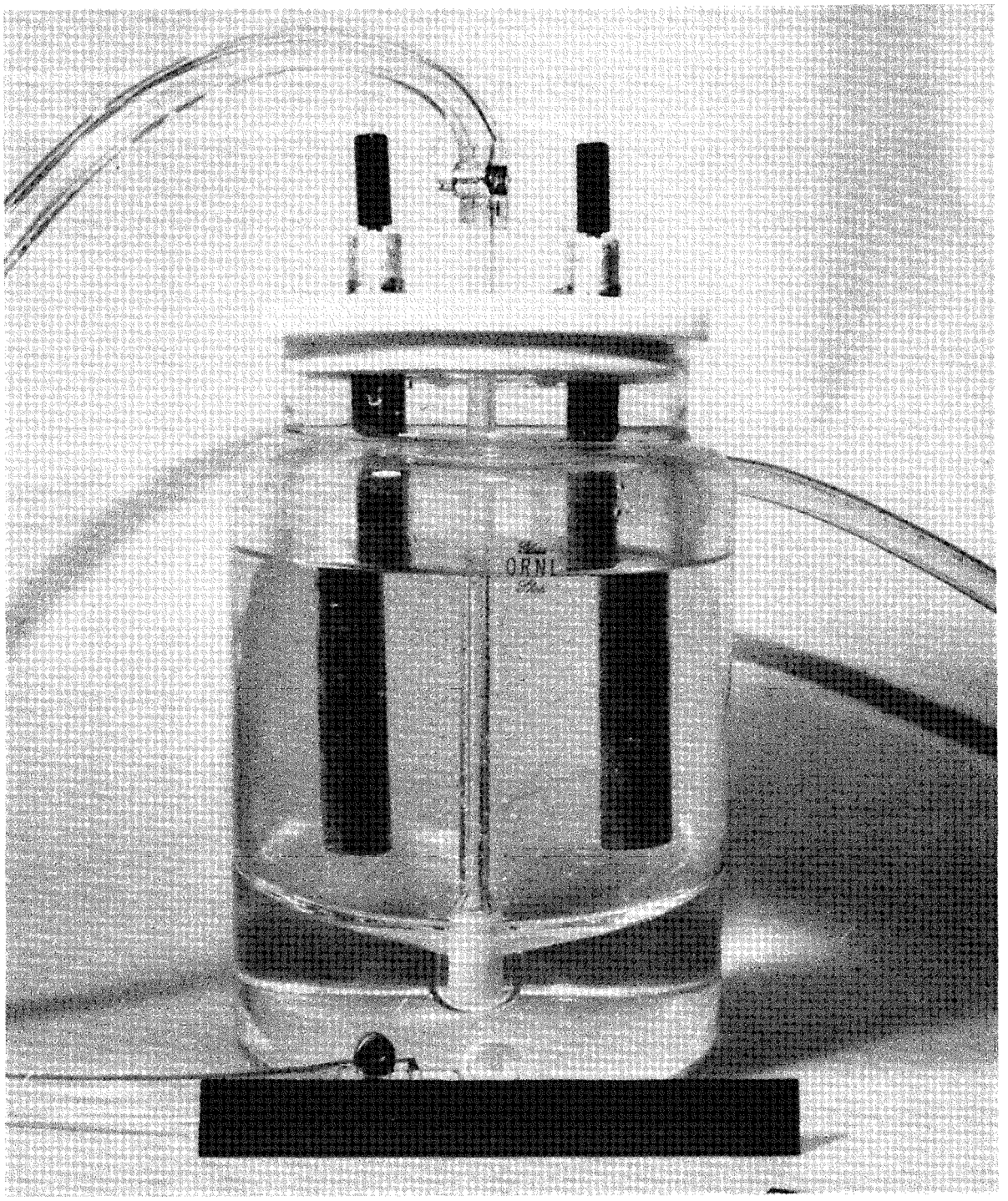



Fig. 1. The electrolysis cell

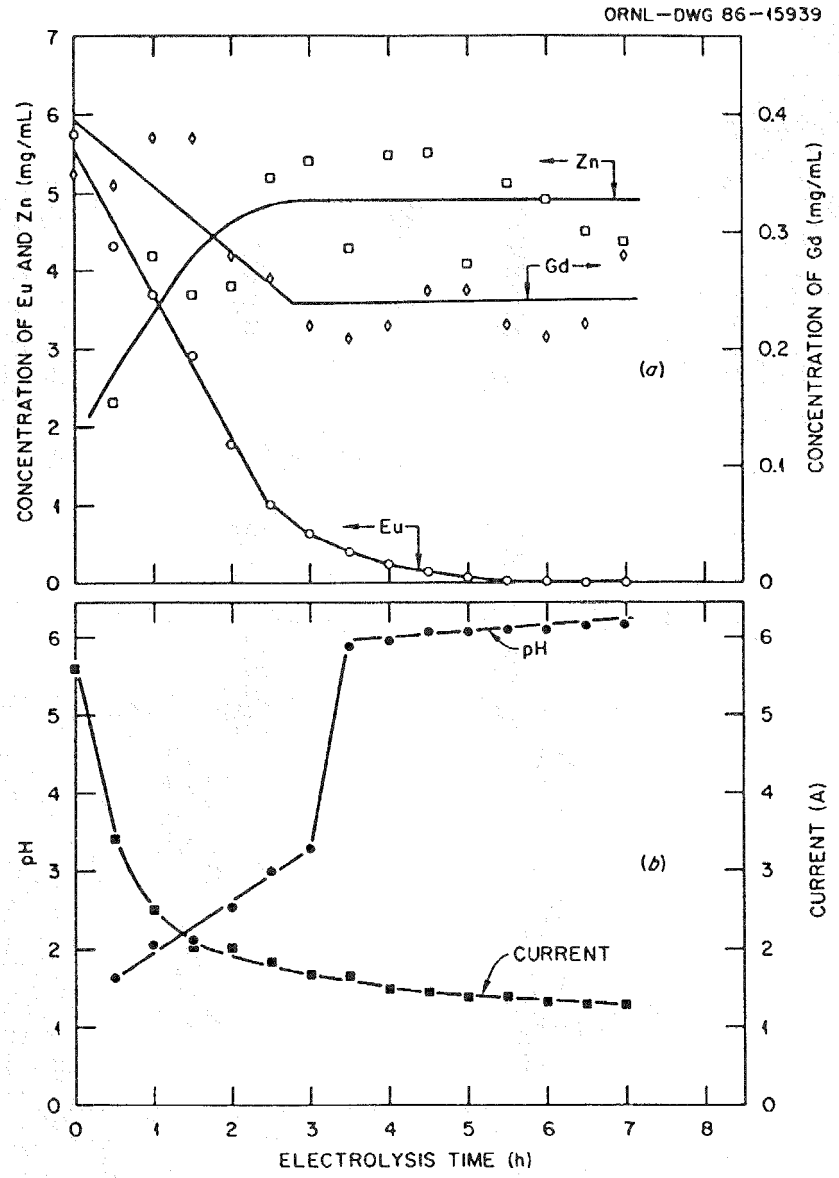



Fig. 2. Constant voltage at 18 V; voltage polarity reversal every 2 min

a. Time dependence of europium (○), gadolinium (◊), and zinc (□) concentrations on the electrolysis time.

b. Solution pH (●) and cell current (■).

remains practically constant. An unexpected feature of the electrolysis at constant voltage is the drop in the gadolinium concentration by about 30%, which takes place within the first 2 to 3 h of electrolysis. The initial cell current is 5.5 A and 3.85 A, dropping off exponentially to reach 1.25 A and 1.0 A for 18 V and 13.5 V, respectively.

It is not clear what is causing the loss in gadolinium during the constant potential electroreduction. It can be speculated that because of the high-current density a local increase in the pH of the solution adjacent to the electrode may have caused partial hydrolysis of gadolinium and its coprecipitation with europium sulfate.

Constant Current. In constant current experiments, a value of 1.25 A was chosen because it appears that at this level no loss of gadolinium would take place.

Three constant current experiments were carried out: (1) polarity switch every 15 min (Fig. 3), (2) polarity switch every 2 min (Fig. 4), and (3) polarity switch every 2 min with 5 mg/mL of $Zn^{2+}$ added to the starting solution (Fig. 5). The results are given in the figures.

There is no significant difference for Experiments 1 and 2, as shown in Figs 3 and 4. In both cases, the europium concentration approaches the zero value after about 7 h. The concentration of gadolinium is not affected. The concentration of zinc reaches a steady-state value of about 5 mg/mL after 4 h, and the pH of the solution reaches the value of approximately 6 after 5 to 6 h of the electrolysis.

Addition of 5 mg/mL of zinc is detrimental to the performance, as shown in Fig. 5. The concentration of europium decreases at a slower rate than in the initial absence of zinc, probably because of the increased competition of Reaction 3 to the europium reduction (Reaction 1). The solution remains acid during the experiment, indicating that the reduction of zinc also competes with hydrogen evolution (Reaction 2). The higher hydrogen ion concentration (acidity) is most likely the cause of the lower voltage during this electrolysis than in the case without added zinc.

The conditions in Fig. 4 were finally adopted for the $^{153}Gd$ production. Cell voltages of the two production runs in the hot cell

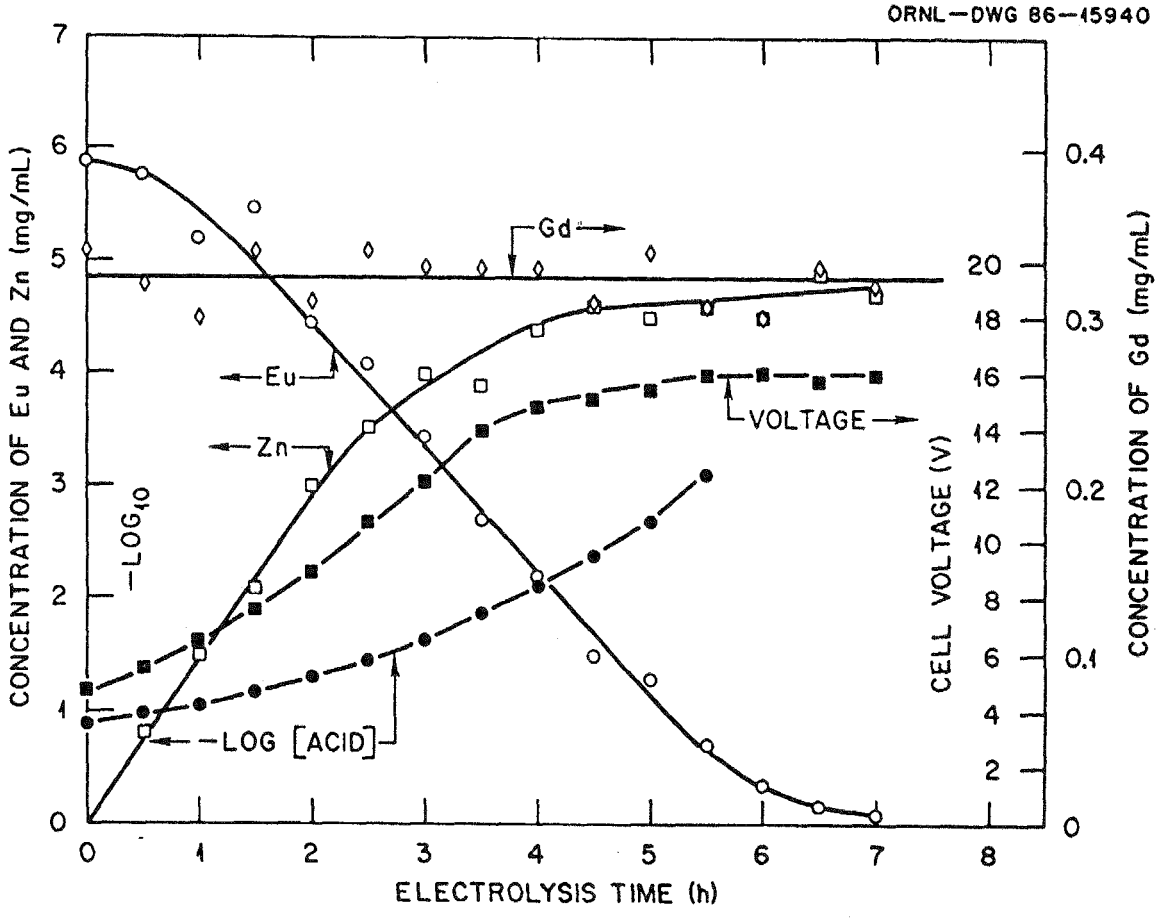



Fig. 3. Constant current at 1.25 A, polarity reversal every 15 min. Time dependence of europium (○), gadolinium (◊), and zinc (□) concentrations, cell voltage (■), and free acid (●) concentration.

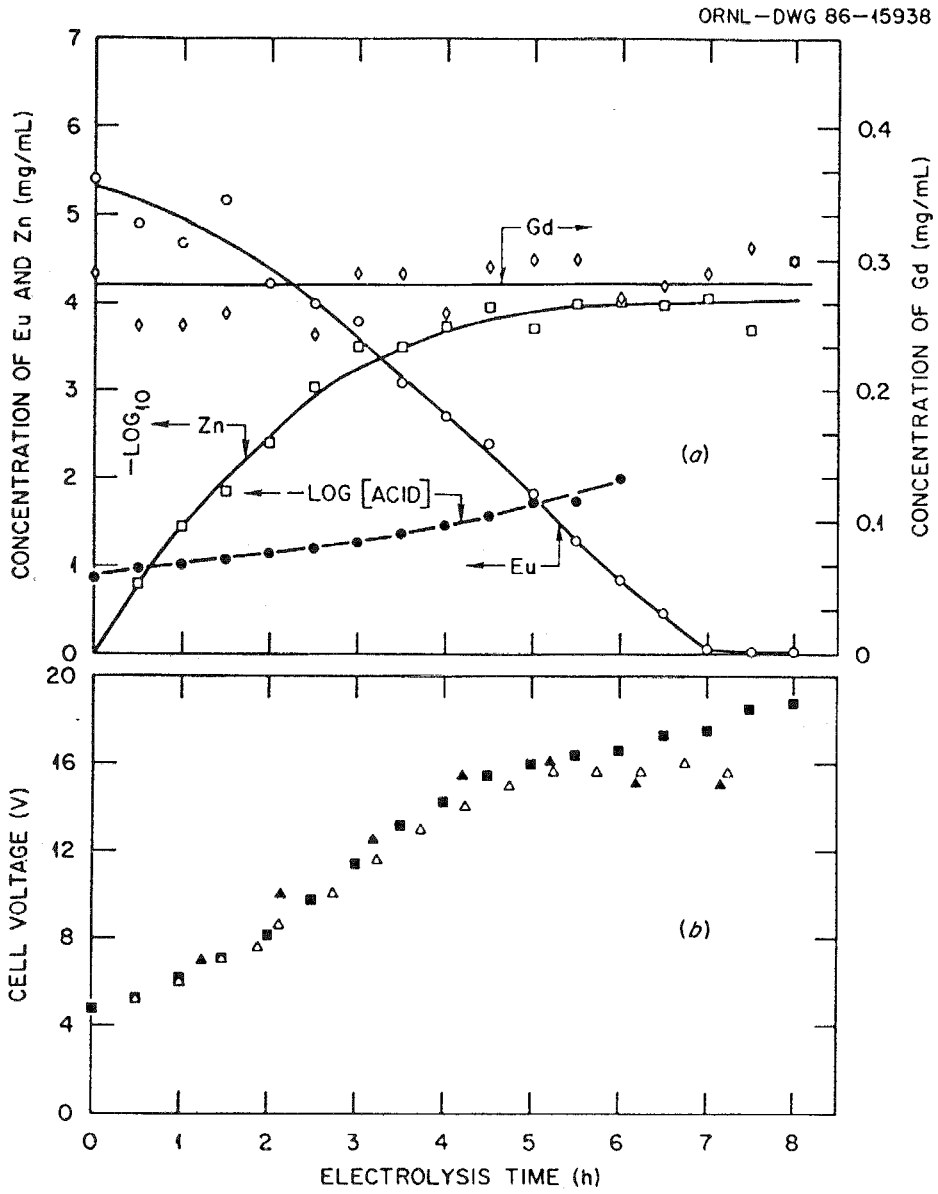



Fig. 4. Constant current at 1.25 A, polarity reversal every 2 min

a. Time dependence of europium (○), gadolinium (◊), and zinc (□) concentrations, and free acid (●) concentration.

b. Cell voltage values of the experimental (■) and the production (▲,△) cell.

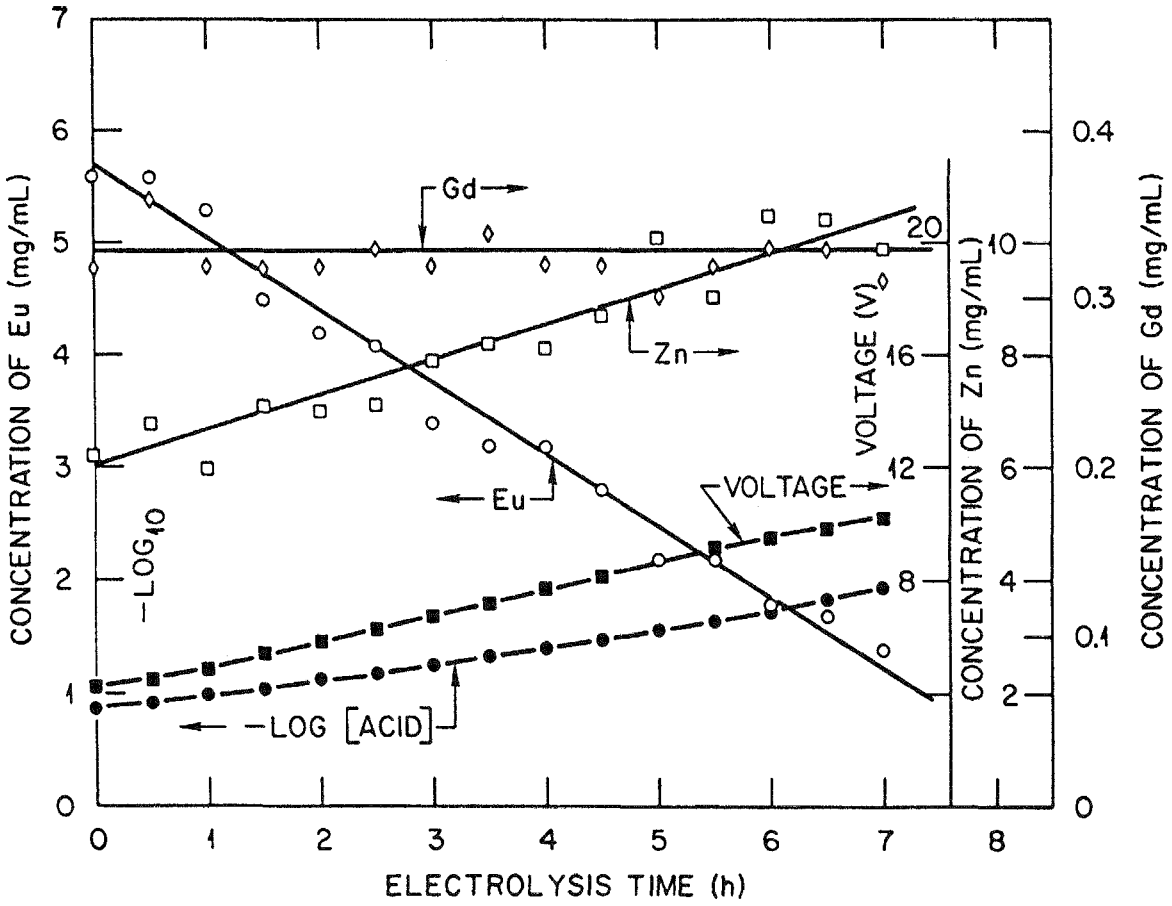



Fig. 5. Constant current at 1.25 A, polarity reversal every 2 min, 5 mg/mL $Zn^{2+}$ added. Time dependence of europium (○), gadolinium (◊) and zinc (□) concentrations, cell voltage (■) and free acid (●) concentration.

are given in Fig. 4b. The higher voltage values for the test run by the end of the process can be attributed to the removal of samples for analysis. A smaller electrode area was available to carry the same current, resulting in a higher current density and somewhat higher resistance.

Although the electroreduction significantly shortened the processing time, the process itself eventually became bottleneck. To avoid this problem, two additional electrodes were added to the original cell design so that the cell current could be doubled and the electrolysis time reduced using the same current density. Two test runs on such a modified cell at a current of 2.5 A showed that in 4 h essentially the same results were obtained as in 7 h using the original cell.

In the first four-electrode run, the cell voltage increased very rapidly so that in about 2.5 h the power supply reached the saturation voltage of 20 V, and the current gradually dropped to 2.2 A (Fig. 6a). For the second run, more sulfuric acid was added (300 mL of 1 N $H_2SO_4$ plus 700 mL of $H_2O$, compared to 250 mL of 1 N $H_2SO_4$ plus 750 mL of $H_2O$ for previous runs) to increase the conductivity of the cell solution which would allow a current of 2.5 A to pass without causing the power supply to reach its limit. The results are shown in Fig. 6b. There is apparently no detrimental effect of this slightly increased acidity. The only noticeable difference is a higher zinc content in the more acidic run. A higher increase in acidity should be avoided, since the preliminary experiments indicated a lower rate of europium removal. Apparently, higher acidity enhances the dissolution of zinc and $Zn^{2+}$, and the rate of both reactions (2) and (3) is increased to the expense of reaction (1).

In all the experiments, some zinc is lost from the electrodes. This happens because some zinc dissolves as $Zn^{2+}$ and some deposits at the anode in fine crystallites of elemental zinc which fluff off the electrodes as the polarity changes. In one example (conditions: 13.5-V constant voltage), a total of 9 g (4.5 g/electrode) of zinc was lost from the electrodes in the 7-h run, 5.5 g of which ended up in the solution as $Zn^{++}$ and about 3.5 g precipitated out as elemental Zn. In

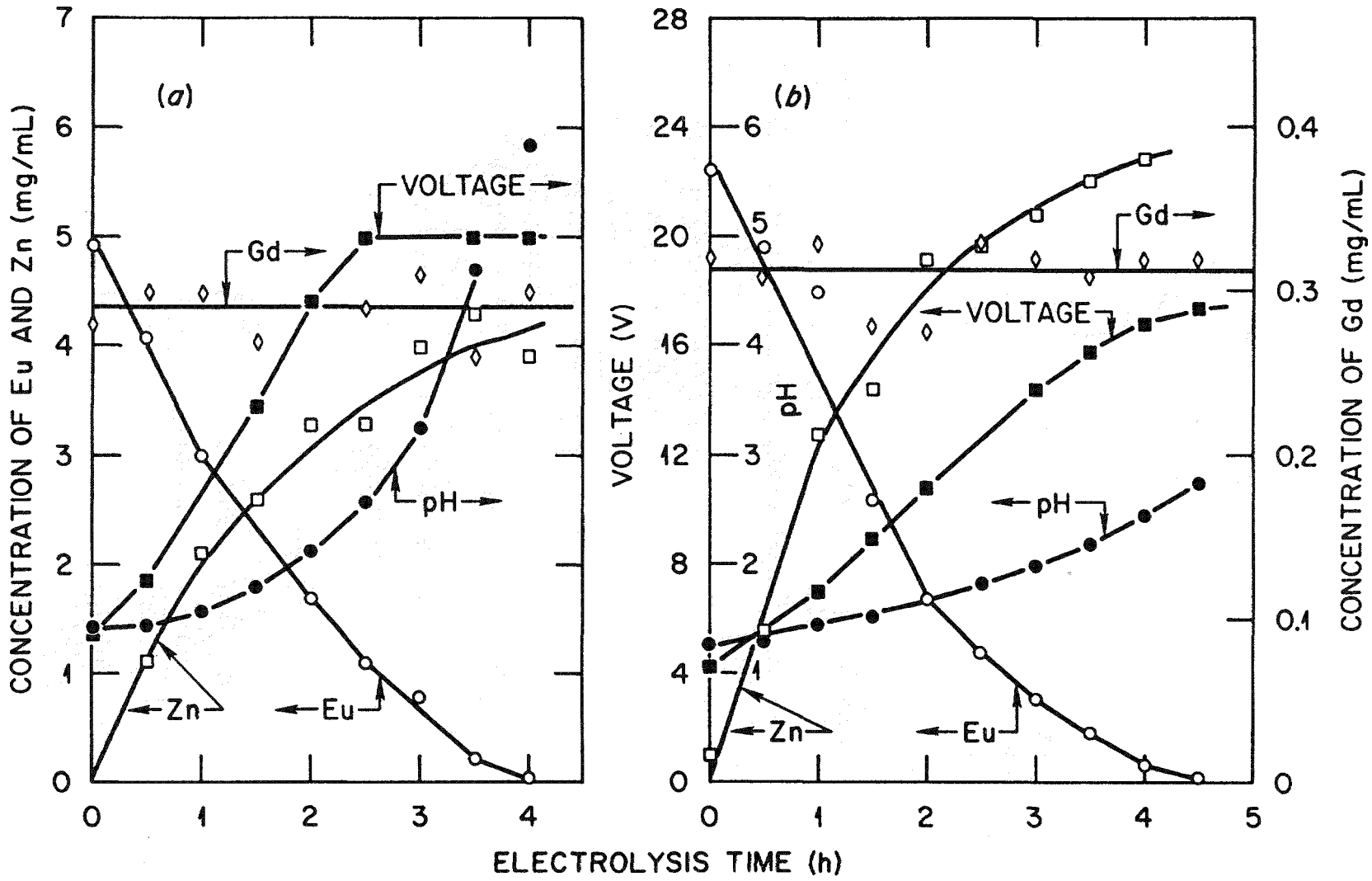



Fig. 6. a. Performance of a four-electrode cell.

b. Performance of a four-electrode cell with slightly increased acidity. Time dependence of europium (○), gadolinium (◊) and zinc (□) concentrations, cell voltage (▪) and free acid (•) concentration.

the experiment with four electrodes (Fig. 6b), zinc loss from all four electrodes was about 10 g (2.5 g per electrode), where about 5.5 g were dissolved as $Zn^{2+}$ and 4.5 g precipitated as the metal.

**Production Improvements.** Before the application of electroreduction separation in the gadolinium process, the product yield was approximately 1.51 Ci of $^{153}Gd$ per gram of irradiated normal $Eu_2O_3$. During the initial phase of implementing the electroreduction process in our production efforts, the electrolysis was carried out at constant voltage rather than constant current. These 38 constant-voltage runs increased the product yield to an average of 2.04 Ci/g. After switching to the constant-current mode of electrolysis, the average product yield for more than 50 runs has been better than 2.6 Ci/g.

## 4. Other Applications of the Electroreduction Process

Along with europium, samarium and ytterbium are the only lanthanide elements with a stable two-valent form. Amalgam extraction was successfully used to separate $^{142}Sm$ from $^{142}Pm$ and to separate $^{167}Yb$ and $^{169}Yb$ from $^{167}Lu$ and $^{169}Lu$ obtained from irradiated tantalum[4]. Ball and Yntema[6] successfully separated ytterbium from a mixture of ytterbium, erbium, and thulium by reducing Yb (III) to Yb (II) in a sulfuric acid solution and precipitating it as the insoluble $YbSO_4$. Therefore, electroreduction with zinc electrodes may also work for removal of samarium and ytterbium from mixtures of other rare-earth elements. Since the standard potentials for the Sm (III)/Sm (II) and Yb (III)/Yb (II) couples are considerably more negative compared to that of Eu (III)/Eu (II) couple, it can be expected that their separation from other rare earths may not be as effective as that of europium (see Table 1).

Table 1. Standard potentials for rare-earth elements[7]

| Couple | Standard potential (V) |
|---|---|
| Eu (III)/Eu (II) | -0.35 |
| Yb (III)/Yb (II) | -1.15 |
| Sm (III)/Sm (II) | -1.2 to -2.0 |
| R.E. (III)/R.E. (O) | -2.1 to -2.4 |

In some organic solvents, the difference of the reduction potentials for the R.E. (III)/R.E. (II) couples and the R.E. (III)/R.E. (O) couples is much bigger than that in water[7]. Use of these solvents instead of water may be worth exploring for electroreductive separation of ytterbium and samarium from other rare-earth elements.

## 5. Conclusions

Zinc electrodes were efficiently used for reducing the bulk concentration of europium in a europium-gadolinium mixture by a factor of approximately 100. As a result, the ion-exchange separation of europium and gadolinium was very efficient, and the yield of $^{153}Gd$ per gram of irradiated $^{151}Eu$ was increased by greater than 70%. The processing capacity was increased by a factor of four.

REFERENCES

1. a. J. C. Posey, Use of High-Pressure Ion Exchange for the Production of Gadolinium-153, Status Report, ORNL/TM-9988, April 1986.

   b. L. C. Brown and A. P. Callahan, High Pressure Ion-Exchange Column Design for Remote Hot-Cell Operation, ORNL/TM-4583, May 1974.

2. F. N. Case, E. H. Acree, and N. H. Cutshall, Production Study of Gadolinium-153, ORNL/TM-2632, August 1969.

3. L. F. Yntema, Journal of American Chemical Society 52, 2782 (1930).

4. A. F. Novgorodov and V. A. Khalkin, Radiokhimiya 10, 554 (1968).

5. "Separation of Samarium, Europium and Gadolinium from Each Other," Japanese Patent, Jpn. Kokai Tokkyo Koho JP 59 76,838 [84 76,838], cf. C.A. 101, 95193 .

6. R. W. Ball and L. F. Yntema, Journal of American Chemical Society 52, 4264 (1930).

7. Encyclopedia of Electrochemistry of the Elements, Ed. A. J. Bard, Marcel Dekker, Inc., 1976, Vol. 6, Chapter 2.

ORNL/TM-10284
Dist. Category UC-4

## INTERNAL DISTRIBUTION

1. W. S. Aaron
2. H. L. Adair
3. B. L. Byrum
4. A. P. Callahan
5. J. R. DeVore
6. L. D. Eyman
7. D. E. Ferguson
8. K. W. Haff
9. F. J. Homan
10. M. W. Kohring
11. E. Newman
17. J. C. Posey
18-22. D. W. Ramey
23. C. R. Richmond
24. J. A. Setaro
25. F. J. Schultz
26. C. D. Scott
27. W. D. Simpson
28. S. H. Stow
29. G. W. Strandberg
30. J. H. Swanks
31. J. A. Tompkins
32. D. B. Trauger
33. J. S. Wike
34. S. E. Williams
35. R. S. Wiltshire
36. Central Research Library
37. Document Reference Section
38-39. Laboratory Records
40. Laboratory Records - RC
41. ORNL Patent Office

## EXTERNAL DISTRIBUTION

42. J. A. Lenhard, Assistant Manager for Energy Research and Development, Oak Ridge Operations Office, U.S. Department of Energy, Post Office Box E, Oak Ridge, TN 37831.

43. J. N. Maddox, Office of Health and Environmental Research, ER-73, G226 GTN, U.S. Department of Energy, Washington, D.C. 20545.

44. L. K. Price, Oak Ridge Operations Office, U.S. Department of Energy, Post Office Box E, Oak Ridge, Tennessee 37831.

45. T. C. Quinby, Iso-Clear Systems Corporation, 601 Scarboro Road, Oak Ridge, Tennessee 37830.

56. J. S. Robertson, Office of Health and Environmental Research, U.S. Department of Energy, Washington, D.C. 20543.

57. S. J. Wolfe, Oak Ridge Operations Office, U.S. Department of Energy, Post Office Box E, Oak Ridge Tennessee 37831.

57-202. Given distribution as shown in TIC-4500 under UC-4 - Chemistry.