Solids
- I. $NaOH \cdot H_2O$ at 50°: NaOH at 75°
- II. hydrated compound with probably 5 or 6 moles of Na_2O per UO_3, at 50°; not studied at 75°
- III. solid solution with $Na_2O:UO_3$ mole ratios from ~8:11 to ~1:3 at 50°; same lower limit at 75°
- IV. compound, probably anhydrous, $Na_2O \cdot 6UO_3$, at 50° and 75°; possibly with slight solid solution on either side of this formula
- V. solid solution with $Na_2O:UO_3$ mole ratios from ~1:12 to ~1:18 at 50°; ~1:16 at 75°
- VI. $UO_3 \cdot 2H_2O$, from 25 to 75°.

Invariant liquids (% Na_2O)

	50°	75°
L + I	45.2	(58.5)[24]
L + I + II	45.2	
L + II + III	42.8	
L + III + IV	0.0106	0.0038
L + IV + V	.00058	.00014
L + V + VI	.00012	.00006

At the higher temperature the lower limit of the solid solution III appears to be about the same as at 50°. Solid IV remains close to the formula $Na_2O \cdot 6UO_3$ in composition, with very little, if any, tendency to take up adjacent solids in solid solution. The composition spread of solid V is possibly becoming narrower with increasing temperature. The fact that the sodium oxide concentrations of the invariant liquids involving the solids III–VI are lower at 75° than at 50° suggests that the actual solubilities of the various solids are decreasing with rising temperature. A solid of approximately the composition $Na_2O \cdot 16UO_3$ is formed at a sodium hydroxide concentration of $\sim 4 \times 10^{-5}$ *M* at 50° and $\sim 2 \times 10^{-5}$ *M* at 75°; and the solid $Na_2O \cdot 6UO_3$ requires NaOH at $\sim 2 \times 10^{-4}$ *M* at 50° but only 4.5×10^{-5} *M* at 75°

Although the solid phases found here to be the equilibrium solids in the aqueous system are not necessarily the same as those to be expected in the anhydrous system Na_2O–UO_3 at high temperatures, the results do seem to rule out the existence of a simple "mono-uranate," or $Na_2O \cdot UO_3$, at least as an equilibrium phase in the aqueous system, despite the formation of the unexpected solid II with a much higher $Na_2O:UO_3$ ratio. As for the familiar "diuranate" formula, $Na_2U_2O_7$, or $Na_2O \cdot 2UO_3$, we see that in these isotherms at least, this is merely a point in the continuous range of compositions comprising the principal solid solution III, although it may be that such a compound becomes a distinct phase in itself at much higher temperature. In some ignitions of wet mixtures of Na_2O and excess UO_3, made for the purpose of testing the result for possible use in analysis of wet residues, it was observed that the weight of the residue obtained at 1000° could be accounted for best (but roughly) in terms of a mixture of $Na_2U_2O_7$ and U_3O_8.

On the basis of the present results, then, all the formulas of sodium uranates previously reported (references 1, 4, 9, 10, 11) through the direct or indirect analysis of precipitates obtained from aqueous solutions, would have to be explained as representing portions of a solid solution, mixtures of equilibrium solids, or decomposed (hydrolyzed) residues of these. Thus the reported $Na_2O:UO_3$ mole ratios 1:2, 9:20, 3:7 and 2:5 would represent regions of the solid solution III; the "compounds" with ratios 2:7 and 1:4, if they were equilibrium solids, would be mixtures of the solids III and IV; and the "compounds" 1:7 and 1:8 probably represent solid IV, or $Na_2O \cdot 6UO_3$, partly decomposed by washing into a mixture of solids IV and V. From the behavior encountered in the present direct study of the system, and from the phase equilibria established, it may be said that it is highly improbable that equilibrium could be expected to hold in ordinary precipitations such as those used in attempting to determine the compositions of the solids by direct analysis or those occurring during the titration of uranyl salt solutions with alkali.

NEW YORK, N. Y.

[24] Seidell (ref. 22), Vol. 1, p. 1284; by interpolation.

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

The Separation of Europium from Samarium by Electrolysis[1]

BY E. I. ONSTOTT

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Europium is efficiently separated from samarium by electrolysis of the europium citrate complex ion at a lithium amalgam cathode. Samarium oxide containing 1.6% europium oxide is quantitatively freed of the europium with one electrolysis. Under optimum conditions, 99.9% of the europium is removed into the mercury phase, while less than 10% of the samarium is removed. Parameters affecting the electrolysis are discussed.

The separation of europium from samarium is not difficult, since europium is easily reduced to the divalent state.[2] However, an efficient method of separating a small amount of europium from a relatively large amount of samarium has not previously been reported.

Marsh[3] has used sodium amalgam to separate europium from samarium, but his method depends on the selective oxidation of samarium after extraction of both samarium and europium. Several extractions are necessary in order to obtain pure samarium. The ion-exchange separation of europium from samarium is possible, but not practical.[4]

McCoy[5] previously has shown that the mercury cathode separation of europium from samarium is practical. Actually the electrode employed by Mc-

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[1] Work done under the auspices of the Atomic Energy Commission.

[2] H. N. McCoy, THIS JOURNAL, **57**, 1756 (1935); **59**, 1131 (1937); L. F. Yntema, *ibid.*, **52**, 2782 (1930).

[3] J. K. Marsh, *J. Chem. Soc.*, 398 (1952); 531 (1943).

[4] B. H. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947); F. H. Spedding, E. I. Fulmer, J. E. Powell, T. A. Butler and I. S. Yaffee, *ibid.*, **72**, 4840 (1950); S. W. Mayer and E. C. Freiling, *ibid.*, **75**, 5647 (1953).

[5] H. N. McCoy, *ibid.*, **63**, 3432 (1941).

Coy was a potassium amalgam cathode, since a large amount of potassium citrate was used to complex the rare earth ions and prevent hydroxide precipitation in the alkaline solutions which were electrolyzed.

The lithium amalgam cathode was chosen for this work, since it is known to have the highest amalgam potential of the alkali and alkaline earth elements.[6] A higher cathode potential allows a more nearly complete removal of europium from the electrolyte phase, and therefore a better separation from samarium is expected. Just why europium and samarium should be separated by this method is not apparent from a consideration of their oxidation–reduction potentials alone, since both are assumed to have about the same value.[7] However, the free energies of amalgamation must also be considered, and there a real difference is apparent. In the metallic state the atomic radius of europium is comparable to that of barium[8] while that of samarium is in line with the other rare earths.[9]

The lithium (or potassium) amalgam cathode serves another useful purpose in that no external control of the applied voltage is required for a reasonably constant cathode potential. Such behavior is general for amalgam cathodes in which the solute metal has a high solubility in the amalgam phase and the solute metal ion has a high solubility in the water phase. A relatively large change in metal ion concentration in either the amalgam or the water phase reflects a small change (a few millivolts) in the equilibrium electrode potential. Hence, such an electrode behaves as a buffer electrode and will maintain a reasonably constant potential as long as an external potential is applied which is in excess of the equilibrium potential.

Experimental

The Sm_2O_3–Eu_2O_3 used was obtained from Société de Produits Chimique des Terres Rares. Spectrographic analysis by O. R. Simi of this Laboratory showed it to contain about 1% Eu_2O_3, but no other rare earths were detected. Other minor impurities were Na, Mg and Ca, each <0.1%. A more accurate value for the Eu_2O_3 content of the stock was obtained after electrolyzing several solutions, then combining the enriched Eu fractions. By a combination of tracer, gravimetric and colorimetric[10] analyses, the Eu_2O_3 content was found to be 1.6%.

The lithium salts were obtained from the Fisher Scientific Co., E. H. Sargent and Co., and the Lithium Corporation of America, Inc. Citric acid was obtained from Eastman Kodak Co.

Stock solutions were made[11] by heating freshly ignited Sm_2O_3–Eu_2O_3 with a slight excess of 20% acetic acid (several hours are needed for complete conversion if the solution is not boiled), then adding the hot solutions to lithium citrate (citric acid plus lithium hydroxide was used also). After adding lithium hydroxide to adjust the *p*H, the solutions were diluted to volume. When potassium citrate was used, the *p*H was adjusted with K_2CO_3.[11]

The electrolysis vessel was a 600-ml. beaker (mercury area, 55 cm.^{2}) modified by attaching a stopcock to the bottom through a capillary tube, and attaching a capillary side arm between the stopcock and the beaker. Electrical contact to the Hg cathode was made by placing a Pt wire in the side arm. The anode was a Pt flag with about 30 cm.^{2} area directly in contact with the electrolysis solution.

Direct current was manually controlled with a selenium rectifier circuit. A Sargent cone drive motor was used to agitate the surface of the Hg at about 100 r.p.m. A cooling coil was placed in the beaker in order to keep the electrolyte temperature close to room temperature. Measurements of *p*H were made with a Beckman Model G *p*H meter. A Cary Spectrophotometer and a Beckman DU spectrophotometer were both used for the colorimetric measurements.

Cathode potential measurements were made with a Rubicon potentiometer and Beckman Type 1170 S.C.E. Direct insertion of the S.C.E. in the solution during the electrolysis gave measurements which were in error because of *IR* drop.[12] Current lines were eliminated by placing a glass sleeve directly on the cathode surface, then inserting the S.C.E. in the solution trapped by the sleeve. The amalgam potential was measured in the same manner except that the electrolysis was stopped and the rectifier leads were disconnected.

The Eu was followed with $Eu^{152,154}$ tracer by gamma counting with a high efficiency scintillation counter made by Group CMR-7 of this Laboratory. The counting vessel was a test-tube in which was placed a 10-ml. aliquot. Precision of counting was ±2%, but by choosing the proper tracer level, the accuracy of the determination of Eu removal was ±0.1%. The rate of electrolysis was determined by removing an aliquot during the electrolysis, counting it, then returning it to the solution as quickly as possible.

The electrolysis generally was continued until it appeared that the Eu removal had stopped, as measured by the tracer.

With Li^+ solutions there was not sufficient CO_2 absorption from the air to give a carbonate precipitate. However, with K^+ present, considerable rare earth carbonate precipitated after a few hours electrolysis time. Some finely divided Hg appeared in solutions electrolyzed at low C.D. or low *p*H. A very thin layer of yellow salt ($EuCO_3$?) was present on the bottom of the beaker under the Hg when solutions containing K^+ were electrolyzed.

The Hg phase was separated as completely as possible by draining it through the stopcock. Any solid amalgam and the beaker walls were washed with distilled water and these washings added to the Sm phase. Solids present, such as finely divided Hg and precipitated salt beneath the Hg and at the junction between the Hg and the solution, were added to the Eu fraction.

The Eu fraction was recovered from the mercury by first treating the amalgam with water, then with dilute nitric acid. Ignition of the precipitated oxalate to the oxide gave the total of Eu_2O_3 and Sm_2O_3, and the Eu_2O_3 was then determined by counting. The Sm from the citrate solution was recovered by acidifying the solutions until about 0.1 *M* free acid was present, then precipitating the oxalate with subsequent ignition to the oxide. With Li^+ present there was practically no co- or post-precipitation of impurities, but with K^+ present, KHC_2O_4 seriously post-precipitated.

Discussion

The Cathode Potential.—The cathode potential at the start of an electrolysis was about -1.6 volts *vs.* S.C.E., but after a few minutes it increased to a value of < -2 volts, and remained reasonably constant throughout the electrolysis (Table I). The current was equally constant and did not vary appreciably unless the temperature changed by several degrees.

The overpotential of the lithium amalgam cathode was measured and found to be generally less than 100 mv. for applied cell potentials of 4.8 to 8.7 volts and current densities of 0.0027–0.0162 amp./cm.^{2}.

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(6) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, p. 489.

(7) D. M. Yost, H. Russel, Jr., and C. S. Garner, "The Rare Earth Elements and Their Compounds," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 54.

(8) L. Pauling, THIS JOURNAL, **69**, 542 (1947).

(9) F. H. Ellinger and W. H. Zachariasen, *ibid.*, **75**, 5650 (1953).

(10) T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1950).

(11) H. N. McCoy, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 65.

(12) J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1953, p. 264.

In several electrolyses at higher current densities, solid lithium amalgam was observed when the main stock solution was electrolyzed for several hours (Table I). The two-phase amalgam potential was measured to be -2.285 ± 0.005 volt *vs.* S.C.E. (current off). Well-formed crystals of potassium amalgam were also observed after electrolysis of the potassium citrate solution at the higher current density, but no potential measurement was made.

TABLE I

SEPARATION EFFICIENCIES

Composition of solutions: Sm^{+++}, 0.447 *M;* Eu^{+++}, 0.0072 *M;* citrate, 1.56 *M* except where noted; acetate, ~ 1.5 *M;* Li, ~ 5.0 *M* except where citrate variable; solution, 200 ml.; temp., 20–25°; Hg, 8–900 g.

Cath. pot. (-volts) *vs.* S.C.E.	Amp. hr. and C.D., amp./cm.^{2} × 10^3	Initial *p*H	% Eu removal	% Sm removal	Rate plot
2.0 –2.1	2.1 at 1.8	9.8	95.4	2.4	
2.05–2.12	3.8 at 2.7	9.8	98.8	4.8	I
2.06–2.16	7.5 at 5.4	9.8	93.9	4.0	G
2.27–2.37^a	12.5 at 9.0	9.8	99.4	6.4	H
2.28–2.38	14.7 at 12.6	9.8	99.2	11.3	E
2.3 –2.4	22.5 at 16.2	9.8	99.9	26.5	
[2.3 –2.4 2.27–2.37^a]	[7.4 at 16.2 7.8 at 9.0]	10.1	99.8	7.8	F
[2.3 –2.4 2.1 –2.2^a]	[4.6 at 6.4 3.0 at 3.6]	9.8	99.9	7.7	
1.97–2.4	17.2 at 12.6	6.0	98.3	47.0	
[2.1 –2.4 2.27–2.37^a]	[3.9 at 12.6 8.0 at 9.0]	7.2	99.3	30.7	
[2.3 –2.4 2.2 –2.3^a]	[4.6 at 12.6 6.2 at 7.2]	8.3	99.8	9.6	
2.3 –2.4^a	17.0 at 12.6	8.4^b	99.9	21.8	D
2.3 –2.4	5.1 at 12.6	8.6^c	99.9	7.4	B
2.3 –2.4	5.7 at 12.6	9.8^d	94.7	17.0	C
2.16–2.26	6.8 at 16.2	8.3^e	74.2	1.8	J
2.05–2.2	12.8 at 9.0	8.3^e	59.4	0.7	K
2.3 –2.4	5.7 at 12.6	9.0^f	99.6	10.1	A

[a] Hg replaced after about 95% of Eu removed; during second part of electrolysis, C. D. (and cath. pot.) sometimes changed. [b] Citrate, 1.05 *M;* Li^+, ~ 3.7 *M.* [c] Citrate, 0.78 *M;* Li^+, ~ 2.9 *M.* [d] Citrate, 0.55 *M;* Li^+, ~ 2.2 *M.* [e] Li^+ replaced by K^+. [f] Citrate, 0.89 *M;* Li^+, ~ 3.7 *M;* Sm^{+++}, 0.426 *M;* Eu^{+++}, 2.3×10^{-4} *M.*

Separation Efficiency.—It is seen from the data in Table I that a higher cathode potential gives a better removal of europium from the electrolyte phase. However, for the same cathode potential, lithium amalgam is better than potassium amalgam as a cathode material. This phenomenon is attributed to a larger ΔF of amalgamation of europium with lithium amalgam than with potassium amalgam.

Any change in a parameter which lowers the citrate ion concentration gives a poorer separation, since relatively more samarium is removed to the mercury phase. Lowering the *p*H of the electrolyte or lowering the citrate concentration directly decreases the separation efficiency, as can be seen in Table I. The effect of lowering the ligand concentration is that of lowering the potential required to electrolyze the samarium citrate complex ion (assuming ideal behavior).

Another parameter which influences the separation of europium is the amount of mercury used. According to the Nernst equation, the equilibrium potential of the $Eu(Hg)/Eu^{+++}$ electrode depends on the ratio of the activity of europium ion in mercury to that in the water phase; thus by keeping the concentration of europium in the mercury low, a better separation is expected. This effect is demonstrated by experiments shown in Table I in which the cathode mercury was replaced with clean mercury after about 95% of the europium had been removed.

The efficiency of separating a very small amount of europium from samarium was tested by electrolyzing a solution made from samarium oxide containing 0.054% europium oxide. As can be seen by the last entry in Table I, the efficiency is nearly as high as with higher europium concentrations. In this latter case the europium content of the samarium-rich fraction was reduced to <0.0003% europium oxide in samarium oxide.

Rate of Electrolysis of Europium.—Experimental conditions at the cathode can be pictured as follows. The voltage and current are sufficiently high and the europium ion concentration is sufficiently low so that all europium ions reaching the cathode surface are transferred to the mercury phase. The current is high (compared to the diffusion current for the reduction of europium ion) since samarium, lithium, hydrogen and probably citrate ions[13] are simultaneously electroreduced with europium ion. Migration of europium ion is eliminated because of the high salt concentration. Hence, replenishment is effected primarily by diffusion, and the rate of electrolysis should be independent of both voltage and current until the concentration of europium in the mercury phase becomes high enough to raise the equilibrium potential of the $Eu(Hg)/Eu^{+++}$ electrode close to the value of the working voltage of the cathode.

Fick's first law may be written[14] to a good first approximation as

$$-\frac{dC}{dt} = \frac{DA}{V\delta}(C - C^e) \qquad (1)$$

where C is the concentration of diffusing ion in the electrolyte, C^e is the concentration at the electrode surface, t is the time, D the diffusion coefficient, A the electrode area, V the volume of electrolyte and δ the diffusion layer thickness. Equation 1 can be integrated after setting C^e equal to zero

$$-\ln\frac{C}{C^0} = \frac{DA}{V\delta}t \qquad (2)$$

where C^0 is the initial concentration. A plot of ln C *vs.* t should give a straight line of slope $-DA/V\delta$, which can be interpreted to be the rate constant. Lingane[15] has used equation 2 in a different form wherein C was measured in terms of diffusion current. Such use was practical since only one electrode process was allowed to proceed, the reduction of copper ion, and thus in his experiments the concentration of copper ion was directly proportional to the current.

Rate data are plotted in Fig. 1. Three families of

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[13] S. Swan, Jr., "Electrolytic Reactions," "Technique of Organic Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1948, p. 183.

[14] J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p. 193.

[15] J. J. Lingane, THIS JOURNAL, **67**, 1916 (1945).

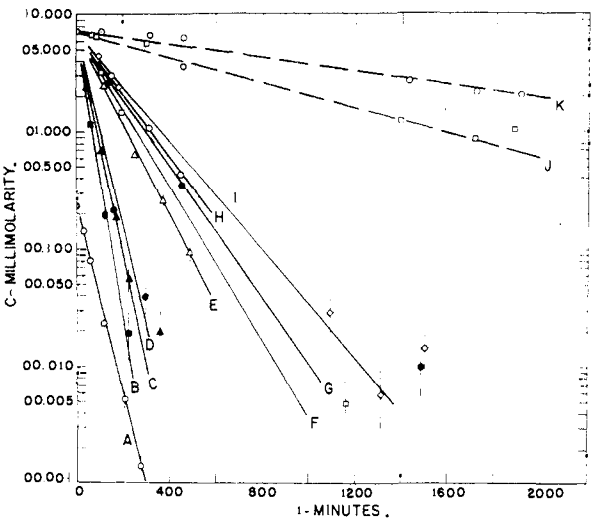

Fig. 1.—Rate of electrolysis of europium: size of symbols approximate accuracy of data. Plots described in Table I.

lines are apparent in which the value of the rate constant changes appreciably. The parameters which were experimentally changed for each family are as follows: Plots A, B, C, D, citrate ion concentration varied, current density constant; plots E, F, G, H, I, current density varied, citrate ion concentration constant, but higher than in plots A, B, C, D (solutions almost saturated with lithium citrate); plots J, K, lithium citrate replaced by potassium citrate, two different current density values.

The variation in the rate of electrolysis in plots E, F, G, H, I is not attributed to an effect of current density directly, but rather to the secondary effect of increased gas stirring with an increase in current. More hydrogen is evolved and consequently the diffusion layer thickness is reduced with the result that the rate of electrolysis is increased. Changing the current density by a factor of six resulted in a change in the rate constant by a factor of about two. The faster rate in the family of plots A, B, C, D, compared to family E, F, G, H, I, is attributed to the secondary effect of a difference in solution viscosity. The solutions electrolyzed in obtaining data in plots E, F, G, H, I were almost saturated with lithium citrate and quite viscous compared to solutions having an appreciably lower citrate concentration. It is seen that the increase in rate in plots A, B, C, D closely parallels a decrease in citrate concentration and expected decrease in viscosity.

Replacement of lithium ion with potassium ion results in a considerably lower rate of electrolysis (plots J and K). There is marked deviation from equation 2 in the initial part of electrolysis, so that it cannot be assumed to be valid. Probably the initial reaction is the preferential electrolysis of potassium ion until the potential of the cathode is sufficiently high to electrolyze europium. Thus the potential of the cathode is essentially the same as the equilibrium potential of the Eu(Hg)/Eu^{+++} electrode, and C^e in equation 1 cannot be assumed to be zero.

The diffusion coefficient of the europium citrate complex ion may be estimated from equation 2 if the diffusion layer thickness is known. Comparison of the value thus calculated to the value obtained by other experiments gives an idea of the validity of equation 2. By taking δ to be 5×10^{-3} cm.,[16] D is calculated to be 0.55×10^{-5} cm.^{2}/sec. for plot A. This value is about the right order of magnitude.[17]

Change in *p*H during Electrolysis.—Electrolytic solutions having an initial *p*H value of about 10 were found to decrease in alkalinity about 1.5 *p*H units during the first few hours of the electrolyses, but after this time the *p*H increased almost to its initial value, provided the C.D. was sufficiently high. If the C.D. was very low, there was only a decrease in *p*H. Solutions having an initial *p*H value of about 8 or less were found to increase in alkalinity (at high C.D. values) such that *p*H values of 9–10 were generally attained. The variation in *p*H is explained by the electrode reactions as follows: the anode reaction is that of oxidizing water to oxygen, and the net reaction produces hydrogen ions. Until the cathode reaches its equilibrium two-phase amalgam potential, the main process is that of electrolyzing lithium ion or potassium ion, and there is no change in *p*H due to the cathode reaction. The over-all change, then, due only to the above two reactions, is an increase in the acidity. However, if after the cathode reaches its equilibrium potential and hydrogen discharge starts, some citric acid is reduced,[13] then hydrogen ions are used up and an alkaline reaction is produced. Indeed, an appreciable amount of organic material was observed to float on all electrolyzed solutions except for two which were electrolyzed at low current density. In the latter case, probably the potential was too low to reduce the citric acid, and no alkaline reaction was produced. A low *p*H favors the electroreduction of organic acids, so that this fact perhaps explains why solutions having an initially low *p*H were found only to increase in *p*H during electrolysis.

Electrolysis of Samarium.—The amount of samarium which was electrolyzed into the cathode was generally less than 10% of that present in the electrolyte. However, in several experiments the amount was greater. Conditions favoring a higher samarium electrolysis are low citrate concentrations, low *p*H values or high cathode potentials.

Purification of Europium.—Thirteen enriched europium fractions were combined (0.12 Eu/Sm) and electrolyzed under optimum conditions as shown by Fig. 1. After 85 minutes electrolysis time, about 90% of the europium of >95% purity was recovered from the amalgam phase. Current efficiency was about 50%. Continuation of the electrolysis resulted in a total yield of europium of 99.5%. Certainly a third electrolysis should give a high yield of europium.

Equation 2 may not be valid when the europium concentration is high, since then the cathode potential during the early part of electrolysis is determined primarily by the europium rather than by the lithium.

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[16] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, p. 144.

[17] Ref. 16, p. 79.