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OXIDATION OF CERIUM (III)
BY OZONE AND BY ELECTROLYSIS

R. E. Lerch

August 1968

AEC RESEARCH &
DEVELOPMENT REPORT

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OXIDATION OF CERIUM(III)
BY OZONE AND BY ELECTROLYSIS

By

R. E. Lerch

Applied Chemistry Section
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OXIDATION OF CERIUM(III)
BY OZONE AND BY ELECTROLYSIS

R. E. Lerch

ABSTRACT

Cerium(III) can be electrolytically oxidized to cerium(IV) on a batch type basis in glass, titanium, or zircaloy vessels, but not in a stainless steel vessel. The process would probably consist of concentrating the cerium to between 0.1M and 0.15M in 2M to 8M nitric acid followed by oxidation and then extraction using 0.3M HDEHP - 0.2M TBP in NPH diluent.

The use of ozone is not feasible for oxidation of cerium(III) to cerium(IV) since the rate of reaction is very slow (even with a catalyst) and because a holding oxidant is necessary during the extraction step.

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OXIDATION OF CERIUM(III) BY OZONE AND BY ELECTROLYSIS

R. E. Lerch

INTRODUCTION

Cerium can be separated from other trivalent rare earth elements by oxidation of cerium(III) to cerium(IV) (in a strong acid medium) followed by extraction of the cerium(IV) into an organic solvent. The purpose of this work was to investigate two possible oxidation methods: (1) oxidation by ozone, and (2) electrolytic oxidation. The experimental work was designed primarily to evaluate only the oxidation step in the separation scheme and not the overall process.

The current separation method at Hanford^(1,2) uses silver-catalyzed persulfate as the oxidant followed by extraction of the cerium(IV) into 0.3M di(2-ethylhexyl)phosphoric acid (HDEHP),* 0.2M tri-n-butyl phosphate (TBP) in normal paraffin hydrocarbon (NHP) diluent. There is some objection to this method due to the high cost of silver and due to the addition of sulfate (from the decomposition of persulfate) to the solution. The two methods described in this paper were appealing since neither one adds any new substance to the solution.

In various oxidation methods that have been proposed and reported, such standard oxidants as potassium permanganate,^(3,4) sodium bismuthate,^(5,6) lead dioxide,⁽³⁾ potassium bromate and potassium chlorate,⁽⁶⁾ and hydrogen peroxide,⁽⁷⁾ as well as electrolytic oxidation,⁽⁸⁾ have been investigated and rejected for one reason or another.

SUMMARY

Ozone was found to be unsatisfactory for oxidation of cerium(III) to cerium(IV). A catalyst as well as a large excess

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* HDEHP will be used as the abbreviation for di(2-ethylhexyl) phosphoric acid rather than D2EHPA since HDEHP is the more standard usage outside of Hanford and since HDEHP distinguishes from the sodium salt of the acid.

of ozone was necessary in order to drive the reaction to completion. Silver(I) was found to catalyze the reaction, but only if the ratio of silver(I) to cerium(III) was ten or greater. Even when complete oxidation was achieved under forcing conditions, however, the cerium(IV) would not extract into an organic extractant. This was probably due to lack of a holding oxidant in the aqueous layer. Temperature and acidity had little effect on the oxidation.

Electrolytic oxidation of cerium(III) to cerium(IV) in a nitric acid solution was successfully demonstrated on a batch type basis in glass, zircaloy and titanium vessels. Good separations ($E_a^0 = 20$ to 105) were obtained both for oxidation followed by extraction of the cerium(IV) into the organic extractant and for oxidation in the presence of an equal volume of organic extractant. Acidity and temperature had little effect on the oxidation. Lack of a holding oxidant in the aqueous phase was of less importance than in the ozone experiments.

Electrolytic oxidation of cerium(III) in a stainless steel vessel followed by extraction of the cerium(IV) into the organic extractant resulted in very low cerium distribution ratios ($E_a^0 = 0.3$ to 0.6) and in dissolution of the stainless steel vessel. This was probably due to surface oxidation of the stainless steel by the cerium(IV) as it formed.

EXPERIMENTAL

OXIDATION BY OZONE

Experimental Setup

The ozone generator used in these experiments was a perchloric acid type electrolytic generator.⁽⁹⁾ By means of electrolysis of perchloric acid at low temperatures (-80°C) one can obtain ozone that is free from nitric oxide and other acid impurities at concentrations above 20 wt%. This amounts to between 0.035 and 0.05 equivalents of ozone per hour.

A reaction train was connected to the outlet of the ozone generator by means of a three-way stopcock. By proper manipulation of the stopcock the stream of ozone could be vented through a potassium iodide scrubber or through the reaction cell connected in series with a potassium iodide scrubber. Thus, once equilibrium was established, the ozone could be directed through the reaction cell for specific periods of time without shutting down the generator. The reaction cell was surrounded by a water jacket for temperature control.

The amount of oxidation taking place was determined by titrating a sample of the cerium solution with a standardized solution of ferrous ammonium sulfate using ferroin as indicator⁽¹⁰⁾ and/or by extracting the cerium(IV) (using ^{141}Ce as tracer) into an organic solvent, then counting aliquots of the aqueous and organic phases to determine the cerium distribution. The organic extractant was 0.3M di(2-ethylhexyl)phosphoric acid (HDEHP), 0.2M tri-n-butyl phosphate (TBP) in normal paraffin hydrocarbon (NPH) diluent. Hereafter, it will be referred to simply as HDEHP. Performance and radiation data for this solvent have been reported previously.⁽²⁾

Results and Discussion

The oxidation potential of ozone is such that one might expect ready oxidation of cerium(III) to cerium(IV):

In addition, no new ions are being added to the system.

Experiments were carried out on ozone oxidation of 0.10M and 0.01M solutions of cerium(III) in nitric acid. Little oxidation of the cerium(III) occurred unless a catalyst was used. Of the various catalysts that were used [iron(II),

iron(III), silver(I), and UV light], only silver(I) was effective. However, silver(I) was effective only if the ratio of silver(I) to cerium(III) was ten or greater. In addition, approximately 20 to 40 times the equivalent amount of ozone had to be added. Under these conditions, nearly complete oxidation of the cerium(III) took place. The effects of silver(I) concentration and the amount of ozone added are shown in Figure 1. The theoretical oxidation time shown in Figure 1 represents the time necessary to oxidize all of the cerium present based on the flow rate of ozone and assuming 100% efficiency in the reaction.

A problem that was encountered during the experiments was the failure of the HDEHP extractant to quantitatively extract the cerium(IV) ion. Typical distribution ratios (E_a^0) of the

(a) Determined by titration

FIGURE 1. Oxidation of 0.01M Cerium(III) by Ozone Using Silver(I) as a Catalyst

cerium were between 0.1 and 18. Normal distribution ratios (organic/aqueous) for 0.01M cerium(IV) in 2M nitric acid using HDEHP as the extractant are greater than 200.⁽¹¹⁾ The low distribution ratios were believed to be due to either the organic extractant reducing some of the cerium(IV) or to the absence of a holding oxidant. The HDEHP extractant was tested by oxidizing cerium(III) with silver-catalyzed persulfate or with sodium bismuthate and then extracting the cerium(IV). In both cases, distribution ratios (E_a^0) between 100 and 300 were obtained. The HDEHP was also checked by comparing the "apparent" cerium oxidation as calculated both from titration data and from extraction data. The results are shown in Table I. The comparison shows that even though >99% of the cerium was oxidized (as determined by titration), partial decomposition of the cerium(IV) occurred during the extraction such that the apparent percent oxidation as calculated from extraction data was less than 80%.

TABLE I. Comparison of Percent Oxidation of Cerium(III) by Ozone as Calculated from Titration and Extraction Data

Nitric Acid Conc., <u>M</u>	Cerium(III) Conc., <u>M</u>	Silver(I) Conc., <u>M</u>	Oxidation Time, min	Percent Oxidation	
				Titration	Extraction ^(a)
2	0.01	0.01	15	29.1	15.6
2	0.01	0.01	30	47.9	31.5
2	0.01	0.10	15	58.1	39.5
2	0.01	0.10	30	99.2	78.2
8	0.01	-	15	16.7	2.5
8	0.01	0.01	15	23.0	6.0
8	0.01	0.10	15	34.2	13.3
8	0.01	0.10	30	35.1	15.1
16	0.01	-	15	99.0	68.6

(a) The percent oxidation calculated from the extraction data assumed complete extraction of all cerium(IV) present in the solution since the normal distribution coefficient for extraction of 0.01M cerium(IV) in 2M nitric acid using HDEHP as extractant is >200.

In order to avoid reduction of the cerium(IV) due to reaction with the organic extractant or its impurities, V. I. Levin et al⁽⁶⁾ reportedly used sodium bismuthate as a "protective oxidizing agent" during extraction of the cerium(IV). However, distinction between the oxidation produced by ozone and that which was due to the sodium bismuthate is not clear.

The effect of nitric acid concentration on the oxidation of 0.01M cerium(III) by ozone was investigated and results are summarized in Table II.

TABLE II. *The Effect of Nitric Acid Concentration on the Oxidation of 0.01M Cerium(III) by Ozone Using Silver(I) as Catalyst*

Oxidation Time, min	Cerium Distribution, E_a^0 at 25 °C				
	0.2M HNO_3	1M HNO_3	2M HNO_3	8M HNO_3	16M HNO_3
3	0.19	0.09	0.08		
5	0.25	0.15	0.14		
7	0.26	0.23	0.22		
9	0.27	0.25	0.28		
11	0.33	0.27	0.39		2.01
15			0.41	0.52	20.1
30			0.92	0.54	
60		16.3	9.27		

Organic/Aqueous: 1.0

Organic: 0.3M HDEHP

0.2M TBP

In NPH

Aqueous: 0.01M cerium

0.10M silver(I)

Theoretical Oxidation Time: ~1 min

In general, the amount and rate of oxidation increased at higher acidity, but the reaction was still very slow unless a catalyst was used. V. I. Levin *et al*⁽⁶⁾ reported that oxidation of cerium(III) in 8M and more concentrated acid occurred almost completely. However, complete oxidation in these experiments was obtained only by using a large excess of ozone and then most of the cerium(IV) was reduced back to cerium(III) during extraction.

The effect of temperature on the oxidation of 0.01M cerium(III) by ozone is shown in Figure 2. In general, there was a slight increase in cerium oxidation with an increase in temperature. The theoretical oxidation time for both reactions was ~ 1 min.

FIGURE 2. The Effect of Temperature on the Oxidation of 0.01M Cerium(III) by Ozone

The data were too incomplete for evaluation of the effect of initial cerium(III) concentration as all the solutions of cerium(III) were poorly oxidized by ozone.

ELECTROLYTIC OXIDATION

Experimental Setup

A Power Designs, Inc., Model 5005R regulated power supply was used for the electrolytic oxidation of cerium(III). Platinum foil and platinum gauze were used for the cathode and anode, respectively. The experiments consisted of generating cerium(IV) electrolytically for measured periods of time, then determining the cerium(III)/cerium(IV) ratio. The cerium(III)/cerium(IV) ratio was determined either by titrating the cerium(IV) with standardized ferrous ammonium sulfate (using ferroin as indicator)⁽¹⁰⁾ or by extracting the cerium(IV) (using ^{141}Ce as tracer) into an organic solvent, then counting aliquots of the aqueous and organic phases. Again, 0.3M HDEHP, 0.2M TBP in NPH diluent was used for the organic extractant. The applied potential was maintained below 3 V in all the experiments in order to minimize gas formation.

Results and Discussion

The electrolytic experiments were carried out using solutions of cerium(III) in nitric acid. Earlier workers^(12,13,14) had theorized that cerium(IV) existed as a hexanitrate complex ion in nitric acid and therefore the solution would not have to be protected from the cathode to prevent reduction of the cerium(IV). More recent work⁽¹⁵⁾ with plutonium(IV) and neptunium(IV), however, has indicated that hexanitrate complex formation in dilute nitric acid solutions probably occurs only to a minor extent. Smith and coworkers⁽¹⁴⁾ were able to show that if the ratio of anode surface area to cathode surface area was large enough, one could obtain rather complete oxidation of the cerium(III) without using a shielded cathode. By using an anode

to cathode surface area ratio of about 200, they were able to obtain 99.7% oxidation of 0.51M cerium(III) nitrate in 2.0M nitric acid. The current efficiency, measured at 80% oxidation, was 84.4%.

Shielded Versus Unshielded Cathodes

In this work, both shielded and unshielded cathodes were used. In general, better current efficiencies were obtained using shielded cathodes. However, this may be due to the fact that the ratio of the anode surface area (86 cm²) to the cathode surface area (4.5 cm²) for the electrodes used in these experiments was small in comparison with that of Smith *et al.* Oxidation efficiencies (used throughout these discussions merely to compare various processes) calculated for 80% oxidation of the 0.01M cerium(III) in nitric acid solutions using shielded and unshielded cathodes are shown in Table III. The theoretical oxidation time using a current of 500 mA was 4 min, 48 sec. More complete oxidation of the cerium(III) is believed possible if a higher ratio of anode to cathode surface area is used.

TABLE III. Electrolytic Oxidation of 0.01M Cerium(III) in Nitric Acid Using Shielded and Unshielded Cathodes

Nitric Acid M	Shielded Cathode				Unshielded Cathode			
	Percent Oxidation ^(a)			Current ^(b) Efficiency	Percent Oxidation ^(a)			Current ^(b) Efficiency
	5 min	10 min	15 min		5 min	10 min	15 min	
0.10	34.8	59.6	74.7		43.4	63.8	83.0	35.3%
0.50					58.7	71.4	81.6	35.7%
1.0	71.0	97.9	>99	82.4%	66.4	89.3	94.7	72.5%
2.0	71.2	90.5	96.5	76.9%	53.2	82.3	92.0	53.6%
4.0	69.0	93.6	97.0	76.1%	58.8	84.3	98.4	56.2%
6.0	67.7	90.8	95.5	73.2%	54.9	84.3	90.7	56.2%
8.0	54.1	81.0	91.0	51.7%	60.1	84.3	97.2	56.2%
10.0	59.1	85.7	95.7	60.5%				
12.0	56.0	83.6	93.0	56.2%				
14.0	53.5	83.9	94.7	54.5%				

(a) Calculated from titration data.

(b) Calculated for 80% oxidation.

Theoretical oxidation time, using a current of 500 mA, is 4 min, 48 sec.

The Effect of Nitric Acid Concentration

The effect of nitric acid concentration on the electrolytic oxidation of 0.01M cerium(III) is shown in Table III. The nitric acid concentration has little effect on the completeness of oxidation. However, the current efficiency drops off sharply at higher nitric acid concentrations. This is probably due to side reactions at the cathode involving possible reduction of the nitrate ion. Possible side reactions could be reduced significantly by using a smaller cathode.

The Effect of Initial Cerium Concentration

Both the completeness and the current efficiency of the cerium(III) electrolytic oxidation reaction increased with an increase in the initial cerium(III) concentration. A comparison of the relative completeness and current efficiency for oxidation of 0.01M and 0.12M solutions of cerium(III) in nitric acid is shown in Table IV. The completeness listed in the table is for a 20% excess of current. To oxidize the cerium(III) in the 0.01M solution to the same percent completeness to which the cerium(III) in the 0.12M solution has been oxidized would require a 100 to 150% excess of current. The better overall reaction obtained with the 0.12M cerium(III) solution is apparent when one compares the relative current efficiencies for 80% oxidation in the various nitric acid solutions (also shown in Table IV). At all three nitric acid concentrations tested, the reactions were >98% efficient for 80% completion of the oxidation. Above 80% oxidation, the efficiencies dropped off. A typical oxidation curve for electrolytic oxidation of 0.10M cerium(III) in 4.0M nitric acid using a shielded cathode is shown in Figure 3. Although the oxidation reaction proceeds at a much faster and more efficient rate with an increase in initial cerium(III) concentration, the effect of even higher initial cerium(III) concentrations was not investigated since the resulting higher concentration of cerium(IV) would be difficult to extract with 0.3M HDEHP.

TABLE IV. *Electrolytic Oxidation of 0.01M and 0.12M Solutions of Cerium(III) in Nitric Acid Using a Shielded Cathode*

Nitric Acid	0.01M Cerium		0.12M Cerium	
	Percent ^(a) Complete	Current ^(b) Efficiency	Percent ^(a) Complete	Current ^(b) Efficiency
1.0M	79.0	82.4	96.3	>98%
2.0M	77.0	76.9	96.9	>98%
4.0M	76.5	76.1	97.2	>98%

(a) *Estimated from titration data at 120% of the theoretical current.*

(b) *The current efficiencies were calculated for 80% oxidation.*

(a) *Determined by titration*

FIGURE 3. *Typical Oxidation Curve for Electrolytic Oxidation of 0.10M Cerium(III) in Nitric Acid*

Effect of Temperature

Temperature was found to have little if any effect on the oxidation of cerium(III) in nitric acid. A comparison of the percent oxidation of 0.10M cerium(III) in 2M nitric acid at 25 °C and 50 °C is shown in Table V.

TABLE V. *The Effect of Temperature on the Oxidation of 0.10M Cerium(III) in 2M Nitric Acid*

Percent Theoretical Current	Percent Completion ^(a)	
	25 °C	50 °C
100%	87.0	85.3
120%	96.1	97.2
150%	97.3	98.1

(a) *Determined by titration.*

Extraction of Electrolytically Generated Cerium(IV) into 0.3M HDEHP, 0.2M TBP in NPH Diluent

Once the cerium(III) has been oxidized to cerium(IV), separation from other trivalent rare earth elements is completed by extracting the cerium(IV) into an organic solvent. The cerium(IV) is then stripped from the organic solvent with 2M nitric acid containing 0.05M sodium nitrite to reduce the cerium to cerium(III).

Electrolytically generated cerium(IV) was found to extract into HDEHP extractant essentially independent of temperature. The extraction was, however, dependent on nitric acid concentration, on the volume ratio of organic extractant to aqueous, on the contact time during extraction, and on the concentration of cerium in the aqueous layer.

Effect of Nitric Acid Concentration

The nitric acid concentration had little effect on the extraction of cerium(IV) except at high concentrations of nitric acid (above 8M HNO_3). The low distribution coefficients (E_a^0) at high nitric acid concentrations were probably a result of slow and incomplete oxidation rather than of incomplete extraction. The extraction data are shown in Table VI for extraction of 0.10M cerium(IV) from various nitric acid solutions. In all cases, the current was sufficient for 150% theoretical oxidation.

TABLE VI. *The Effect of Nitric Acid Concentration on Extraction of 0.10M Cerium(IV) into 0.3M HDEHP - 0.2M TBP in NPH Diluent*

<u>Nitric Acid Concentration</u>	<u>Cerium(IV) Distribution, E_a^0</u>
0.5M	69.3
1.0M	87.1
2.0M	80.5
4.0M	72.0
6.0M	63.5
8.0M	44.2
10.0M	10.5

Temperature: 25 °C

Contact Time: 2.0 min

Organic/Aqueous: 1.0

Oxidation Current: 150% of theoretical

The organic extractant was added after complete oxidation.

Effect of Extractant Ratio

The dependence of extraction on the volume ratio of organic extractant to aqueous is shown in Table VII. The relatively low distribution ratios (E_a^0) are probably due to lack of a holding oxidant in the aqueous phase or to incomplete oxidation as a result of using too small a ratio of anode surface area to cathode surface area during the electrolysis. In each case the

aqueous layer was initially 0.12M in cerium(III) and the current was sufficient for 120% of theoretical oxidation.

TABLE VII. The Effect of the Organic/Aqueous Ratio on Extraction of 0.12M Cerium(IV) into 0.3M HDEHF - 0.2M in NPH Diluent

Volume Ratio Organic/Aqueous	Aqueous Acid Concentration					
	1.0M HNO ₃		2.0M HNO ₃		4.0M HNO ₃	
	E _a ^o	Percent ^(a) Oxidation	E _a ^o	Percent ^(a) Oxidation	E _a ^o	Percent ^(a) Oxidation
1.0/1.0	26.11	96.3	28.92	96.7	25.88	96.3
2.0/1.0	16.14	94.2	15.89	94.1	13.52	93.1
3.0/1.0	12.26	92.5	10.64	91.4	11.53	92.0
Percent Oxidation by Titration		96.1		96.4		95.6

Temperature: 25 °C

Contact Time: 2.0 min

The organic extractant was added after complete oxidation.

(a) Calculated from E_a^o assuming complete extraction of all of the cerium(IV) that was present.

Contact Time During Extraction

The contact time of the organic extractant and aqueous solution was shown to have a definite effect on the amount of cerium(IV) that was extracted. In general, longer contact times gave lower cerium(IV) distribution ratios (E_a^o). This is probably due to reduction of the cerium(IV) by the organic extractant (or its impurities) or the lack of a holding oxidant in the aqueous layer. Typical data for extraction of 0.12M cerium(IV) into 0.3M HDEHP using contact times of 2.0 min and 5.0 min (and for various volume ratios of organic extractant to aqueous) are shown in Table VIII. The current was sufficient for 120% of theoretical oxidation.

Effect of Cerium Concentration

The effect of cerium concentration on the extent of extraction is shown in Figure 4. All the experiments were run at 25 °C

TABLE VIII. *The Effect of Organic/Aqueous Contact Time on Extraction of 0.12M Cerium(IV) into 0.3M HDEHP - 0.2M TBP in NPH Diluent*

Ratio Organic/Aqueous	Distribution Ratio, E_a^0	
	2 min Contact	5 min Contact
0.60/1.0	15.24	12.71
0.80/1.0	49.01	35.41
1.0/1.0	37.47	32.73
1.2/1.0	33.59	23.52
1.4/1.0	24.40	17.96

Temperature: 25 °C

Oxidation Current: 120% of theoretical

Organic: 0.3M HDEHP

0.2M TBP

In NPH diluent

Aqueous: 0.12M Ce(III)

2M HNO₃

FIGURE 4. *The Effect of Cerium Concentration on the Extraction of Cerium(IV) into 0.3M HDEHP - 0.2M NPH in Diluent*

in 2.0M nitric acid, using a current sufficient for 150% theoretical oxidation. The extractions were done with an organic/aqueous volume ratio of 1.0. It appears that the best distributions were obtained with a cerium concentration between 0.08M and 0.16M. The actual distribution ratios (E_a^0) between these concentrations were difficult to reproduce, probably due to slight differences in stirring rates and also due to lack of a holding oxidant. The cerium(IV) distributions fell off rapidly at high and low concentrations of cerium. At low cerium concentrations, incomplete oxidation was probably the cause of the low cerium(IV) distributions (E_a^0). At high cerium concentrations, the low cerium(IV) distributions (E_a^0) were probably due to overloading the organic extractant. This would be the case if two moles of HDEHP were required for each mole of cerium(IV).⁽¹¹⁾ The generally low overall cerium(IV) distributions were believed due to lack of a holding oxidant or due to incomplete oxidation of the cerium(IV). Previous work has shown that the distribution coefficients for 0.01 to 0.10M cerium(IV) extraction into 0.4M HDEHP, 0.2M TBP were greater than 400.⁽¹¹⁾

Oxidation in the Presence of Organic Extractant

Successful cerium oxidation-extraction experiments were carried out by oxidizing 0.10M cerium(III) in the presence of an equal volume of organic extractant. The experiments were carried out in a glass vessel using a platinum gauze anode and an unshielded platinum foil cathode. The anode was placed half in the aqueous and half in the organic phase while the cathode was placed only in the aqueous phase. The mixture was stirred at a rate just fast enough to maintain 500 mA current through the cell using an applied potential of <3 V. (Excessive stirring caused the current to drop to less than 500 mA and the potential to exceed 3 V causing gas evolution at the anode.)

The mixture was oxidized for a given period of time, then vigorously stirred for 2 min, then sampled. The results of a typical experiment using 0.10M cerium(III) in 2.0M nitric acid, an organic to aqueous extraction ratio of 1.0 and a temperature of 25 °C are shown in Table IX. The organic extractant was HDEHP. The results indicate that electrolytic oxidation of a 0.10M solution of cerium(III) could be carried out in the presence of an equal volume of organic extractant although it would be done with some sacrifice in current efficiency. The decrease in current efficiency is probably a direct result of two things: (1) a two-fold decrease in the cathode to anode surface area, and (2) the slightly higher electrical impedance due to the presence of the organic extractant.

TABLE IX. Electrolytic Oxidation of 0.10M Cerium(III) in the Presence of an Equal Volume of Organic Extractant

Theoretical Current, %	Cerium Distribution
	E_a^0
150	10.50
200	19.97
250	23.69

Temperature: 25 °C

Organic/Aqueous: 1.0

Organic: 0.3M HDEHP

0.2M TBP

in NPH

Aqueous: 0.10M Ce(III)

2M HNO₃

Contact Time: 2 min

Electrolytic Oxidation of Cerium(III) in the Presence of Stainless Steel

Electrolytic oxidation of cerium(III) in a stainless steel vessel resulted in very low cerium distribution ratios (E_a^0 , 0.3 to 0.6) and in dissolution of the stainless steel vessel. This apparently was due to surface oxidation of the stainless steel by the cerium(IV) as it formed. Results of a typical experiment using a solution of 0.10M cerium(III) in 2.0M nitric acid, an organic to aqueous extraction ratio of 1.0 and a temperature of 25 °C are shown in Table X.

TABLE X. *Electrolytic Oxidation of 0.10M Cerium(III) in a Stainless Steel Vessel*

<u>Theoretical Current, %</u>	<u>Cerium Distribution E_a^0</u>
100	0.402
112.5	0.407
125	0.389
137.5	0.386
187.5	0.378

Temperature: 25 °C

Organic/Aqueous: 1 0

Organic: 0.3M HDEHP

0.2M TBP

in NPH

Aqueous: 0.10M Ce(III)

2M HNO₃

Contact Time: 2 min

The resulting aqueous layer had a very pronounced iron(III)-chromium(III) color to it. Subsequent analysis of a sample of the aqueous layer following two hours of oxidation gave the following analysis: 0.115 g/liter chromium, 0.720 g/liter iron,

and 0.15 g/liter nickel. Later measurements of the corrosion rate (at 25 °C) indicated that 304L type stainless steel corroded at a rate of 1.4 in/yr ($\sim 3.2 \text{ mg/cm}^2/\text{hr}$) in a 0.10M cerium(IV)-2.0M nitric acid solution. The results of the experiments on corrosion of stainless steel in cerium(IV)-nitric acid solutions will be reported in a separate document.

Several side experiments were run in an effort either to protect the stainless steel vessel from attack by the cerium(IV) or to extract the cerium(IV) into an organic layer before it could react with the stainless steel. Data for electrolytic oxidation of a solution of 0.10M cerium(III) in 2.0M nitric acid in the presence of an equal volume of 0.3M HDEHP are shown in Table XI. The main difficulty in trying to extract the cerium(IV) into the organic layer before it has a chance to react with the stainless steel is maintaining an adequate stirring rate without increasing the electrical resistance of the mixture. Faster stirring requires an increase in the applied potential such that oxygen rather than cerium(IV) is generated at the anode; too slow a stirring rate doesn't mix the aqueous and organic layers enough to extract the cerium(IV) before it reacts with the stainless steel.

Attempts at protecting the stainless steel vessel electrolytically were unsuccessful. The vessel was given both cathodic and anodic protection ($\sim 2.5 \text{ V}$) in an attempt to repel the cerium(IV) as it formed. Cerium distribution ratios (E_a^0) indicated that the anodic protection was more effective than the cathodic protection which would mean that the cerium(IV) was reacting with the stainless steel before it formed the hexanitrate complex ion. In either case, the cerium distribution ratios (E_a^0) were low, indicating only partial oxidation of the cerium(III) taking place. Higher potentials (which might be

TABLE XI. *Electrolytic Oxidation of 0.10M Cerium(III) in Stainless Steel in the Presence of Organic Extractant*

Theoretical Current, %	Cerium Distribution E_a^0
111	1.64
148	1.98
185	5.15
222	5.72
260	14.59
296	11.47
333	11.03

Temperature: 25 °C

Organic/Aqueous: 1.0

Organic: 0.3M HDEHP

0.2M TBP

in NPH

Aqueous: 0.10M Ce(III)

2.0M HNO₃

Contact Time: 2 min

more effective in protecting the stainless steel vessel) were not investigated in these experiments. The results for oxidation of 0.10M cerium in 2.0M nitric acid using electrolytic protection for the stainless steel vessel are shown in Table XII.

Electrolytic oxidation of cerium(III) in other types of containment vessels was also investigated. In particular, 0.10M cerium(III) solutions in 2.0M nitric acid were found to be easily oxidizable and extractable in both zircaloy and titanium reaction vessels. The data for these experiments are shown in Table XIII. Either type of vessel would probably work for electrolytic oxidation of cerium(III). No degradation of the vessel was noted in either experiment.

TABLE XII. *Electrolytic Oxidation of 0.10M Cerium(III) in Electrolytically Protected Stainless Steel*

Theoretical Current, %	Anodic Protection	Cathodic Protection
	E_a^O	E_a^O
100	0.81	0.23
150	0.91	0.24

Temperature: 25 °C

Organic/Aqueous: 1.0

Organic: 0.3M HDEHP

0.2M TBP

in NPH

Aqueous: 2.0M HNO₃

0.10M Ce(III)

Contact Time: 2 min

TABLE XIII. *Electrolytic Oxidation of 0.10M Cerium(III) in Zircaloy and Titanium Vessels*

Theoretical Current, %	Cerium Distribution, E_a^O	
	Zircaloy	Titanium
100	5.02	8.41
125	54.0	63.7
156	69.5	69.4
188	68.8	81.7

PROCESS RECOMMENDATIONS

Cerium(III) can be successfully oxidized to cerium(IV) on a batch type basis and with good current efficiency in glass, titanium, or zircaloy vessels, but not in a stainless steel vessel. Results of laboratory experiments using tracer quantities of ¹⁴¹Ce dictate the following process recommendations:

1. Concentration of cerium between 0.08M and 0.15M.
2. Oxidation in 2M to 8M nitric acid.

3. Oxidation in a titanium, zircaloy, or in a glass-lined stainless steel vessel.
4. Oxidation temperature between 25 °C and 50 °C.
5. Extraction of the cerium(III) into an equal volume of 0.3M HDEHP-0.2M TBP in NPH diluent, either during or following oxidation.
6. A high (>100) ratio of cathode to anode surface area.
7. Short organic/aqueous contact times during extraction.

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