

APR 2 1968

RI bureau of mines
report of investigations **7123**



RECOVERY OF CERIUM AND LANTHANUM BY OZONATION OF LANTHANIDE SOLUTIONS



UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

May 1968

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By D. J. Bauer and R. E. Lindstrom

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This publication has been cataloged as follows:

Bauer, Donald J

Recovery of cerium and lanthanum by ozonation of lanthanide solutions, by D. J. Bauer and R. E. Lindstrom. [Washington] U.S. Dept. of the Interior, Bureau of Mines [1968]

9 p. illus., tables. (U. S. Bureau of Mines. Report of investigations 7123)

Includes bibliography.

1. Cerium. 2. Lanthanum. I. Lindstrom, Roald E., jt. auth. II. Title. (Series)

TN23.U7 no. 7123 622.06173

U. S. Dept. of the Int. Library

CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	1
Materials, apparatus, and procedure.....	2
Discussion and results.....	3
Conclusions.....	8
References.....	9

ILLUSTRATIONS

Fig.

1. Effect of reaction time on CeO_2 recovery from lanthanide chloride solution at ambient temperature.....	4
2. Effect of reaction time on CeO_2 recovery from lanthanide chloride solution at 85°C	5

TABLES

1. X-ray fluorescent analysis of rare-earth-oxide feed material.....	3
2. Recovery and purity of CeO_2 and La_2O_3 as a function of pH and time, at ambient temperature.....	6
3. Recovery and purity of CeO_2 and La_2O_3 as a function of pH and time, at 85°C	7
4. Two-step recovery of CeO_2 and La_2O_3	7

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by

D. J. Bauer¹ and R. E. Lindstrom²

ABSTRACT

Oxidation of mixed lanthanide solutions with ozone at pH 4.5 and at ambient temperature resulted in precipitation of 98 percent of the original cerium present. Corresponding cerium purity was increased from 50 to 98 percent. A second ozone oxidation-precipitation step produced cerium of 99.9 percent purity in high yield from the 98-percent-pure material.

Alternately, ozonation at pH 6.5 and 85° C differentially precipitated cerium and rare-earth elements heavier than cerium and left 89 percent of the original lanthanum in solution at a purity of 95 percent. Subsequent recovery of cerium from the heavier rare-earth elements in the precipitate was accomplished by dissolving the precipitate in dilute mineral acid and reoxidizing the cerium with ozone at pH 4.5 and at ambient temperature. The filtrate contained an enriched praseodymium-neodymium-samarium-europium mixture that is amenable to separation by ion exchange or solvent extraction.

INTRODUCTION

Cerium and lanthanum are among the most abundant of the rare-earth elements, and their recovery and purification have considerable economic importance. Cerium compounds find their main use as glass-polishing agents; they also are of value as glass-coloring agents and as opacifiers in glazes and enamels. Lanthanum, in addition to being used in glass, is being used in increasing quantities as a petroleum-cracking catalyst.

The separation of cerium and lanthanum from a wide variety of source materials has been accomplished by several methods including fractional crystallization (4, 6),³ basicity precipitation (3), ion exchange (5), and solvent

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³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

extraction (2, 7). Probably the best known and most widely used techniques for cerium purification are those based on the oxidation of cerium in solution to the tetravalent state. Persulfates, permanganates, and hypochlorites are frequently used for this oxidation reaction. The tetravalent cerium can be recovered from the rare-earth solution by precipitation of the comparatively insoluble cerium (IV) by pH control (3) or by extraction of a ceric salt into an organic extractant (7). Under some conditions a ceric salt (for example, ceric nitrate) will precipitate if the pH of the solution is raised to 2 or higher. A few repetitions of this process will produce a basic ceric salt more than 99-percent pure, but the effort involved in the procedure is considerable, and the yield is relatively low.

A solvent extraction process employing tri-n-butyl phosphate solvent has been used to extract ceric nitrate, probably as the hexanitrate-cerate complex. This procedure is capable of producing high-purity cerium compounds with high yields in a few countercurrent stages. In another method, cerous hydroxide is oxidized to hydrated ceric oxide by heating the solid rare-earth mixture in air. Leaching of this material under controlled pH conditions will dissolve the trivalent rare-earth hydroxides, whereas the ceric salt remains insoluble.

Lanthanum, having but one oxidation state, is considerably more difficult to purify than cerium. One traditional technique utilizes the addition of ammonia to a hot solution of rare-earth salts. Because of its greater basicity, the lanthanum remains in solution at pH values approaching neutrality, while the less basic heavier rare-earth elements are precipitated. This procedure will produce a lanthanum salt of >90-percent purity, but recovery is rarely greater than 75 percent.

A possible technique for oxidizing and purifying cerium that has received little attention is based on the well-known capabilities of ozone as an oxidant (1). Ozone, which has an oxidation potential of minus 2.07 volts in acid solution, is surpassed in electronegative oxidation potential only by fluorine among the commonly used oxidizing agents. Ozone is known to oxidize ferrous ion to ferric, chromous to chromate, sulfide to sulfate, and nitrite to nitrate. Based on the known oxidation potential of minus 1.74 for the $Ce^{+3}(aq) \rightleftharpoons Ce^{+4}(aq) + e^-$ couple, ozone would be expected to oxidize a cerous salt in solution to the ceric form.

This report is concerned with a Bureau of Mines investigation of the ozone oxidation of cerium ion in aqueous solution and the simultaneous precipitation of a purified cerium product. Another goal of the study was to investigate the oxidation-precipitation reaction as a means of coprecipitating rare-earth elements heavier than cerium with the cerium to provide an upgraded lanthanum fraction in the filtrate.

MATERIALS, APPARATUS, AND PROCEDURE

Charge solutions were prepared by dissolving cerium-group rare-earth oxides in sulfuric, nitric, or hydrochloric acid and, for the majority of tests, diluting to a final concentration of 12 g/l (RE_2O_3 basis). The

rare-earth oxides were obtained from the mineral bastnasite and had the composition listed in table 1.

TABLE 1. - X-ray fluorescent analysis of rare-earth-oxide feed material

Rare-earth species	Analysis, percent
CeO ₂	50.0
Eu ₂ O ₃1
La ₂ O ₃	36.0
Nd ₂ O ₃	9.7
Pr ₆ O ₁₁	3.5
Sm ₂ O ₃7

Ozone was produced in a Welsbach-type ozonator⁴ operating at 15,000 volts and 60 cps. The generator was controlled to deliver approximately 2.5 grams of ozone per hour with an oxygen flow of 0.02 cfm at 8 psi. Breathing oxygen was used because of its low moisture content. Toxic ozone fumes were confined in a hood.

Individual experiments were conducted with 800-ml of charge solution in 1-liter, open-top, glass reaction vessels. Solutions were stirred and heated to 85° C during selected experiments. It was usually necessary to add water to the solution during the high temperature experiments to maintain a constant volume. Addition of ammonia was necessary to neutralize acid formed during the oxidation reaction. Ozone and ammonia gases were introduced into the rare-earth solution through fritted glass tubes. In any given experiment the addition of ozone was continued until essentially all of the cerium had precipitated or until a predetermined reaction time was reached. Precipitation of the cerium was complete when the pH of the solution remained constant without the addition of ammonia. The precipitated CeO₂ was recovered by filtration.

Cerium precipitation was followed by a Ce¹⁴⁴ tracer for the initial reaction-time studies. Rare-earth elements remaining in solution were precipitated with oxalic acid, and the rare-earth oxalates were roasted to the oxide at 1,700° F. All rare-earth oxide products were analyzed by X-ray fluorescence. Inasmuch as the cerium products were roasted to CeO₂ before weighing, and analytical results were reported on an oxide basis, the cerium precipitates are referred to as CeO₂ or ceric oxide throughout this report. However, it should be noted that the cerium probably precipitated as hydrated ceric oxide, CeO₂·2H₂O.

DISCUSSION AND RESULTS

Since cerium compounds are oxidized under certain conditions by oxygen, preliminary experiments were conducted with air or oxygen to establish a basis for comparison with results subsequently obtained with ozone. Negative results

⁴Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

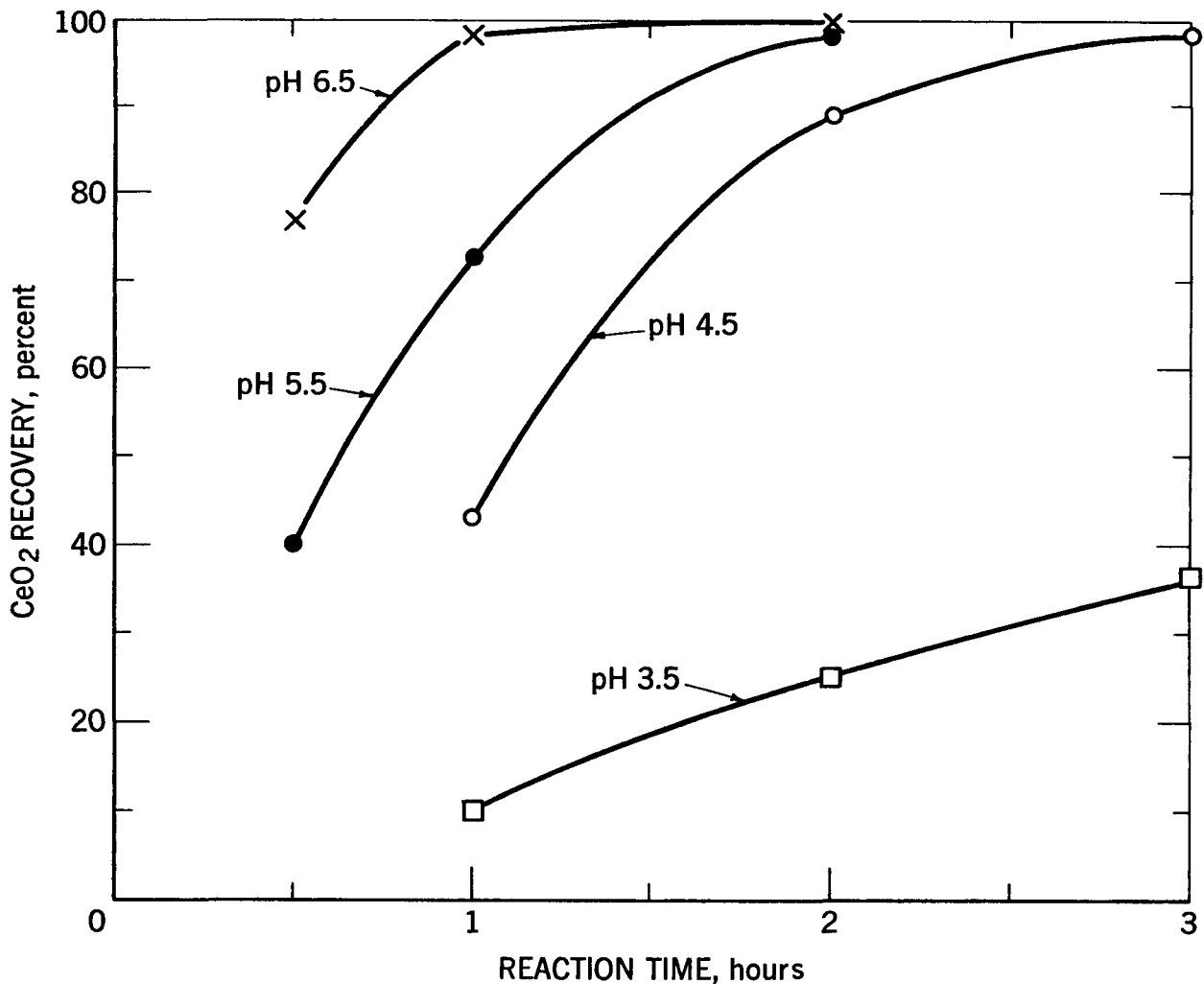


FIGURE 1. - Effect of Reaction Time on CeO₂ Recovery From Lanthanide Chloride Solution at Ambient Temperature.

(for example, no cerium oxidation) were obtained with pH values as high as 5.5 at ambient temperature. Oxidation-precipitation started when the temperature was increased to 85° C and the pH to 6.5 with either air or oxygen. Under these conditions considerable quantities of trivalent hydroxides were coprecipitated with the tetravalent cerium oxide. Although the CeO₂ precipitate was badly contaminated, the rare-earth elements contained in the filtrate analyzed 91 percent lanthanum oxide when oxygen was used for oxidation. Lanthanum recovery, however, was only 77 percent. Slightly less favorable results were obtained with air. Neither gas produced a sharp pH stabilization, such as occurred when ozone was the oxidant. This factor was a considerable disadvantage, because the stabilizing of the solution pH was a reliable indication of complete CeO₂ precipitation. A further disadvantage in the use of air or oxygen streams is that extended operation at high temperature and high pH resulted in the complete precipitation of all the rare-earth elements in the charge solution.

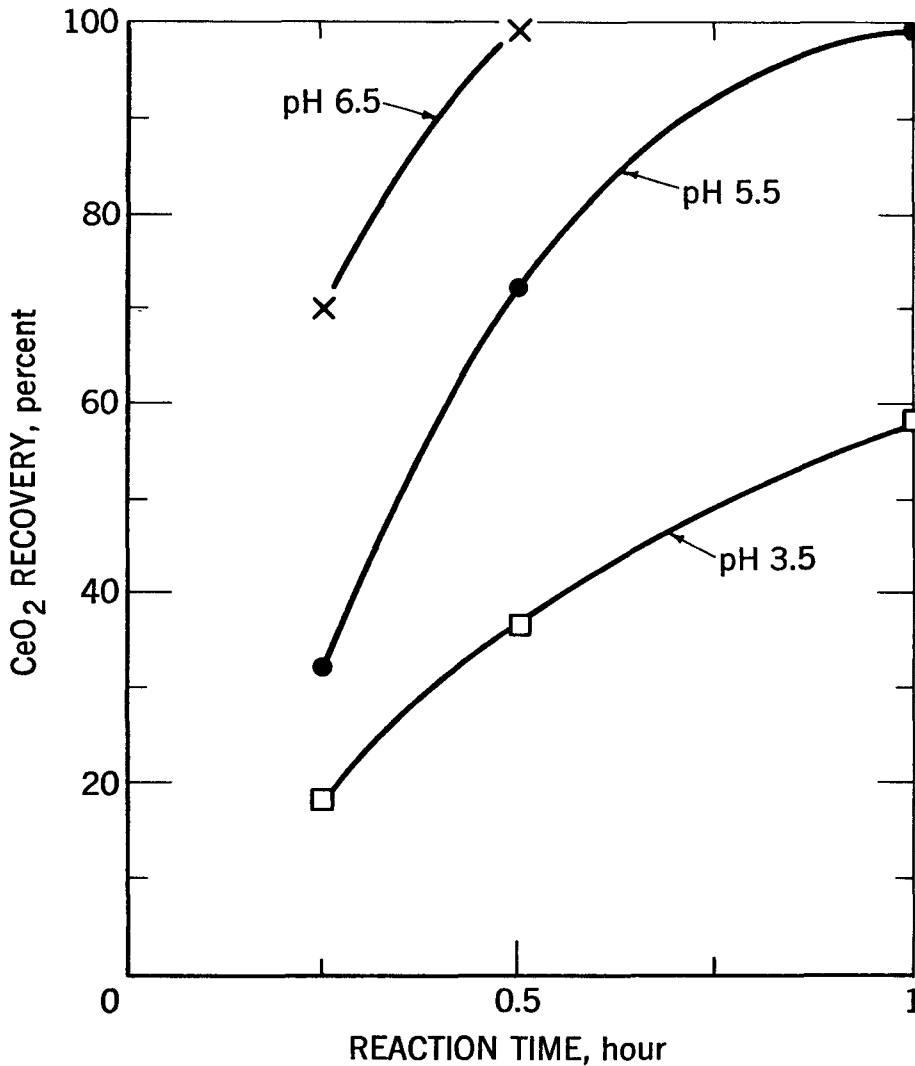


FIGURE 2. - Effect of Reaction Time on CeO_2 Recovery From Lanthanide Chloride Solution at 85°C .

Initial experiments with ozone were conducted to determine the variation of CeO_2 precipitation from chloride solutions with time at varied pH values and temperatures. Figure 1 shows that CeO_2 precipitation increases with both increasing reaction time and increasing pH at ambient temperature. At 3-hours reaction time, CeO_2 precipitation increased from 36 to 98 percent when the pH was increased from 3.5 to 4.5. Greater than 99-percent precipitation of CeO_2 occurred in 2 hours at pH 5.5, whereas only 1 hour was required for 99-percent precipitation at pH 6.5. Hydrogen ion concentrations above pH 6.5 were not investigated because of the formation of rare-

earth hydroxides. The same trend can be seen in figure 2 for precipitation at 85°C ; however, at the higher temperature the rate of CeO_2 precipitation increased considerably. Complete precipitation of CeO_2 occurred in 1 hour at pH 5.5, and only one-half hour was required at pH 6.5.

Subsequent experiments with ozone were conducted using rare-earth sulfate, nitrate, or chloride solutions to obtain recovery and purity data for cerium and lanthanum compounds. The three anion species were included in the study, because it was not known if the differences in their abilities to form complex ions with the rare-earth elements would affect the recovery and purity of the CeO_2 precipitate. In table 2 CeO_2 recovery and purity data obtained with the sulfate, nitrate, and chloride solutions at ambient temperature are summarized. A maximum CeO_2 purity of 98 percent was obtained with the chloride solution, while a maximum purity of 92 to 93 percent was obtained with

the sulfate and nitrate solutions. CeO_2 recovery values of approximately 99 percent were common for all three anion species with pH values above 4.5. However, with pH values below 4.5, precipitation from the sulfate solution resulted in recovery values markedly superior to those obtained with chloride or nitrate solutions. Presumably, complete CeO_2 precipitation would occur using any of the three anionic species in the pH ranges covered if the ozone oxidation-precipitation reactions were continued for a sufficiently long time.

TABLE 2. - Recovery and purity of CeO_2 and La_2O_3 as a function of pH and time, at ambient temperature

Anion	pH	Reaction time, hours	CeO_2 in precipitate		La_2O_3 in filtrate	
			Recovery, percent	Purity, percent	Recovery, percent	Purity, percent
SO_4	1.5	3	93	79	88	63
	2.5	2	97	86	92	67
	3.5	2	99.3	85	93	69
	4.5	2	99.8	86	93	70
	5.5	2	99.6	92	95	75
NO_3	3.0	3	73	93	(¹)	(¹)
	4.5	3	99.2	93	97	75
	5.0	2	99.1	93	98	73
	5.5	1	98.8	89	(¹)	(¹)
Cl	3.5	3	36	89	(¹)	(¹)
	4.5	3	98	98	98	70
	5.5	2	99.2	92	94	75
	6.5	1	99.8	76	90	88

¹Not determined.

The effect of temperature on CeO_2 recovery was determined at 85° C in the nitrate and chloride systems. Solubility limitations prevented investigation of rare-earth sulfate solutions at the higher temperature. Comparison of tables 2 and 3 shows that although the reaction time required to reach a given percentage of ceric oxide recovery at 85° C is substantially less than at ambient temperature, the cerium product is less pure. In one case a ceric oxide product of 95 percent purity was obtained in 1 hour with the chloride system, but recovery was only 58 percent. It is concluded that operation at ambient temperature is preferable for producing high-purity ceric oxide in high recovery.

Complete precipitation of pure cerium oxide would leave a trivalent rare-earth mixture in solution containing a theoretical maximum of 72-percent lanthanum oxide. However, the lanthanum recovery and analytical data obtained during the recovery of CeO_2 (tables 1 and 2) show that at pH values of 4.5 and above the praseodymium, neodymium, and samarium started to precipitate selectively with the cerium, thereby leaving a more purified lanthanum product in the filtrate. The purity of the lanthanum in the filtrate increased with increasing pH up to the maximum value investigated, pH 6.5.

TABLE 3. - Recovery and purity of CeO_2 and La_2O_3 as a function of pH and time, at 85° C

Anion	pH	Reaction time, hours	CeO_2 in precipitate		La_2O_3 in filtrate	
			Recovery, percent	Purity, percent	Recovery, percent	Purity, percent
NO_3	5.5	$\frac{1}{2}$	99.4	72	78	90
	6.5	$\frac{1}{2}$	99.9	70	80	96
Cl	3.5	1	58	95	94	51
	4.5	1	99.9	90	97	75
	5.5	1	99.3	80	90	82
	6.5	$\frac{1}{2}$	99.7	72	88	94

The increase in purity occurred at ambient temperature as well as at 85° C, although the highest lanthanum purity values were obtained at the higher temperature. At 85° C and pH 6.5, 80-percent recovery of 96-percent-pure lanthanum (oxide basis) was obtained with the nitrate system, and 88-percent recovery of 94-percent-pure lanthanum with the chloride system. At ambient temperature, the best results were 88-percent recovery of 90-percent-pure lanthanum. The best results seem to be obtained with operation at elevated temperature, especially since the reaction time was decreased from 1 hour to one-half hour by heating the solution to 85° C. The lanthanum results obtained in the ozone system were notably superior to those obtained in the oxygen system mentioned previously.

Isolation and purification of both cerium and lanthanum in the bastnasite mixture would require a two-step operation. In the first step, the primary precipitation of cerium and heavier rare-earth salts at 85° C would provide a purified lanthanum product in the filtrate. In the second step, the filtered precipitate would be redissolved in mineral acid at ambient temperature and reozonated to provide a pure CeO_2 precipitate. Data given in table 4 are typical of the results obtained with such a two-step process.

TABLE 4. - Two-step recovery of CeO_2 and La_2O_3

Treatment	Anion	Temperature	pH	Reaction time, hours	Recovery, percent	Purity, percent
Step 1, lanthanum recovery.	{ NO_3 Cl }	85° C	6.5	$\frac{1}{2}$	89	95
		85° C	6.5	$\frac{1}{2}$	83	95
Step 2, cerium recovery.	{ NO_3 Cl }	Ambient	4.5	3	94	98
		Ambient	4.5	3	97	96

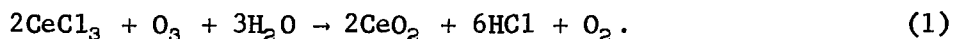
The rare-earth fraction in the first filtrate from the ozone oxidation-precipitation reaction at 85° C and pH 6.5 analyzed 95 percent lanthanum oxide for both the chloride and nitrate systems. Corresponding lanthanum recoveries were 89 percent for the nitrate system and 83 percent for the chloride system. Subsequent recovery of cerium from the heavier lanthanides by a second ozonation step at ambient temperature and pH 4.5 produced a slightly purer CeO_2

product from the nitrate system than from the chloride system (98 percent versus 96 percent), but the CeO_2 recovery from the chloride system was higher (97 percent versus 94 percent). In general, the anion is of minor importance, and it should be noted that it can be changed when redissolving the precipitate from the first step. This change of anionic specie could be of importance for subsequent separation of the rare-earth elements heavier than cerium.

Production of high-purity ceric oxide was shown to be feasible by dissolving the 98-percent ceric oxide ozonation product in hydrochloric acid and repeating the ozone oxidation-precipitation step at ambient temperature and pH 4.5. The purity of the resulting ceric oxide precipitate was in excess of 99.9 percent, and recovery was essentially complete.

The effect of rare-earth concentration on cerium recovery and purity was investigated by ozonating a 200-g/l solution of bastnasite-type chloride salts at ambient temperature and pH 4.5. Typical CeO_2 recovery values were in the 97 percent range, and the corresponding CeO_2 purity decreased from the 98 percent obtained at a concentration of 12 g/l to 93 percent. The reduced product purity was partially mitigated, however, by an increase in the precipitation rate to 1.8 times that obtained at the lower concentration.

The stoichiometry of the reaction occurring between ozone and cerium in solution was investigated by oxidizing high-purity cerous nitrate, chloride, or sulfate solutions at ambient temperature. No ammonia was added during the tests, and the pH dropped from an initial value of 6 to 2.5 for the chloride solutions. No precipitation occurred in the nitrate solution, possibly because of the stability of the anionic ceric nitrate complex at low pH. For the chloride and sulfate solutions, the ratios between the CeO_2 recovered, the ozone consumed, and the hydrogen ions produced at ambient temperature correspond to the following equation given for the chloride system.



The experimental data checked within 5 percent for equation 1. It is of interest in equation 1 that the ozone furnishes only 25 percent of the oxygen necessary to form the ceric oxide.

CONCLUSIONS

Cerium can be effectively recovered from complex rare-earth mixtures in solution by a simple, ambient temperature, oxidation-precipitation process utilizing ozone to precipitate CeO_2 . Operation in the pH range from 4.0 to 5.0 is recommended. The ozonation technique is also applicable to lanthanum purification by operating at 85° C, preferably at pH values greater than 5.0. The techniques involved are simple, relatively rapid, and produce commercial-grade cerium and lanthanum compounds in high yields. In addition, separation and purification are accomplished without introducing contaminants into the system.

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⁵Titles enclosed in parentheses are translations from the language in which the item was originally published.