

ELECTROWINNING CERIUM AND LANTHANUM METALS
FROM THEIR OXIDES

UNIVERSITY OF NEVADA

STATEMENT OF THE REQUIREMENTS FOR THE

DEGREE OF METALLURGICAL ENGINEER

BY

EDWARD MURPHY

1941

A THESIS SUBMITTED TO THE FACULTY OF
THE UNIVERSITY OF NEVADA IN PARTIAL FUL-
FILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF METALLURGICAL ENGINEER

by

EDWARD MORRICE

1964

Thesis

65 ✓

Procedures for electrowinning high-purity cerium and lanthanum metals from their oxides were developed at the Reno Metallurgy Research Center of the Federal Bureau of Mines. Experiments requisite to developing these procedures were planned and performed under the supervision of Edward Morrice, Extractive Metallurgist. Mr. Morrice is the senior author of the attached Reports of Investigation, 5549, 5868, and 6075, which contain the pertinent metallurgical laboratory data.

Claude W. Hammond

Thesis Director

Vernon E. Scheid

Department Head

W. P. Brinn

Dean, Graduate School

RI

bureau of mines
report of investigations 5549

METALLURGICAL LABORATORY DATA ON
REDUCTION AND REFINING OF CERIC OXIDE
AND CEROUS FLUORIDE TO CERIUM INGOT

By E. Morrice, J. Darrah, E. Brown, C. Wyche,
W. Headrick, R. Williams and R. G. Knickerbocker



UNITED STATES DEPARTMENT OF THE INTERIOR

METALLURGICAL LABORATORY DATA ON
REDUCTION AND REFINING OF CERIC OXIDE
AND CEROUS FLUORIDE TO CERIUM INGOT

By E. Morrice, J. Darrah, E. Brown, C. Wyche,
W. Headrick, R. Williams and R. G. Knickerbocker

* * * * * report of investigations 5549



UNITED STATES DEPARTMENT OF THE INTERIOR
Fred A. Seaton, Secretary

BUREAU OF MINES
Marling J. Ankeny, Director

This publication has been cataloged as follows:

Morrice, Edward.

Metallurgical laboratory data on reduction and refining of ceric oxide and cerous fluoride to cerium ingot, by E. Morrice [and others. Washington] U. S. Dept. of the Interior, Bureau of Mines, 1960.

36 p. illus., tables. 27 cm. (U. S. Bureau of Mines. Report of investigations, 5549)

Bibliography: p. 35-36.

1. Cerium—Electrometallurgy. 2. Cerium compounds. I. Title. (Series)

[TN23.U7 no. 5549] 622.06173

U. S. Dept. of the Int. Library

CONTENTS

	<u>Page</u>
Summary.....	1
Introduction.....	2
Preparation of anhydrous cerous fluoride.....	5
Details of Reno ammonium bifluoride method.....	6
Fluoride electrolytes.....	7
Vacuum drying.....	9
Electrowinning.....	9
Laboratory cell development.....	9
Cell type No. 1.....	9
Cell type No. 2.....	11
Cell type No. 3.....	12
Cell type No. 4.....	12
Reno cerium electrowinning cell (cell type No. 5)...	14
Electrowinning cell and electrode assembly.....	14
Melting of bath.....	17
Cerium electrowinning run (CE-42).....	18
Analyses of cell-box gases.....	20
Lithiothermic reduction and vacuum refining.....	21
Ceramics.....	23
Electrical conductivity of cerium metals.....	25
Investigations with chamber No. 1.....	26
Investigations with chamber No. 2.....	28
Discussion.....	29
Future work plans.....	33

ILLUSTRATIONS

Fig.

1. Cerium electrowinning cell type No. 5.....	15
2. Electrowinning gloved cell box and accessories.....	17

TABLES

	<u>Page</u>
1. Typical cell temperatures and cerium nodule analyses.	13
2. Analytical comparison of two cerium nodules from run CE-42.....	19
3. Analytical comparison of cerium metals.....	24
4. Electrical conductivity and purity comparisons of vacuum-refined, cold-rolled cerium metal samples at 0° C.....	27
5. Electrical conductivity and purity comparisons of machined cerium metal samples at -187° C.....	28
6. Typical data and results for electrowinning cerium from Reno electrolyte.....	31
7. Typical cell-box atmosphere and cerium nodule analyses.....	31

METALLURGICAL LABORATORY DATA ON REDUCTION AND REFINING
OF CERIC OXIDE AND CEROUS FLUORIDE TO CERIUM INGOT

by

E. Morrice, J. Darrah, E. Brown, C. Wyche, W. Headrick,
R. Williams and R. G. Knickerbocker

ERRATA

<u>Page</u>	<u>Par.</u>	<u>Line</u>	<u>Now reads in part</u>	<u>Should read</u>
2	7	4	(15, 23)	(26, 17)
3	1	3	(12)	(14)
3	1	4	(17)	(19)
3	2	3	(19)	(22)
3	3	3	(20)	(21)
4	3	1	(20)	(1)
4	3	2	(20, 4)	(22, 4)
6	1	6	(21)	(24)
6	1	9	(16)	(18)
8	2	1	(13)	(15)
8	5	3	A pool of molten alkali was	A pool of molten alkali <u>metal</u> was
9	1	7	(22)	(25)
14	4	4	A 40-volt, 200-ampere,	A 40-volt, <u>300</u> -ampere,
16	4	5	The air-lock inside diaen-	The air-lock inside dimen-
18	7	2	the 40-volt, 200-ampere	the 40-volt, <u>300</u> -ampere
20	3	4	(18, 14)	(20, 16)
20	4	2	(13)	(15)
21	5	5	cerous fluoride ce obtained	cerous fluoride <u>he</u> obtained
21	6	8	(20)	(22)
21	7	3	P. M. G. Gray	P. M. <u>J.</u> Gray
21	7	5	(17)	(19)
25	6	3	(20)	(22)
28	3	12	dislocations the	dislocations <u>in</u> the

METALLURGICAL LABORATORY DATA ON REDUCTION
AND REFINING OF CERIC OXIDE AND CEROUS
FLUORIDE TO CERIUM INGOT^{1/}

by

E. Morrice,^{2/} J. Darrah,^{3/} E. Brown,^{4/} C. Wyche,^{4/} W. Headrick,^{5/}
R. Williams,^{5/} and R. G. Knickerbocker^{6/}

SUMMARY

The metallurgical laboratory data developed in this study indicate an improved electrowinning process for producing higher purity cerium ingot.

A typical sample of the Reno electrocerium contains 99.9 weight-percent cerium and the following impurities: Total other rare-earth elements, less than 0.04 percent; iron not detected; silicon and aluminum, less than 0.02 percent each; calcium plus magnesium, less than 0.01 percent; carbon, 0.01 percent; oxygen, 0.002 percent; hydrogen, 0.0003 percent; and nitrogen, 0.0015 percent.

Equipment under development included the molten-bath container or electrolytic cell, electrodes, and related items, as well as an enclosure or cell box resembling that of a vacuum furnace. The cell box is designed to allow molten electrolysis to be performed in an atmosphere that can be closely controlled as to composition, temperature, and pressure. The molten electrolysis was conducted in a graphite cell, in which the temperature was also under close control and which prevented contact between cerium and carbon and permitted deposition of cerium metal at a temperature as close as possible to 805° C. Cell off-gases were sampled and analyzed. A section of this report describes these procedures and discusses the relation of cell-gas composition to metal purity.

In an experimental study of the suitability of several mixtures of metallic halides as the solvent phase of molten-salt electrolytes, the mixture of cerium, barium, and lithium fluorides in the proportion of 73, 12, and 15 percent, respectively, showed the greatest promise. Nevertheless, studies on the compounding and properties of cerium electrolytes are being continued, as the electrolyte is the cornerstone of the process.

^{1/} Work on manuscript completed January 1959.

^{2/} Metallurgist, Bureau of Mines, Region II, Reno, Nev.

^{3/} Physicist, Bureau of Mines, Region II, Reno, Nev.

^{4/} Chemist, Bureau of Mines, Region II, Reno, Nev.

^{5/} Physical science aid, Bureau of Mines, Region II, Reno, Nev.

^{6/} Supervisory metallurgist, Bureau of Mines, Region II, Reno, Nev.

Electrocerium nodules were formed in the small cells described in this report. These irregular, rounded nodules resulted from cerium metal being deposited in a molten condition and slipping down the cathode to the end where they sank into the bath and solidified. However, it is believed that in a larger cell and under favorable conditions the nodules will coalesce.

One of the interesting phenomena observed, which is still under investigation in this higher purity cerium electrowinning laboratory, is the large variation in purity of different nodules of metal from the same cathode in the same cell run. For example, although 0.01 percent calcium plus magnesium is typical in electrocerium analysis, a number of nodules of cerium have been made in which no magnesium or calcium has been detected. A method of comparing the nodules by air corrosion was used to classify higher- from lower-grade metal.

As an indicator of metal purity and an aid to learning more about certain properties of cerium, electrical conductivity measurements of the metal over a span of temperatures in a low range have yielded valuable data. Equipment for measuring electrical conductivity, like the electrowinning equipment, is still in a developmental stage. However, data obtained to date have shown a distinct correlation between electrical conductivity and metal purity. For example, at 0° C. the conductivity of a nodule of Reno electrocerium 99.9 percent pure was more than three times that of a sample of 95.8-percent cerium metal obtained from a commercial source.

A laboratory lithiothermic reduction procedure for preparing cerium regulus on a 50-gram scale by lithium-iodine reduction of cerous fluoride and the vacuum refining of this regulus to cerium metal are also described.

INTRODUCTION

The growth and future importance of the rare-earth metals in commercial industry may depend largely upon improved methods of extracting and refining these elements. It is proposed to use the data on the reduction and refining of cerium given in this report for this objective.

Cerium is one of the elements in a group comprising 65 percent of the known metallic elements that have never been prepared in sufficient quantity and quality to allow development of their important use patterns; more than 80 percent of all known elements are metallic, and only 35 percent of the metallic elements are being applied commercially to any major extent.

Cerium is the most abundant element of the rare-earth group. Mine-run ores of cerium from Mountain Pass, Calif., contain 3.6 percent cerium; monazite minerals from Florida beach sands, South Carolina, India, and Brazil range from 25 to 26 percent cerium (15, 23).^{7/}

^{7/} Underlined numbers in parentheses refer to items in the bibliography at the end of this report.

Cerium is a metallic element with a silvery luster, atomic weight of 140.13, density of 6.9, and atomic volume of 20, which forms crystals of face-centered cubic and close-packed hexagonal structures (12); it has a melting point of $804^{\circ} \pm 5^{\circ}$ C., according to F. H. Spedding (17).

Because of its superreactive nature, cerium alloys or forms compounds with virtually all metallic, nonmetallic, and gaseous elements. Felix Trombe (19) reports that cerium metal has distinctive elemental or metallic properties, such as its volume abnormalities, either under pressure or at low temperatures. In a study of metallic cerium in 1934, a nonreversible magnetic cycle was identified that did not seem to depend on the quantity of iron (of the order of 100 p.p.m.) in the cerium. These data have been confirmed after some years by Charlotte Henry La Blanchetais (12) who succeeded in preparing cerium with less than 5 p.p.m. of iron. This higher purity metal follows the Curie-Weiss law; that is, the reciprocal of the magnetic susceptibility is a straightline function of the absolute temperature. However, with 100 p.p.m. iron, the temperature-susceptibility relationship was altered markedly, showing that the magnetic properties of cerium are very sensitive to traces of iron. Other scientists did not confirm this phenomena, and the possible influence of iron was debated. In 1945 Trombe and Foex presented new data showing that the magnetic cycle is accompanied by a dilatation cycle of considerable importance, corresponding to a contraction in volume at diminishing temperature and an expansion in volume of 10 percent at increasing temperature. Instead of the 10-percent contraction at 109° K., there is a certain inertia and expansion around 175° K., then the two curves rejoin.

As the metal already has a dense structure (face-centered cubic) at ordinary temperatures and a contraction of 10 percent at lower temperatures, Linus Pauling (20) presented the idea that this phenomenon is electronic; that is, he considered that an electron changes orbit at lower temperatures, which caused contraction of cerium's atomic radius. Actually, cerium is again face-centered cubic at lower temperatures but has different parameters.

If pure cerium is submitted to successive heatings and coolings within a certain temperature range, the importance of magnetic and dilatation cycles diminishes progressively until their suppression is nearly complete. Cerium is then changed into another form, likewise compact but hexagonal.

Felix Trombe and Marc Foex (23) have established that certain impurities are responsible for the absence of cycles, regardless of the thermal treatment of the metal. It has been reported that calcium and magnesium, especially, are deterrents to obtaining the contracted form of cerium. In 1949 Lawson and Tang (13) obtained a transformation at 15,000 kg. per sq. cm. corresponding to a decrease in volume of 16.5 rather than 10 percent. This transformation was produced under pressure at ordinary temperature, whereas under standard pressure a temperature of 109° K. would be required.

These observations, reported by Trombe and other investigators, illustrate the importance of purity on certain properties of metallic cerium. Even the minute amount of contaminants in the purest cerium that has been studied may camouflage some as-yet undiscovered properties of still purer

metal. It is possible that one or more of the elusive properties of cerium will lead to important new uses. Another approach to greater utilization of this abundant but little-used natural resource is to find less expensive ways of producing a marketable-grade product. The aim of the Bureau's research is to develop processes that will yield high-purity metal that has commercial potentialities. Refining techniques for producing ultrapure metal, such as single-crystal or "whisker" products, are beyond the scope of present research at Reno but will become an essential phase of reduction and refining work in the near future.

Since the work reported by F. Trombe in 1956 and 1957, the Bureau's reduction and refining laboratory at Reno has reported the presence of molybdenum and tantalum in cerium metal where these metals are held in contact above 820° C. for any appreciable time.

Cerium metal has been prepared by calcium reduction (20) and has been electrowon from chloride and fluoride electrolytes (20, 4). W. J. Kroll (10) states:

Fluorine metallurgy is in its infancy, and it is much less advanced than that of chlorine. The advent of large fluorine cells has brought about considerable advance in organic fluorine compounds, and it is hoped that this movement will make itself felt also in the field of inorganic chemistry and its application to metallurgy.

The electrolysis of aqueous solutions of inorganic salts of cerium does not deposit pure metal, because the nascent cerium atoms react with water or hydrogen to form metallic oxide and hydrated oxide, or cerium hydride.

Electrolysis of alcoholic solutions of the anhydrous chlorides of cerium has been investigated (9).

Recent literature describes the hydrogen reduction of CeO_2 to Ce_2O_3 and nonstoichiometric intermediate oxides at temperatures between 250° and 1,400° C. The extent of reduction increases with the temperature (7).

The Reno process for electrowinning cerium from CeO_2 in fluoride electrolytes is similar to electrowinning aluminum from Al_2O_3 in cryolite baths, except for the more reactive nature of molten cerium. The Reno type of cerium electrowinning cell, with its controlled temperature and atmosphere, was a natural laboratory development which was partly suggested by previous work on the inert-atmosphere, electric-arc welding of tantalum and molybdenum cans for lithium-bomb reduction of cerous fluoride. In the lithiothermic work it was found that both tantalum and molybdenum alloy with cerium metal at the temperatures, pressures, and other conditions encountered in bomb reductions. The analysis of cerium metal from the tests showed tantalum 0.3 percent and molybdenum 2.7 percent.

The development of the 6-inch diameter, laboratory graphite cell was the result of investigations which proved that graphite was an excellent

refractory or corrosion-resistant material with molten rare-earth fluorides and oxyfluorides under controlled temperature-and-atmosphere electrolytic conditions. Graphite also costs much less than any suitable metallic container, can be easily fabricated into any size or shape, and is stable at 900° C. in the cell atmosphere consisting of argon or helium with CO₂, CO, and a small amount of O₂.

The following basic data guided the selection and composition of the CeF₃-BaF₂-LiF solvent-phase electrolyte for electrowinning of cerium from CeO₂:

1. The electrolyte has a melting point 75° to 80° C. below that of cerium.
2. The fluorides were chosen instead of the chlorides because they are less hygroscopic. Hydrogen forms cerium hydrides with molten cerium.
3. Sodium and potassium fluorides were found to be electrolytically unstable at the temperatures and pressures used in the cell.
4. The relation of density of cerium metal at 6.9 and the oxyfluoride electrolyte at 4.3 was advantageous.
5. Electrical resistivities of the molten bath were in the proper range for temperature control, electrolytic oxidation-reduction reactions, or transfer of cerium cations and oxyfluoride anions.

When these investigations on rare metals were initiated in 1956 at Reno, Nev., considerable metallothermic effort had been devoted to the preparation of rare-earth metals at Ames, Iowa, by F. H. Spedding and his coworkers and by the Bureau of Mines station at Albany, Oreg. Therefore, the metallothermic work at Reno was limited to lithium-iodine reductants. This phase of the reduction and refining laboratory work was completed in fiscal year 1958, and the data are given in this report.

PREPARATION OF ANHYDROUS CEROUS FLUORIDE

Anhydrous cerous fluoride was made for the preparation of cerium metal by lithiothermic reduction and for an electrowinning bath constituent.

Anhydrous cerous fluoride was made by the reaction of ammonium bifluoride with ceric oxide at 500° to 600° C. in air. Attempts to make cerous fluoride at temperatures lower than 500° C. resulted in contamination with ceric oxide. When temperatures exceeded 600° C. cerium oxyfluoride was formed. Platinum dishes or sintered cerous fluoride boats were used as reaction containers. When porcelain, iron, nickel, and fused alumina containers were used, the cerous fluoride product contained silicon, iron, nickel, and aluminum.

Two other methods of preparing anhydrous rare-earth fluorides are described in the literature. One method is precipitation from aqueous solution with hydrofluoric acid and dehydration (6). The principal difficulties are in the mechanics of washing and drying the hydrated fluoride to prepare anhydrous cerous fluoride consistently free from oxyfluorides. Another method is the gaseous fluorination of ceric oxide with HF or ClF₃ (21). According to Von Wartenberg, CeF₃ was made by passing anhydrous HF over CeO₂ in a platinum tube at temperatures above 400° C. Popov and Knudson describe the fluorination of the oxides lanthanum to samarium with ClF₃ (16).

The ammonium-bifluoride method used at Reno does not require the handling of a gelatinous precipitate and is simpler than either of the above methods for preparing small laboratory batches of anhydrous cerous fluoride.

Details of Reno Ammonium Bifluoride Method

Ceric oxide, obtained from a commercial company or from other work at the Reno station, was pulverized in a porcelain mortar with approximately 10 percent excess of the stoichiometric quantity of commercial ammonium bifluoride flakes. The mixture was placed in a platinum dish or CeF₃ boat in a laboratory muffle open to the air. The muffle was maintained at 500° to 600° C. for 2 hours before the product was removed. Some ammonium fluoride collected on the inside of the muffle.

The purity of cerous fluoride batches was determined by the X-ray and spectrographic analytical laboratories. A typical spectrographic analysis indicated that aluminum, calcium, iron, lithium, magnesium, nickel, platinum, silicon, and zinc were not detected. An X-ray diffraction pattern showed CeF₃. No ceric oxide or cerium oxyfluoride was detected. A sample of the CeF₃ was reported by the Bureau of Mines Boulder City station to contain 0.004 percent nitrogen.

One-hundred-and-fifty grams of cerous fluoride made by this method was sent to K. K. Kelly, Chief, Berkeley Thermodynamics Research Laboratory, at Berkeley, Calif. Analyses in the Berkeley station laboratory showed:

	<u>Determined</u>	<u>Theoretical</u>
Cerium.....percent..	71.14	71.09
Fluorine.....do.....	28.87	28.91

In order to prepare larger batches of cerous fluoride without contamination and to eliminate the use of platinum ware, sintered cerous fluoride boats were developed. Cerous fluoride, prepared in platinum dishes as described, was mixed with Carbowax and pressed at 56,000 p.s.i. into 1-13/16-inch, i.d. cylinders. The cylinders were cut in half longitudinally and the resulting boats placed in a 2-9/16-inch i.d. vitrified alumina tube within a horizontal tube furnace. The boats were heated in air at 250° C. for 2 hours to remove the Carbowax and sintered by bringing them to 530° C. in 15 hours.

The sintered cerous fluoride boats were loaded with the ammonium bifluoride-ceric oxide mixture (proportions as previously given), and the

tube furnace was brought from room temperature to 500° C. in 4 hours. The charge was maintained at 500° to 600° C. in the air for 2 hours. Eight-hundred-gram batches of cerous fluoride were made by this method.

In a typical spectrographic analysis no aluminum, calcium, iron, lithium, magnesium, nickel, platinum, silicon, and zinc were detected. X-ray diffraction showed no $CeOF_2$ or CeO_2 .

High-temperature heat-content measurements were made at the Berkeley Thermodynamics Research Laboratory, Berkeley, Calif., on samples of cerous fluoride prepared by the ammonium bifluoride method in platinum dishes and in sintered CeF_3 boats at the Reno station.

FLUORIDE ELECTROLYTES

A prime requisite of a successful molten-salt electrowinning process is a suitable electrolyte. Such factors as cathode, anode, and cell construction materials, composition of the atmosphere surrounding the cell, and voltage and current requirements are also essential but are largely contingent on characteristics of the electrolyte. Accordingly, the electrolyte might be considered the heart of the high-purity-metal electrowinning process.

Surprisingly little basic data have been published on fluoride electrolytes. Because of the key function they perform and the dearth of information on them, considerable effort is being applied to basic studies of electrolytes--the preliminary of cell-box electrowinning investigations. The electrolyte experimentation is on a much smaller scale than the electrowinning studies; its purpose is to define the physical, chemical, and electrochemical characteristics of combinations of fluoride solvent-phase constituents and of electrolytic baths.

Measurements desired and phenomena about which better understanding are needed concern melting points, viscosity, density, vapor pressure, tendency to wet graphite, solubility of solute in solvent, ionization, transfer of ions, equilibria, polarization, and effects of anode gases.

These investigations on electrolytes require special measuring devices for use with melting and atmosphere-control equipment. Obtaining accurate data is complicated by the extremely corrosive nature of the molten fluorides. Many of these studies are in a formative stage, and a search is still in progress for instruments suitable for making some measurements. However, during the period covered by this report, melting points, conductivities, and solubilities of components were measured, and preliminary electrolyses were conducted on several fluoride baths. The small scale of the operations conserved time and materials in developing suitable electrolytes for trial in the larger cerium electrowinning cells.

Several types of small-scale cells were used for fluoride melting-point determinations and electrolysis of short duration. One cell comprised a carbon pot (welding-rod carbon) 5/8 inch i.d. and 2-3/4 inches deep, set inside a 1- by 7.9-inch Vycor glass tube. The anode (a carbon rod 1/8-inch

in diameter) and the cathode (a molybdenum strip 1/32 inch wide and 0.01 inch thick) were attached to a 3/16-inch-diameter brass rod and insulated from each other with sheet mica. The brass rod served as the electrical lead to the anode, and a copper wire served as the lead to the cathode. The electrical assembly was introduced into the cell through rubber sleeves set over nipples in a Pyrex glass head. The glass head also had outlets, permitting evacuation and flushing with argon and introduction of a thermocouple protection tube, and was sealed in place in the mouth of the Vycor glass test tube with Apiezon wax. The wax was kept cool with a jet of air.

Neidrach and Dearing (13) have suggested that adding small amounts of chlorides to molten fluoride solvents increases fluidity and electrical conductivity. The described apparatus was used in investigating the effect of adding 5 percent by weight of $MgCl_2$ to part of a CeF_3 -LiF- BaF_2 bath from the Reno cerium electrowinning cell. The $MgCl_2$ lowered the bath melting point from 740° to 690° C., but chlorine gas was produced during electrolysis and anode effect was noted.

The loss of lithium from the CeF_3 -LiF- BaF_2 bath during electrolysis suggested the investigation of a new bath containing less LiF. With the previously described apparatus and the electrode assembly removed, a series of melting points was measured on various CeF -LiF- BaF_2 mixtures by the thermal-analysis techniques and visual observations. A bath having a satisfactory melting point of 735° C. was prepared, comprising 77.3 percent CeF_3 , 12.7 percent BaF_2 , and 10.0 percent LiF by weight. P. M. J. Gray's bath (4) contained 26.9 weight-percent LiF.

MgF_2 was investigated as a substitute for LiF in the CeF_3 -LiF- BaF_2 bath because it has a lower vapor pressure. The melting points of various CeF_3 - MgF_2 - BaF_2 mixtures were measured. As the lowest melting point was 930° C., no mixture investigated was suitable as a solvent-phase electrolyte for electrowinning of cerium. However, MgF_2 may serve as a bath constituent for electrowinning of uranium ingot and the rare-earth metals melting above $1,000^\circ$ C.

Using a KF-LiF-NaF solvent-phase electrolyte and adding CeF_3 , the authors carried out electrolysis in a tantalum cell within a controlled-atmosphere glove box. A pool of molten alkali was noticed around the cathode at the top of the bath during electrolysis. X-ray diffraction patterns of cell products showed that no cerium metal had been produced. With a $BaCl_2$ - $CaCl_2$ - CeF_3 bath, electrolysis in a Vycor cell within the controlled-atmosphere glove box produced massive cerium metal and chlorine gas. Spectrographic analysis showed 0.01 to 0.1 percent calcium in the cerium metal.

Several small-scale cells were designed and investigated to measure the electrical conductivity of molten fluoride systems with alternating current. The fabrication of a suitable cell has been hampered by lack of a nonconducting material resistant to fluoride corrosion.

A cell requiring about 75 grams of bath material was built and gave results in good agreement with values in the literature for the electrical conductivities of molten KCl and NaCl. All parts of the cell in contact with

the molten bath were made of graphite or molybdenum, except a Vycor glass tube that provided an insulated electrolyte path between the two molybdenum electrodes. Fluoride corrosion of the Vycor glass prevented good reproducibility in electrical-conductivity measurements of molten fluoride systems with this cell. A new cell is being developed in which the Vycor glass tube is replaced by a hot-pressed boron nitride tube. Data obtained in this laboratory and by other workers (22) have indicated that boron nitride is resistant enough to corrosion by molten fluorides for short periods to serve these experimental purposes.

Vacuum Drying

The constituents for the solvent phase of the cerium electrolyte, that is, CeF_3 , BaF_2 (reagent-grade), and LiF powder (reagent-grade), were mixed in air in the proper proportions. The mixture was placed in a glass-stopcocked Pyrex flask within a wire-wound resistance furnace. The flask was evacuated to about 10 microns, and the furnace turned on. All vacuum readings were taken with a Pirani gage. As the furnace heated, the flask was pumped out continuously by a mechanical high-vacuum pump with a dry-ice-acetone trap. A furnace temperature of approximately 280°C . and about 15 hours were necessary for the mixture to reach a vacuum of 10 to 15 microns. The powder mixture was then tested for moisture as follows: Moisture removed after dehydration of the electrolyte components was captured in a dry ice-acetone cold trap for 5 to 10 minutes. The trap was then warmed to room temperature and flushed with dry argon through a sensitive moisture-determining instrument, the moisture monitor. When no moisture was detected above the level of the argon blank, the sample was considered dry.

The powder, comprising 73 percent CeF_3 , 15 percent LiF , and 12 percent BaF_2 , contained approximately 1 percent moisture before vacuum drying. This mixture will be referred to in this report as the Reno fluoride solvent-phase electrolyte, or the Reno fluoride electrolyte. The procedure removed about 70 percent of the moisture. An experiment indicated that most of the remaining moisture was removed as the temperature was increased to the melting point of the bath. CeO_2 , the solute phase of this electrolyte, was vacuum-dried in a similar manner.

ELECTROWINNING

Laboratory-Cell Development

Cell Type No. 1

A carbon cell 8 inches high by 4 inches i.d. was designed. P. M. J. Gray (4) used a similar cell. This cell, made of grade CS-31 carbon, was heated externally by a wire-wound resistance furnace through a type-316 stainless-steel can; the inside bottom of the carbon cell was covered with molybdenum sheet that extended 1 inch up the sides. A small 1- by 1-3/16-inch-diameter molybdenum crucible for holding the molten cerium product was placed under the 0.2-inch-diameter molybdenum cathode. The cathode was protected to 1 inch above the bath by a carbon sheath, which also served as an

entrance tube for the argon gas that continuously purged the space above the bath. The small molybdenum crucible was suspended from the carbon sheath with molybdenum ribbons so that it could be raised above the molten bath when electrolysis was complete. No evacuation of contained air or occluded gases in the carbon or charge was possible in a cell of this type. A 0.625-inch-diameter, grade CS-31 carbon anode was used with 1-inch spacing between electrodes. The cell was covered with a water-cooled carbon lid, and the lid was covered with 2 inches of transite insulation.

In a cell of this type ceric oxide cannot be added continuously during electrolysis, thus the operation was of short duration or a batch-type one. It is doubtful whether the data obtained can be compared with continuous-operation data in which the oxide feed is added during electrolysis.

Preparation of Charge

A fluoride electrolyte composed of 60.8 percent by weight of CeF_3 , 26.9 percent LiF , and 12.3 percent BaF_2 was used. This mixture was reported to be capable of dissolving 3 to 5 percent by weight of CeO_2 at 850°C . The density of the mixture was approximately 4.0 grams per cubic centimeter. The dry-powder mixture required to form a bath 2 inches deep in the cell was calculated to be of the following weight composition:

	<u>Grams</u>
Cerous fluoride.....	972.8
Lithium fluoride.....	430.4
Barium fluoride.....	196.8
Ceric oxide.....	160.0

The cerous fluoride (99.8 percent pure) used in this experiment was prepared from ceric oxide purchased from a commercial source and mixed with ceric oxide prepared from bastnasite in the Extraction Section of the Reno laboratory. The mixture was fluorinated with ammonium bifluoride, as already described. The lithium fluoride powder was reagent grade; spectrographic analysis showing less than 0.1 percent barium, 0.001 percent magnesium, and other metallic and nonmetallic elements as traces. The barium fluoride was also reagent grade, spectrographic analysis showing less than 0.01 percent calcium, 0.001 percent magnesium, 0.001 percent silicon, 0.1 percent strontium, and 0.001 percent titanium.

The mixed charge was made into briquets in a laboratory hydraulic press at 20 tons per square inch. This permitted charging the complete 1,760 grams of mixture into the carbon cell where the charge was dried for 16 hours at 140°C . After the briquets were charged and the cell was covered, purified argon was passed through the cell for 30 minutes before initial heating.

Melting of Charge

While the purified argon continued to flow through the cell, the furnace temperature was raised. The time required for melting was 4 hours, and the

bath was molten at a furnace temperature of 900° C. Furnace temperatures were taken on the outside bottom of the carbon cell with a base-metal thermocouple. The actual temperatures of the molten bath were taken at intervals with a bare platinum-rhodium thermocouple through the port at the top of the lid. Part of the molten bath adhered to a molybdenum strip. This light-blue vitreous slag analyzed 0.1 percent iron, 0.01 percent magnesium, 0.1 percent molybdenum, and 0.001 percent silicon. The slag adhering to the molybdenum strip indicated a bath depth of 2-1/4 inches.

Electrolytic Operations

The bath was electrolyzed at a temperature of 820° to 890° C. for 108 minutes. The amperage ranged from 20 to 15 and the voltage between the electrodes from 6.3 to 5.6.

The cathode and the molybdenum crucible were lifted above the molten bath before allowing it to freeze. Purified argon continued to flow through the cell until the bath had reached room temperature, approximately 13 hours.

The molybdenum crucible, which was easily removed from the supporting basket, was filled to the top with nodules of cerium metal in light-blue electrolyte. The cerium metal when cleaned of electrolyte was found by the X-ray laboratory to contain traces of iron and molybdenum. The cathode density was calculated to be approximately 6 amperes per square centimeter. The cerium metal analyzed 0.1 percent barium, 0.01 to 0.1 percent iron, 0.001 percent magnesium, 0.1 percent molybdenum, 0.001 percent silicon, and traces of other metallic elements.

Five separate electrowinning experiments were made with this cell. The temperature of the electrolyte ranged from 890° to 820° C., the voltage between electrodes from 6.2 to 4.4, the amperage from 19.0 to 15.0, and the electrode immersion depth from 3/4 to 5/8 inch; the distance between electrodes was held at 1 inch. The time of electrolysis ranged from 1.6 to 3.5 hours per experiment. The following conclusions were drawn: (1) CO₂ gas was identified as a product of the electrolysis, and (2) no fluorine gas could be detected as a result of the electrolytic action.

The metal made in these five experimental runs in the No. 1 type cell contained cerium carbide. Considerable electric current was lost through poor insulation between the electrodes and carbon cell top, and it was difficult to keep the electrodes adjusted to their proper positions. The inability to see the molten bath and make necessary adjustments was a major handicap. Purging the space in the cell above the bath with inert gas at pressure did not remove air and moisture, as was indicated by the yellow (CeO₂) surface of the solidified bath. The highest current efficiency attained in any of the five runs was less than 35 percent. The melting temperature of the fluoride electrolyte was approximately 715° C.

Cell Type No. 2

The first alterations made on the No. 1 carbon cell were to line it with sheet molybdenum, remove the carbon sheath surrounding the cathode, and

improve the transite bushings on the electrodes in the carbon cell top so as to eliminate the stray current losses. The charge to cell No. 2 was the same as that to cell No. 1, comprising the same mixture of CeF_3 -LiF-BaF₂ and ceric oxide. The molybdenum cup was fastened to the bottom of the molybdenum liner and not attached to the cathode.

The bath was electrolyzed at 778° to 814° C. for 178 minutes with the electrodes immersed three-fourths inch. The amperage ranged from 20 to 29 and the voltage from 7.4 to 8.2.

The electrodes and molybdenum cup were allowed to freeze in the bath. The molybdenum lining was eaten through immediately above the bath, and some of the bath contacted the carbon cell. The molybdenum cup was displaced from under the cathode. A small amount of cerium adhered to the molybdenum cathode, and some nodules were dispersed in the frozen bath.

Cell Type No. 3

Inability to observe the cell operations and control the essential factors in Nos. 1 and 2 cells led to the development of cell type No. 3, which was operated in an argon atmosphere. Cell operations were visible through safety glass and controlled by gloved hands through ports in a steel box.

The cell, furnace, and electrode assembly were arranged within a mild-steel glove box. The electrode assembly consisted of a steel frame with an adjustable electrode holder carrying two electrodes and direct-current conductor arms. The fluoride bath was kept molten by external heating with a resistance furnace made of nichrome wire wound in a 5-inch-i.d. alundum sleeve. The box atmosphere was pumped down and purified argon introduced before melting the "Gray" electrolyte. The argon atmosphere was tested with a gas master instrument and moisture monitor to control purity. One 0.375-inch-diameter carbon-rod anode and one 0.200-inch-diameter molybdenum-rod cathode were used.

Iron, Vycor glass, carbon, and graphite were investigated as cell materials. Cerium metal prepared in the externally heated iron cell, but not in contact with the iron, contained 5.27 percent iron. Vycor glass was corroded with the molten fluoride bath and the cerium metal. Cerium metal that had contacted the carbon or graphite cell walls or bottom contained up to 2.2 percent carbon.

When molten electrolyte and cerium metal contacted the CS-31 carbon cell walls and bottom, cracks developed, resulting in loss of bath. AGX-grade graphite was substituted for CS-31 carbon and did not crack under similar conditions.

Cell Type No. 4

Preventing the molten cerium from contacting the graphite cell walls and bottom was investigated, using the furnace and electrode assembly described in the cell type No. 3.

In one experiment with the Reno fluoride solvent-phase electrolyte, a sintered cerous fluoride disk was placed in the cell bottom. The disk prevented the cerium metal from contacting the graphite cell, and no evidence of carbide formation was noted. However, the CeF_3 disk dissolved slowly in the bath.

In another experiment (CE-30), an air-cooled copper coil was placed under the graphite cell bottom and a frozen layer of electrolyte maintained. Two hundred grams of massive cerium metal was deposited and held above the cell bottom. Analysis of a nodule of CE-30 cerium metal by the Boulder City station showed 0.01 percent carbon. Table 1 gives analyses of this nodule for metallic and nonmetallic impurities.

TABLE 1. - Typical cell temperatures and cerium nodule analyses

Run No.	Nodule No.	Elements, weight-percent							
		Total rare-earths	Fe	Si	Al	Ca + Mg	Li	Ba	Mo
CE-30 ^{1/}	1	0.04	(2/)	0.02	0.02	0.01	0.001	0.001-.01	0.02
CE-41 ^{3/}	1	(2/)	(2/)	(2/)	.04	(2/)	.01	(2/)	.02
	2	.01	0.03	(2/)	.04	.006	.01	(2/)	.02
	3	(2/)	.06	(2/)	.06	(2/)	.01	(2/)	.05
CE-42 ^{3/}	2S	(2/)	.03	(2/)	(2/)	(2/)	.01	(2/)	(2/)
	2T	(2/)	.06	(2/)	.08	(2/)	.01	(2/)	.05
	1S	(2/)	.04	.01	.03	.001	(2/)	(2/)	.04

Run No.	Nodule No.	Elements, p.p.m.				Total impurities, weight, percent	Temperature, °C.					
		C	O	N	H		Bath		Anode		Cell bottom	
							Average	Maximum	Average	Maximum	Average	Maximum
CE-30 ^{1/}	1	100	20	15	3	0.125	820	850	780	818	622	749
CE-41 ^{3/}	1	34	523	5	5	.126	845	932	785	822	675	728
	2	(4/)	(4/)	(4/)	(4/)							
	3	(4/)	(4/)	(4/)	(4/)							
CE-42 ^{3/}	2S	207	569	6	9	.119	878	920	817	869	605	683
	2T	55	594	6	4	.266						
	1S	(4/)	(4/)	(4/)	(4/)							

- 1/ Cell type 4.
 2/ Not detected.
 3/ Cell type 5.
 4/ Not determined.

A mixture comprising 1,178 grams of the Reno fluoride electrolyte and 1,622 grams of old bath was dried using the procedure described under vacuum drying, page 9.

This bath was melted in a 4-inch-i.d. by 4-5/8-inch-deep graphite cell, using a wire-wound resistance furnace within the controlled atmosphere and temperature cell box. A bath temperature of 772° to 850° C. and a cell-bottom temperature of 590° to 749° C. were maintained during electrolysis.

A 0.200-inch-diameter molybdenum-rod cathode and a 0.625-inch-diameter carbon anode, three-fourths inch apart, were immersed 1 inch in the molten bath.

Ceric oxide was added to the molten bath at a rate of approximately 2.5 grams per 5 minutes during the 510 minutes of electrolysis, and an average current of 19.6 amperes and 6.0 volts was maintained.

Reno Cerium Electrowinning Cell (Cell Type No. 5)

As a result of previous data semicontinuous cell type No. 5 was developed. It differs mainly from the earlier types in that the electrode arrangement for melting the bath is the same as that for electrolysis. Although this 6-inch-diameter graphite cell is the latest cell development reported at this time, plans have been made to develop a continuous 12-inch-diameter electrowinning cerium cell in the near future.

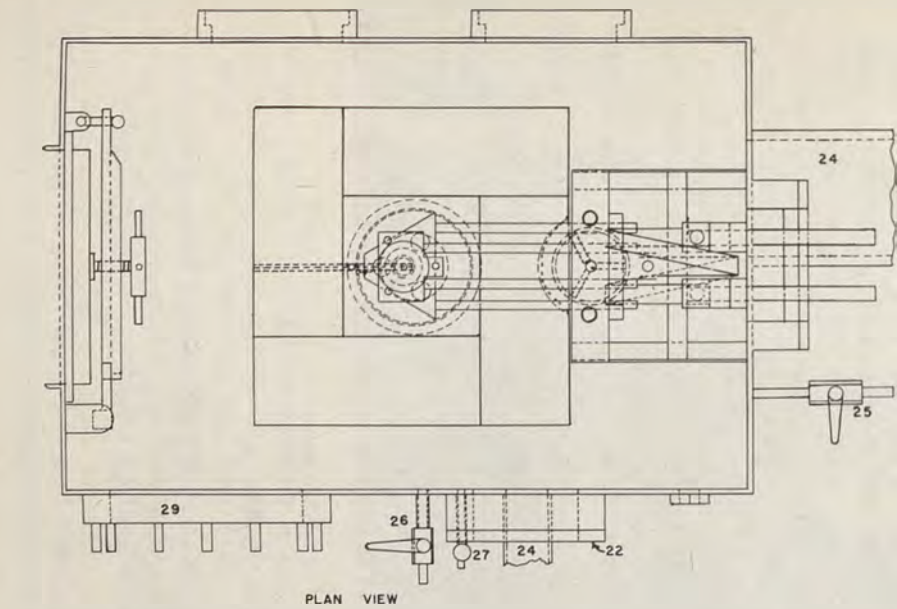
In order to have more positive control of the temperatures of the cathodes, anodes, cell walls, and cell bottom and maintain a layer of frozen electrolyte on the cell walls and bottom, a triangular electrode arrangement adapted to internal melting was designed and built. A 40-volt, 200-ampere, silicon, a.c.-d.c. rectifier unit and a 300-ampere, 40-volt, a.c. arc-welding unit were used as power sources. The No. 5 cell was operated in a controlled atmosphere and temperature glove box. Figure 1 shows the principal features of this cell and glove box.

The meltdown of the Reno fluoride electrolyte was initiated by passing current through the electrodes and through graphite-ring resistors that contact the bottom ends of the electrodes. The resistors are set on minus-10-mesh old-bath material within the graphite cell and are removed after enough bath has melted to carry the current.

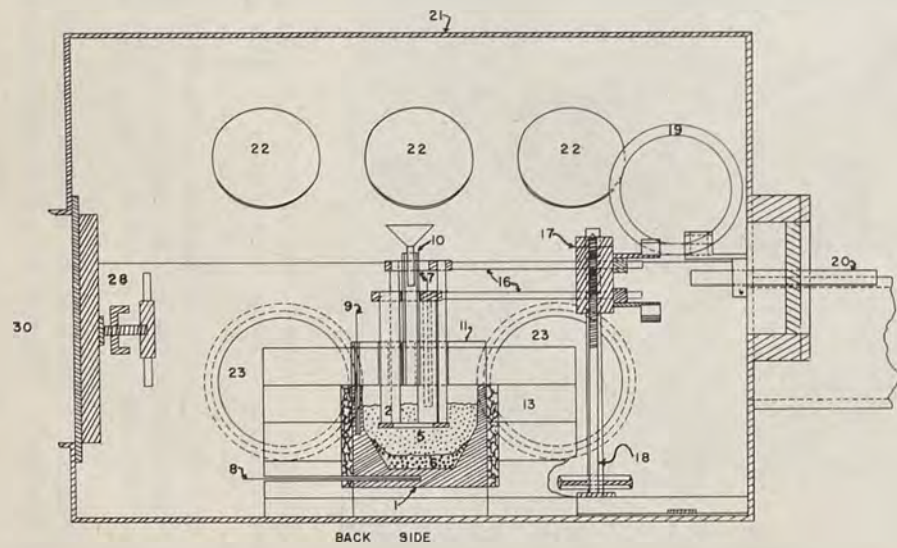
Electrowinning Cell and Electrode Assembly

The electrowinning cell is AGX-grade graphite, 6-1/8 inches inside top diameter by 4-1/2 inches deep. The cell tapers to 6 inches i.d. at a depth of 2-1/4 inches and to 3-1/2 inches i.d. in the remaining 2-1/4 inches. The graphite cell walls are 1/2 inch thick and the bottom 1 inch thick. One thermocouple well is drilled longitudinally in the graphite cell wall; another thermocouple well is drilled in the graphite cell bottom. Chromel-alumel thermocouples in sillimanite protection tubes are placed in the thermocouple wells.

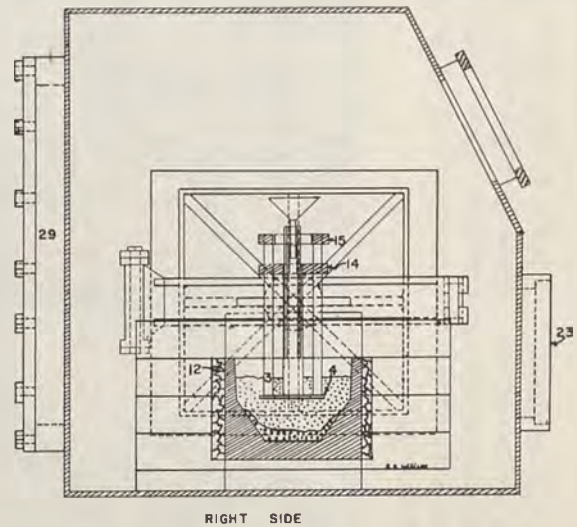
The cell is insulated on the sides with 4 inches of insulating brick with 1/2 inch of minus-4-mesh fire-clay brick grog between the graphite and the insulating brick. The bottom of the cell rests on 1-1/2 inches of insulating brick, allowing more heat loss and helping to maintain a bottom layer of frozen bath or skull. The cell cover is fire-clay brick 2-1/2 inches thick. The central brick of the cell cover is drilled to accommodate electrodes and feed tube. A 3/8-inch-i.d. sillimanite tube with a Pyrex funnel for feeding cell charge materials and ceric oxide terminates at the bottom of this brick cover.



PLAN VIEW



BACK SIDE



RIGHT SIDE

- | | |
|--------------------------------|-------------------------------------|
| 1. GRAPHITE CELL | 16. POWER-CONDUCTOR RODS |
| 2. CARBON ANODE | 17. TRANSITE BLOCK |
| 3. MOLYBDENUM CATHODE | 18. ELECTRODE ADJUSTING SCREW |
| 4. GRAPHITE-RING RESISTORS | 19. POWER CABLES |
| 5. MOLTEN-FLUORIDE BATH | 20. POWER FEEDTHROUGHS |
| 6. FROZEN-BATH LAYER | 21. STEEL GLOVE BOX |
| 7. ANODE THERMOCOUPLE | 22. GLASS-VIEWING PORTS |
| 8. CELL-BOTTOM THERMOCOUPLE | 23. GLOVE PORTS |
| 9. CELL-WALL THERMOCOUPLE | 24. GLOVE-BOX PUMPOUT |
| 10. SILLIMANTE FEED TUBE | 25. ARGON OR HELIUM INLET VALVE |
| 11. FIRE CLAY BRICK CELL COVER | 26. OUTLET VALVE FOR GAS SAMPLES |
| 12. FIRE CLAY BRICK GROG | 27. " " " MOISTURE " |
| 13. INSULATING BRICK | 28. GLOVE-BOX - AIRLOCK ACCESS DOOR |
| 14. ANODE HOLDER PLATE | 29. GLOVE-BOX ACCESS DOOR |
| 15. CATHODE HOLDER PLATE | 30. AIR LOCK |

FIGURE 1. - Cerium Electrowinning Cell Type No. 5.

The electrode assembly consists of an adjustable three anode- three cathode triangular system. (See fig. 1.) A thermocouple well is drilled longitudinally in a carbon anode within 1 inch of the bottom. A chromel-alumel thermocouple in a sillimanite protection tube is placed in the anode thermocouple well.

Two copper power-conductor rods from the anode and cathode holder pass through a transite block that is raised and lowered on a steel frame by operating an adjusting screw to position the electrodes vertically.

Rubber-insulated power cables carry the current to the conductors from power feedthroughs, which are vacuum-sealed in a rubber-gasketed Micarta plate on the end of the glove box. Rubber-insulated power cables carry current from the a.c.-d.c. rectifier and a.c. welder heater to the ends of the power feedthroughs outside the steel glove box.

Steel Glove Box

The electrode assembly and graphite cell are centrally located in the controlled atmosphere-temperature-pressure (C.A.T.P.) steel glove box. The glove box and air-lock enclosures are made of welded 1/4-inch mild-steel plate. (See figs. 1 and 2.) The inside dimensions of the glove box are 24 inches wide by 36 inches long by 26 inches high. The air-lock inside dimensions are 12 inches wide by 12 inches high by 18 inches long. The room air-lock door and the glove box-air lock access door are sealed with flat rubber gaskets. A 10- by 18-inch mild steel door is sealed to the rear side of the glove box with a flat rubber gasket. This glove-box access door is removed for setting up and dismantling the electrowinning cell and electrode assembly.

The inside of the glove box and air lock were sandblasted and painted with a water solution of 1-percent "Siliclad." No noticeable corrosion had taken place on the inside surfaces of the mild steel glove box after exposure to vapors from various melting and electrolytic experiments with fluoride baths over a period of 9 months.

The 1-inch-thick, laminated, safety-glass viewing ports were slightly etched after several electrolytic runs and were removed and buffed to restore transparency. A 100-watt light bulb within the box was used for illumination.

Replacing Air With Inert Atmosphere

Figure 2 shows the oil-diffusion pump, a welded-steel cold trap, and a mechanical fore pump connected to the end of the glove box opposite the air lock. The 6-inch-diameter oil-diffusion pump and the mechanical fore pump can be used to evacuate the glove box through a 6-inch steel pipe and the air lock through a 4-inch steel pipe. The box and air lock can also be evacuated through a 2-inch pipe attached directly to the mechanical pump.

Argon or helium is admitted to the glove box through the 1/4-inch copper tube shown in figure 1. Box atmosphere pressures were measured through this

tube using a mercury manometer. Samples of box and air-lock atmospheres for gas master tests and Orsat gas analyses were obtained through the 1/4-inch valve shown in figure 1. Box atmosphere samples for moisture determinations were transferred into the moisture monitor through a copper Teflon tube system connected to a vacuum pump.

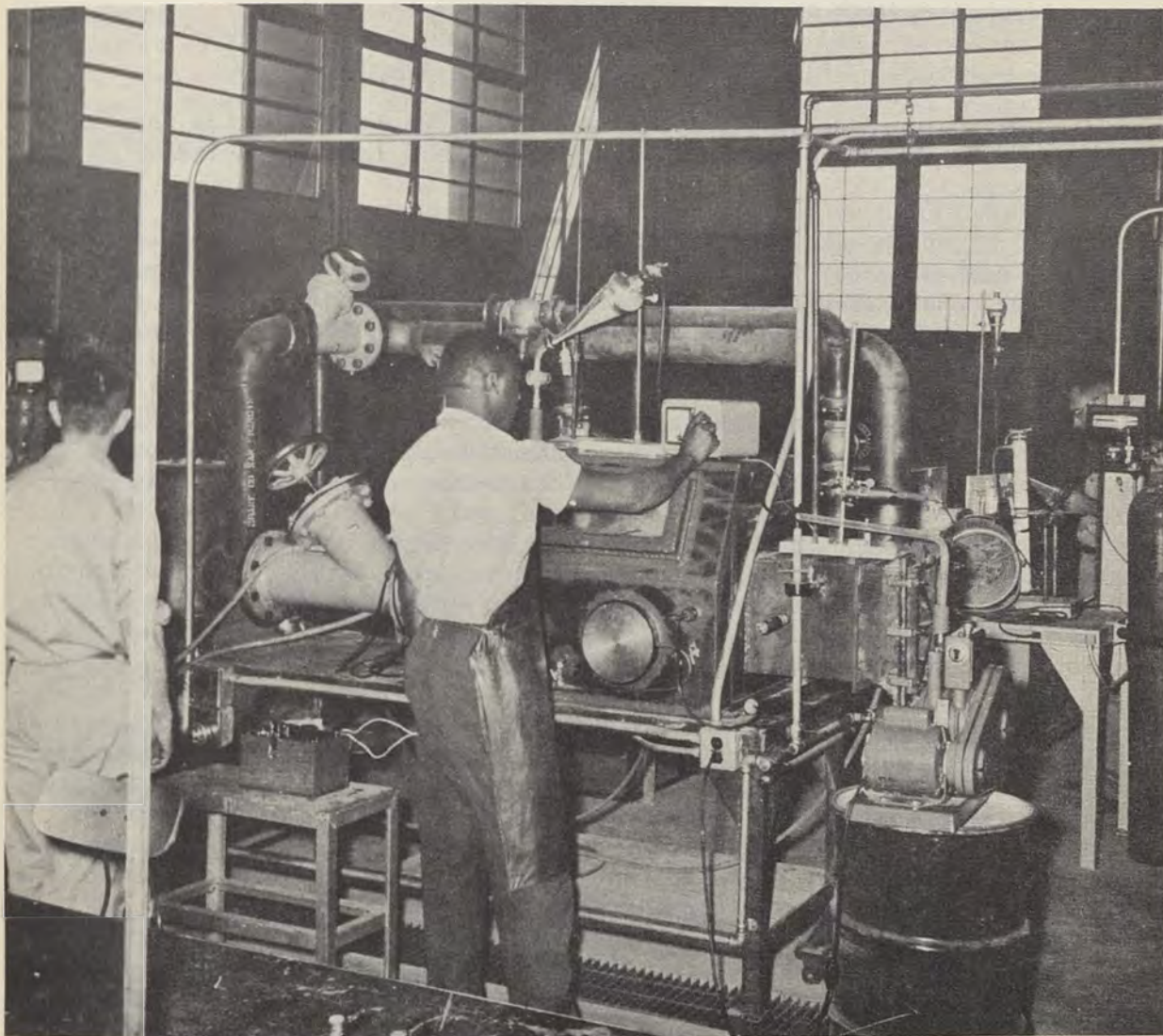


FIGURE 2. - Electrowinning Gloved Cell Box and Accessories.

Melting of Bath

Electrocerium fluoride charges were melted by passing direct current through the graphite resistors contacting the bottoms of the electrodes. The 40-volt 300-ampere, silicon, a.c.-d.c. rectifier unit was the d.-c. source. Arcing was noted with erratic voltage and current conditions. Moreover, cerium carbides were formed, as cerium-metal deposition began with the initial melting of the charge when graphite resistors were present. Analysis of

a cerium metal sample, where part of a graphite resistor remained in the bath during electrolysis, showed 5,200 p.p.m. carbon.

Several attempts were made to use cerium metal strips as resistors in melting with direct current. In all instances the cerium metal melted, breaking the circuit before enough molten bath had been obtained to carry the current. Additional work on this problem is planned in the future.

Cerium Electrowinning Run (CE-42)

A cerium electrowinning run was made using the Reno fluoride solvent phase of the electrolyte and CeO_2 solute with a.-c. internal meltdown in the type No. 5 cell.

The C. A. T. P. glove box containing the triangular electrode assembly and the 6-inch-diameter insulated graphite cell described previously were pumped down to 75 microns. High-purity tank argon was run into the glove box to 3/4-p.s.i. The box atmosphere and high-purity tank argon were compared with the gas master and found to have equal thermal conductivities.

Three thousand one hundred and thirty grams of minus-10-mesh charge, made from the old bath of a previous electrowinning run and vacuum dried, were loaded into the cell. Two graphite half-ring resistors, 3/16 inch thick by 3-3/4 inches o.d. by 3/8 inch wide, were placed on top of the minus-10-mesh charge. The electrodes were lowered to contact the resistors. The resistors were placed 1-3/4 inches from the top of the cell, and 1 inch of vacuum-dried, Reno fluoride, solvent-phase electrolyte powder was placed on top of the resistors. When the graphite resistors were placed on fresh powder, arcing was caused by shrinkage of the bath.

Alternating current at an average of 7 volts and 300 amperes was passed through the graphite resistors for 2 hours using the 40-volt 300-ampere arc-welding unit. About 1,500 grams of Reno fluoride solvent-phase electrolyte was added to the cell by the gloved operator through the feed tube during the alternating-current meltdown. No arcing was noted. When a fluoride bath was obtained around the electrodes and the bath temperature was 750° C., the graphite resistors were removed, using molybdenum tongs.

The current was then switched from a.c. on the welding unit to d.c. on the 40-volt, 200-ampere silicon rectifier. Ceric oxide (CeO_2) powder was charged into the molten bath by the gloved operator through the sillimanite feed tube, using a calibrated glass spoon. A ceric oxide feed rate of 2 grams per minute was maintained during the 146 minutes of electrolysis.

An average direct-current voltage of 6.7 and an average amperage of 203 were maintained during electrolysis. The electrodes were immersed in the bath three-quarters inch, giving an initial cathode current density of 11.3 a. per sq. cm. and an initial anode current density of 4.5 a. per sq. cm. Adjoining cathodes and anodes were 0.75 inch apart and 1.25 inches from the cell wall.

During electrolysis the temperature of the anode having the thermocouple well averaged 817° C. and the cell-bottom temperature 605° C.

Samples of the cell-box atmosphere were taken for Orsat gas analysis at approximately 15-minute intervals. At intermittent intervals the box was partly pumped down, and high-purity argon was introduced to maintain the box atmosphere at about 66° C. which enabled the operator to work in the box. A maximum of 17.6 percent CO₂ and 1.8 percent CO was reached in the box atmosphere. Usually, the pumpdowns and introduction of argon maintained the box atmosphere below 12 percent CO₂ and 1 percent CO. Qualitative tests of box-atmosphere samples for fluoride ion, using zirconium alizarin solution, were negative.

Some of the bath foamed over the side of the graphite cell during this run. A small amount of a white, powdery sublimate collected on the anodes above the bath. Previous X-ray diffraction patterns indicated that this sublimate was chiefly LiF. The glass viewing ports were also coated with a white, powdery sublimate and were slightly etched.

The bath with immersed electrodes was allowed to freeze in the cell-box atmosphere upon completion of the run and remained there for 15 hours. The frozen bath was then readily lifted from the graphite cell by means of the electrodes. The graphite cell was not visibly corroded.

Six hundred and six grams of massive cerium metal nodules, mostly 1/2- by 1/2- by 1-inch, were found scattered in the frozen bath beneath the electrodes. None of the cerium nodules touched the electrodes, walls, or bottom of the graphite cell. Only a very small amount of cerium metal adhered to the molybdenum cathodes.

Each cerium metal nodule under molybdenum cathode No. 2 in electrolytic run CE-42 was filed in the air to obtain one or two bright surfaces. The filed surfaces were examined megascopically after the nodules had remained in air 40 hours. Some nodules were tarnished and others remained silvery. Table 2 compares a silvery-surfaced nodule, 2S, with a tarnished-surfaced nodule, 2T.

TABLE 2. - Analytical comparison of two cerium nodules from run CE-42

Run No.	Nodule No.	Elements, weight-percent							Elements, p.p.m.				Total impurities, weight, percent
		Fe	Si	Al	Ca+ Mg	Ba	Li	Mo	C	O	N	H	
CE-42	2S	0.03	(1/)	(1/)	(1/)	(1/)	0.01	(1/)	207	569	6	9	0.12
CE-42	2T	.06	(1/)	0.08	(1/)	(1/)	.01	0.05	55	594	6	4	.27

1/ Not detected.

This method has been used to classify low- and high-grade cerium metal nodules from several electrolytic runs. Generally, nodules with silvery surfaces are higher grade than those with tarnished surfaces. Investigation of the air-corrosion classification method is being continued.

Current efficiency, computed from massive cerium metal produced, was 94 percent. Current efficiencies ranged from 70 to 94 percent, depending upon the amount of old bath reused in the charge and other factors inherent to small research cells and short electrolyzing periods.

Analyses of Cell-Box Gases

Gas analyses were performed during each run in cell type Nos. 3, 4, and 5. Gas samples were removed from the cell box by means of an evacuated gas-sample bottle 10 inches long and 1-1/2 inches in diameter with a stopcock at both ends. The sample bottle was evacuated to 20 microns pressure or less, then attached with a short piece of rubber tubing to a valve near the top center of the glove box. After the tubing was flushed with argon to remove any air, the valve and stopcock were opened and a sample of the glove-box atmosphere was sucked into the sample tube. The sample was then transferred to an Orsat apparatus and analyzed for CO₂, CO, and O₂ by standard Orsat procedure. The Orsat apparatus had a capacity of 50 ml., and gas volumes could be measured to 0.1 ml. or 0.2 percent of the total gas volume. Qualitative tests were also made for HF and F₂ by bubbling samples of the box gas through a zirconium-alizarin solution prepared according to Feigl (2).

The major gaseous product of the electrolysis was CO₂, and small amounts of CO were present. In this respect the current cerium cell is similar to the aluminum cell, in which CO₂ is known to be the principal anode gas and CO is formed by the reduction of CO₂ by anode carbon or by metal fog (18, 14). The amount of CO seldom exceeded 2 percent of the total volume of the gas in the glove box and usually remained within a range of 0.8 to 1.6 percent, despite the length of the runs. The concentration of CO₂ continued to build up as the runs proceeded. By partly evacuating the glove box and adding pure argon at intervals, the operator diluted the CO₂ and CO and controlled the box atmosphere. The maximum concentration of CO₂ permitted in any run was 18 percent. The correlation between CO₂ content of the box atmosphere and metal purity is to be investigated. Possibly, a greater CO₂ concentration may be tolerated.

CF₄ has been reported in the off gases of both aluminum (5) and uranium cells (13) and would be expected to be present in preference to F₂ in any electrolysis of a fluoride bath using a carbon anode at temperatures greater than 450° C. (10).

In the uranium cell the CF₄ was usually present in concentrations of 0.19 percent or less, and in the aluminum cell the gas was detected only during an anode effect caused by depletion of Al₂O₃ in the cell.

There are no convenient chemical tests for the fluorocarbons, because of their extreme inertness. It is planned to have mass spectrometric analyses made of the cerium cell gas. Attempts to trap out CF₄ by means of liquid oxygen traps did not indicate the presence of the gas in detectable quantities. It is believed that some CF₄ and possibly other higher fluorocarbons may be present in the off gases of the cell but in too small amounts to be detected by available procedures.

Oxygen has been detected occasionally in the box gas sample, but its presence has usually been traced to small leaks in the glove box that developed after the run had begun.

At least 1 percent HF has been reported in the off gases of the aluminum cell, due to moisture in the fluoride baths and hydrogen from anode hydrocarbons (5). No HF or F₂ has been detected in the off gases from the Reno cerium cell. However, the slow etching of gas-sample tubes, glass viewports, and other pieces of glass apparatus seems to indicate the presence of at least small amounts of HF.

Typical moisture analyses of the high-purity argon and helium gave moisture contents of less than 10 p.p.m. by volume.

The purity of the cell-box gas before melting and electrolysis was determined by an instrument that compares the thermal conductivity of a sample gas with that of a standard gas. High-purity argon and helium were used as standard gases. When the thermal conductivities of the box gas and tank gas matched, the box atmosphere was considered to be of proper purity.

LITHIOTHERMIC REDUCTION AND VACUUM REFINING

Anhydrous cerous fluoride and chloride have been used by previous investigators in preparing cerium regulus by metallothermic reductions. P. M. J. Gray (4) obtained only finely dispersed cerium regulus in the lithium-bomb reductions of cerous chloride in molybdenum cans. In similar reductions of cerous fluoride he obtained buttons of massive cerium regulus. He attributes the failure of the dispersed metal to coalesce in the chloride reduction to an oxide or oxychloride skin on the metallic surface. This skin is derived from small amounts of water retained by the cerous chloride after dehydration or picked up from the air during loading.

In the Reno experiments cerous fluoride was chosen owing to the relative ease of preparing it in an anhydrous form and its stability in air at ordinary temperatures. Cerous fluoride also has a lower vapor pressure than cerous chloride. Lithium metal was chosen as the reductant because the LiF slag has a low melting point (870° C.), thus facilitating coalescence of the cerium. Calcium and magnesium fluorides melt at 1,360° and 1,396° C., respectively. Cerium from the calcium reduction of cerous chloride contains up to 2 percent calcium (1) and magnesium forms alloys with cerium (20).

Massive cerium regulus was prepared by the lithium-iodine reduction of anhydrous cerous fluoride in welded molybdenum and tantalum cans, lime-lined steel-pipe reactors or bombs, in a Globar resistance furnace. P. M. G. Gray (4) reported that cerium metal prepared by lithium-bomb reduction in a molybdenum can had negligible molybdenum pickup. Spedding (17) found that cerium prepared by calcium reduction in tantalum crucibles contained less than 0.05 percent tantalum. As much as 2.7 percent molybdenum and 0.3 percent tantalum were reported by X-ray fluorescent analysis in Reno bomb cerium regulus prepared in molybdenum and tantalum cans.

Because the vapor pressure that builds up in a properly fabricated molybdenum or tantalum container is a primary factor in bomb reduction efficiencies, techniques for fabricating and welding molybdenum and tantalum cans for reduction containers were developed in these laboratories. The cans were welded in a dry argon atmosphere in a glove box using a special direct-current tungsten arc welder.

A procedure was developed for preparing 50-gram buttons of cerium regulus by bomb reduction. The cerous fluoride made by the thermal fluorination of ceric oxide with ammonium bifluoride was heated under a vacuum of 42 microns 300° to 400° C. for 12 hours to remove moisture and other gases. A tantalum or molybdenum can, 1-3/4 inches in diameter by 2-1/2 inches in height, was made from 0.005-inch sheet with a welded bottom and side seam. The can was degassed in the induction furnace, then transferred to an argon atmosphere glove box and loaded with thin alternate layers of charge comprising 78.17 grams of CeF_3 , 9.6 grams of silvery Li metal, and 20 grams of resublimed I_2 . The purity of the glove-box atmosphere was controlled by comparing the atmosphere with high-purity tank argon using the gas master.

A molybdenum or tantalum plug was placed in the top of the loaded can, and the can was packed in a wrought-iron pipe reactor 2-1/4 inches i.d. by 8-3/4 inches high, with a liner of recalcined lime. The pipe reactor had a welded bottom and was sealed with a threaded pipe cap using litharge and glycerine.

The bomb was removed from the dry-argon-atmosphere glove box and charged in the Globar furnace at 1,280° C. If reduction was begun with a cold furnace, a finely dispersed cerium metal in a lithium fluoride-lithium iodide slag was produced. The outside of the pipe was maintained at 1,100° to 1,150° C. for 40 minutes, then the reactor was removed from the furnace and air-quenched for 15 hours before opening.

Recoveries of massive cerium regulus as a button ranged from less than 50 to 95 percent. The lithium-fluoride-lithium-iodide slag broke away readily from the cerium button. When a molybdenum can was used, the molybdenum adhered to the cerium, making it necessary to machine the molybdenum from the cerium button. When a tantalum can was used, the tantalum could be peeled away readily from the cerium button, however, the can was sacrificed in the reduction.

Leaks in the plugs of the molybdenum or tantalum can and voids in the lime packing, which allow the reaction gases to force unreduced charge out of the reduction zone, are believed to be the principal causes for the failure to reproduce consistently high reduction efficiencies. Extreme care is required in making and loading molybdenum or tantalum containers and bombs.

Cerium reguli from the lithium-iodine bomb reductions of cerous fluoride in tantalum and molybdenum cans were melted and refined using quartz-tube vacuum induction and vacuum resistance furnaces.

The tantalum and molybdenum cans, 1 inch in diameter by 4 inches high, were fabricated in the Reno laboratories from 0.005-inch gage sheet and welded in an argon-atmosphere glove box. They were degassed in the quartz-tube induction furnace.

Several pieces of bomb cerium regulus were scraped clean of slag and oxide with a molybdenum knife and loaded into a degassed tantalum or molybdenum can in an argon-atmosphere glove box. Then the loaded can was transferred under argon to the 3-inch-diameter quartz-tube induction furnace.

To facilitate better low-range temperature control in the vacuum induction furnace, a secondary coil was connected in series with the furnace coil. This coil allowed degassing of the cerium regulus below its melting point and prevented ejection of molten cerium from the can by the sudden evolution of gases. Vacuum refining experiments also were performed using a resistance furnace surrounding the quartz tube to bring the cerium regulus slowly from room temperature to its melting point.

In a typical vacuum refining experiment, the cold quartz tube was evacuated to 3 microns and the temperature of the cerium regulus, measured by optical pyrometer, was varied from 740° to 920° C. in a degassing period of 4.65 hours. The vacuum rose from 3 to 230 microns and dropped to 15 microns at the end of the experiment. When Reno electrocerium metal was vacuum-refined, as previously described, the vacuum varied by only a few microns.

Several pieces of cerium regulus had melted into one ingot with several blowholes at the top. Machining was necessary to remove the molybdenum, but the tantalum could be peeled readily from the refined cerium ingot. Some of these round ingots were cold-rolled in an argon atmosphere and shaped into 0.1- by 0.2- by 1-inch specimens for electrical conductivity investigations.

In table 3 a Reno bomb cerium regulus, before and after vacuum refining in a tantalum can, is compared analytically with Reno electrocerium and a commercial cerium metal.

CERAMICS

Titanium oxynitride crucibles were prepared and used at Reno for vacuum refining commercial cerium metal. L. S. Foster (3) describes titanium and zirconium oxynitride crucible preparation and cerium melts under vacuum in these crucibles. According to Foster, cerium does not attack the crucibles, but no data are given on contamination of the cerium.

A mixture of 70 percent titanium nitride and 30 percent titanium oxide by weight with Carbowax was molded under pressure in a steel die. The green crucibles were calcined at 250° C. to remove the Carbowax binder, then fired in a dry argon atmosphere in the induction furnace at 1,550° to 1,600° C.

Commercial cerium metal was vacuum-melted in the titanium oxynitride crucibles in the quartz tube using an induction furnace. Approximately

20 grams of cerium was melted in each crucible, and temperatures of approximately 1,000° C. were attained. The cerium adhered to the crucible walls and bottom, and spectrographic analysis indicated contamination of the cerium with titanium at an approximate weight-percent of 0.1 to 0.01 titanium.

TABLE 3. - Analytical comparison of cerium metals

Type of cerium	Elements, weight percent								
	Total rare earths, weight-percent	Fe	Si	Al	Ca + Mg	Li	Ba	Ta or Mo	I
Reno bomb cerium regulus	0.05	0.05	0.06	0.01	(1/)	1.00	(1/)	0.20	0.31
Reno bomb cerium regulus, refined.....	.01	.05	.06	(1/)	(1/)	.01	(1/)	.30	(1/)
Reno electrocerium.....	.04	(1/)	.02	.02	.01	.001	.005	.02	(1/)
Commercial cerium metal ^{3/}	3.1	.12	.05	.01	.16	(1/)	(1/)	(1/)	.05

Type of cerium	Elements, p.p.m.				Total impurities, percent
	C	O	H	N	
Reno bomb cerium regulus	(2/)	(2/)	(2/)	(2/)	1.68
Reno bomb cerium regulus, refined.....	(2/)	(2/)	(2/)	(2/)	.42
Reno electrocerium.....	100	20	3	15	.12
Commercial cerium metal ^{3/}	36	147	11	15	3.49

^{1/} Not detected.

^{2/} Not determined.

^{3/} Commercial metal is prepared from an intermediate chloride salt, which may account for the high concentration of other rare-earth metals.

In summarizing his experimental results, Foster (3) states that CeS is in no way superior to TiN or ZrN for melting cerium.

Some grades of graphite have proved satisfactory as cell construction materials at 810° C. in the Reno cerium electrowinning runs. Unlike Vycor glass and iron they were not attacked by the molten fluoride electrolyte. As the graphite surface was not wet with the Reno fluoride electrolyte, the frozen electrolytes could be easily removed, making possible reuse of the graphite cells.

In cerium electrowinning runs using cells of a certain grade of carbon, carbides were formed and the cells cracked when molten cerium contacted the carbon, resulting in loss of the molten electrolyte. Under parallel conditions in graphite cells, the molten cerium formed carbides on contacting the graphite, but no cracking took place at temperatures of 810° C.

When a frozen layer of electrolyte is maintained next to the graphite, as in cell type No. 5, electrocerium low in carbon impurity can be prepared in a graphite cell under properly controlled atmosphere and temperature conditions.

The development of laboratory use of CeF_3 as a ceramic liner in the fluorination tube furnace at Reno is reported on page 6.

ELECTRICAL CONDUCTIVITY OF CERIUM METALS

The Bureau's Physics of Metals unit has expended much of its effort on the design, fabrication, and operation of equipment to give reproducible values of electrical conductivity of cerium from room temperature to that of liquid oxygen. The purpose is: (1) To assess the relative purity of samples of electrocerium and (2) to determine the true electrical conductivity of cerium over this range of temperature. Progress and development toward these goals are as follows:

The relative purity of the cerium samples can be measured by their conductivity, as the electrical resistance of most elements of atomic numbers 57 to 71 decreases with temperature, although not linearly, finally reaching a value independent of temperature. This low-temperature residual resistivity is a function of the purity of the metal and the strains and dislocations in the sample. Thus, if the strains and dislocations can be minimized or held approximately constant, electrical conductivity will be a very sensitive measure of the purity. Control of strain level and dislocations is not too formidable a problem, as purity is by far the most sensitive parameter according to previous investigators. (8)

In addition to the complications imposed by impurities, the electrical conductivity of cerium is further complicated by at least three reversible allotropic changes between its melting point and absolute zero. A study of the literature shows that the inner state of the metal is not one of equilibrium but of simultaneous coexistence of two or more of these changes.

The equipment is being developed so that a wide range of temperature rates will be possible; thus, the area of the hysteresis loop can be investigated as a function of the temperature rates.

The Reno electrocerium is usually spectrographically free of calcium and magnesium, two major impurities in the cerium used by most investigators. As previous studies (20) of the allotropic transformations have revealed that calcium and magnesium are particularly interfering impurities, the values of electrical conductivity obtained in this investigation may be of considerable significance.

Correlation of this type has been done on other elements with great success. For instance, Bell Telephone Laboratories reports in a recent article on low-temperature resistance of "varistor"-type high-purity copper (11):

It is planned to use the foregoing correlation as an aid in selecting some varistor coppers in the near future. However, while this method may prove useful in selecting varistor coppers, the present results are reported primarily to call attention to a particular example of the practical utility of low-temperature

resistance measurements in assessing the relative purity of metals, since it is felt that the method may have more general utility as a criterion of purity than is generally recognized.

The importance of obtaining the true electrical conductivity of cerium, is evident from examining the atomic structure of the rare-earth elements. They have similar electronic structures, although their nuclear structures differ. As the atomic weight of the series increases there is, with few exceptions, a regular decrease in atomic volume.

The chemical reactivities of the rare-earth elements, which are a function of their electronic structures, are quite similar. Their physical properties, which depend on their nuclear structures as well as other factors, show significant differences. Thus, they offer an excellent opportunity for checking present theories of metals and possible correlation of the properties of the metals and their structures. However, as they are extremely reactive and small amounts of impurities can drastically change their properties, accurate reproducible measurements of their characteristics are generally lacking.

Investigations With Chamber No. 1

The first chamber was fabricated from 3-inch-i.d. by 7-inch-long steel pipe, welded shut at the bottom, and a 3-inch-i.d., 5-inch-o.d. O-ring flange welded to the top. The cover was a 5-inch-diameter Bakelite disk 1/2 inch thick, to which the entire bridge circuit was rigidly attached. The bridge comprised separate current and potential contacts with a copper-constantan thermocouple at either end of the sample. The sample was held tightly against the contacting edges by a spring-loaded Bakelite sheet. The cover also contained an outlet for evacuating the test chamber and a 1/2-inch-diameter brass rod for supporting the chamber in the Dewar of liquid oxygen. Vacuum-tight electrical connections were made by sealing the leads in a cold-setting plastic where they pass through the Bakelite cover.

Temperature of the sample was controlled by variable electric heaters, one in a thin-walled copper tube connecting the sample block to the bottom of the test chamber and another between the O-ring flange and the Bakelite cover.

A Kelvin bridge circuit was chosen to measure the resistivity, because the null detector method of measuring would eliminate errors due to contact resistances. These resistances will be present when working with reactive metals such as cerium, and because the total resistance of the sample is small the errors would be large.

The bridge consists of separate current and potential contacts to the sample. The potential drop across the sample is measured by a Rubicon type-B precision potentiometer; the current, which is supplied by five 6-volt, low-discharge-type storage batteries, is measured by the potential drop across a standard resistance of 1 ohm.

The resistance, R , of the sample is given by Ohm's law as the quotient of the potential drop and current. The resistivity, ρ , of specimens is then computed from the relation $\rho = \frac{RA}{L}$, where A is the cross-sectional area and L the distance between potential contacts. The temperature of the sample is indicated by two copper-constantan thermocouples, one at either end of the sample.

Specimens for comparing electrical conductivity were made originally as follows: Samples of Reno electrolytic and bomb cerium metals and commercial cerium metals were vacuum-melted in degassed, 1/2-inch-i.d. tantalum cans. Then these samples were prepared in an argon atmosphere in the glove box for X-ray lattice constant and electrical conductivity measurements. Disks 1/4 inch thick were cut with bolt cutters from the 1/2-inch-diameter cerium cylinders. The disks were cold-rolled into strips 1/8 inch thick with a hand rolling mill. The strips were squared into approximately 0.2 by 0.1 by 1-inch samples with a steel file and polished on grit 1/0 emery paper. All machining, rolling, polishing, and sample preparation were performed in an argon atmosphere.

Conductivity values obtained in chamber No. 1 on samples of cerium produced by three methods showed a distinct correlation with purity. (See table 4.)

TABLE 4. - Electrical conductivity and purity comparisons of vacuum-refined, cold-rolled cerium metal samples at 0° C.

Metal, type	Conductivity, ohm. ⁻¹ -cm. ⁻¹	Cerium, percent
Reno electrolytic cerium.....	8.3×10^4	99.8
Reno lithiothermic cerium.....	2.7×10^4	98.5
Commercial cerium.....	2.5×10^4	95.8

The apparatus, although useful in gathering preliminary data, had several disadvantages: (1) It was extremely difficult to achieve zero flow of heat at the start of the run without considerable fluctuation in temperature. As the resistivity of cerium is a function of the thermal history of the metal, it would be necessary to duplicate this cycle every run. (2) The temperature gradient across the sample could not be held at the desired maximum of 1/2° C., because the heat was being exchanged primarily from either end of the sample. (3) The danger of thermoelectric effects was present, as the bridge circuit was not in an isothermal region. (4) Finally, it was very difficult to reproduce the thermal cycles.

After some effort was made to eliminate these faults from the equipment, it became apparent that a drastic change was needed in the basic design, and chamber No. 2, was designed and constructed. This chamber proved very successful.

Investigations With Chamber No. 2

Chamber No. 2 was fabricated from high-conductivity copper and has provisions for running three samples simultaneously. The chamber is surrounded by several inches of polystyrene foam, and temperature is controlled by circulating gases at various temperatures through coils soldered to the outside of the container. The same bridge circuit used with chamber No. 1 was also used with chamber No. 2. A technical paper, describing the equipment in detail, is being prepared for publication. The use of a small jeweler's lathe in making the samples did not introduce as many dislocations as rolling.

As it is impossible at present to remelt cerium without introducing impurities, the length of the conductivity samples is limited to that of the nodules. The average conductivity sample is approximately 0.125 inch in diameter and 1 inch long; thus, uniformity of cross section and measurement of the 0.8 inch between potential edges represent the largest uncertainties in the computed conductivity, being plus or minus 1.5 percent.

An axis is chosen through the longest dimension of the irregular nodule so that the finished sample will be as long as possible. A cold-setting plastic is cast around the nodule in a 3/4-inch cylindrical tube with the chosen axis of the nodule coinciding with the axis of the cylinder. The cylinder is mounted in a jeweler's lathe and machined under vacuum oil to approximately 0.135 inch in the section containing the metal, leaving plastic knobs on the ends for mounting for the final cut. The semifinished samples are then stored in a desiccator. Just before measurement they are mounted again in the lathe and machined to 0.125 inch plus or minus 0.0005 inch, then mounted in the inert-atmosphere test chamber. Although much work remains to be done on controlling grain size, orientation, stress level, and dislocations the polycrystalline samples, preliminary investigations indicate that these factors were approximately constant in the samples used in this investigation.

By means of chamber No. 2 it was possible to compare Reno electrocerium with commercial cerium at liquid-oxygen temperatures. Samples for the comparison were machined, then measured simultaneously. A constant temperature rate of 0.2° C. per minute was used throughout the experiment, and the samples were held at the low point for 36 hours to insure equilibrium before the return cycle was begun. As was true with chamber No. 1, the conductivities with chamber No. 2 were greater for the purer metal. (See table 5.)

TABLE 5. - Electrical conductivity and purity comparisons
of machined cerium metal samples at -187° C.

Metal, type	Conductivity, ohm. ⁻¹ -cm. ⁻¹	Cerium, percent
Reno electrolytic cerium (Sample No. CE-42-2S).....	17.8×10^2	99.9
Commercial cerium.....	13.0×10^2	95.8

No direct comparison can be made between the data from experiments in chamber Nos. 1 and 2 because of differences in temperature and sample fabrication. The large temperature gradient in the bridge circuit of chamber No. 1 probably affected the values obtained.

No low-temperature transition was evidenced in the commercial metal, nor was there any hysteresis. Reno electrolytic cerium (CE-42-2S) showed a normal transition and hysteresis pattern with the curves rejoining at minus 90° C. The measurement given for CE-42-2S is valid only for this sample, as the nodules produced in the same run vary. For example, another sample, CE-42-2, had a conductivity of 18.0×10^{-2} , ohm.⁻¹cm.⁻¹.

DISCUSSION

High-purity cerium ingot was prepared in Nos. 4 and 5 cells by maintaining a cell liner of frozen electrolyte and a controlled argon-carbon dioxide-carbon monoxide cell atmosphere. Control of the anode and cell-bottom temperatures in the cerium electrowinning runs given in tables 1 and 6 prevented molten cerium from contacting the graphite.

Analyses for metallic, nonmetallic, and gaseous impurities show that the cerium nodules from the same electrowinning run, as well as those from different runs, vary widely in composition. (See table 1.) Each set of analyses represents only the nodule sampled and illustrates the extreme reactivity of cerium metal.

The authors believe that the carbon in the cerium comes from the CO₂ released at the anode. The variation in carbon content of the nodules shows the need for careful control of the composition of the cell-box atmosphere and the temperature and viscosity of the electrolyte. For example, samples of cerium metal nodules from CE-30 were analyzed for carbon at the Rolla (Mo.) station of the Federal Bureau of Mines, using the conductometric carbon analyzer. Ten determinations averaged 1,590 p.p.m. carbon with a low of 20 p.p.m. and a high of 6,200 p.p.m. The nodules were exposed to the atmosphere, and pieces picked from nodules having the least surface corrosion on four determinations averaged 35 p.p.m. carbon with a low of 20 p.p.m. and a high of 50 p.p.m.

The aluminum, silicon, and iron impurities in electro-cerium are attributed mainly to the fire-clay-brick cell cover and the carbon-welding-rod anodes. Iron also may be introduced in crushing old electrolytes for reuse. Lithium and barium impurities in cerium are low, although their fluorides are solvent-phase electrolyte constituents. Molybdenum cathodes and a molybdenum tool used to remove the graphite resistors after meltdown are the sources of molybdenum contamination of the electrocerium.

During the 3.65 hours of electrolysis it is doubtful whether the electrolyte reached a state of equilibrium, regarding either oxyfluoride content or cation versus anion balance. The considerable difference in the analysis of separate cerium nodules indicates that the selective purification of the electrolyte did not proceed to completion.

Before bath temperatures, cell-box-atmosphere temperatures, pressures, bath equilibrium, and compositions can be correlated with the amounts of impurities in the electrocerium, electrolytic runs of 72 hours or more are believed necessary. A cerium electrowinning cell has been designed for semi-continuous operation of 72 hours or more. A mechanical feeder for CeO_2 will be used in operating this cell.

Coalescence depends upon the surface condition of the metal and upon surface tension, viscosity, and relative density of metal and electrolyte, manner of feeding ceric oxide, and possibly other factors. The authors believe that longer runs in a larger cell, with a deeper zone of electrolyte at a temperature above the cerium melting point, would aid in nodule coalescence.

The work in the Reno laboratories has been confined solely to fluoride electrolytes, the electrowinning of cerium from CeO_2 , and the lithiothermic reduction of CeF_3 . The problem of rare-earth metal coalescence in chloride systems has been reported by other workers.

P. M. J. Gray (4) reported on the metallothermic reduction of cerous chloride with lithium metal:

This reaction was carried out in a manner very similar to that for the reduction of the trifluoride but was not nearly so successful. In every run a reaction took place satisfactorily but the metal produced would not coalesce and remained finely dispersed throughout the reaction cake * * *. The failure of the metal globules to coalesce is almost certainly due to the presence of oxide or oxychloride which forms an infusible skin on the surface of the metal.

Table 6 compares the apparent current efficiencies of three cerium electrowinning runs. The short duration of the runs, the presence of old electrolyte, lack of information as to the exact valence of the cerium in the compound being electrolyzed, and other cell conditions prevented calculation of actual current efficiencies. For example, in run CE-30 the bath was kept molten by external heating with alternating current, whereas in runs CE-41 and CE-42 direct current was used both for electrolytic and thermal energy.

Apparent current efficiencies, calculated on the basis of total direct current and a valence of 4 for cerium, although useful in comparing one electrolytic run with another, should not be regarded as absolute values.

Average and maximum CO_2 and CO in the cell-box atmospheres for runs CE-30, 41, and 42 show no correlation with the amounts of carbon and oxygen in the cerium metal nodules. (See table 7.)

The present work indicates that the 73 percent CeF_3 , 15 percent LiF, 12 percent BaF_2 mixture is satisfactory for the solvent phase of the electrolyte. With longer runs, however, loss by volatilization may necessitate finding a substitute for LiF.

TABLE 6. - Typical data and results of electrowinning cerium from Reno electrolyte

Run No.	Apparent current efficiency, percent ^{1/}	Electrolyte composition, weight-percent		Current density, a./cm. ² ^{2/}	
		Fresh Reno solvent-phase electrolyte	Old electrolyte	Anode	Cathode
CE-30 ^{3/}	85	48	52	1.5	4.8
CE-41 ^{4/}	78	80	20	4.1	10.0
CE-42 ^{4/}	94	37	63	4.5	11.3

Run No.	CeO ₂ added		Electrode immersion, inch	Ampere-minutes x 10 ⁻³
	Amount, g.	Rate, g./min.		
CE-30 ^{3/}	227	0.6	1.00	10.0
CE-41 ^{4/}	444	1.8	.75	43.4
CE-42 ^{4/}	575	2.2	.75	32.4

1/ Calculated using the weight of cerium ingot recovered, the ampere-minute value of the run, and a valence of 4 for cerium.

2/ Calculated using the weighted average amperage for the run and the starting electrode curved surface areas.

3/ Cell type No. 4.

4/ Cell type No. 5.

TABLE 7. - Typical cell-box atmosphere and cerium nodule analyses

Run No.	Nodule No.	Cell-box-atmosphere volume, percent				Cerium nodule, p.p.m.	
		Maximum CO ₂	Average CO ₂	Maximum CO	Average CO	C	O
CE-30.....	1	15.2	8.4	0.8	0.6	100	20
CE-41.....	1	15.2	7.9	2.0	.7	34	523
CE-42.....	2S	17.6	9.3	1.8	1.0	207	569
CE-42.....	2T	17.6	9.3	1.8	1.0	55	594

Considerable cerium and misch metals are prepared commercially by electrowinning from cerous chloride in the air, using the frozen electrolyte as a cell cover. At present, cerous chloride is reported to be cheaper than ceric oxide because it is an intermediate product from the processing of monazite concentrates for thorium. Future electrowinning investigations using cerous chloride as the source of high-purity cerium metal, under controlled atmospheric and temperature conditions similar to those described in this paper, might be worthwhile.

Although there are many important points of similarity between the basic electrochemistry and mechanics of transfer of ions in the commercial aluminum cell and the electrowinning of cerium at the Reno laboratories, two essential differences are apparent to the laboratory investigator.

The first difference is the smaller working volume of the 6-in-diameter pilot cerium electrowinning cell as compared to that of the commercial aluminum cell. The most direct and harmful effect of the smaller volume is that it forces a technique of intermittent operation of the cell; that is, the time of electrolysis is limited by the volume under the electrodes and above the protecting layer of frozen electrolyte available for collecting cerium metal. For example, in test run CE-41, 716 grams of cerium metal accumulated in an electrolysis of 3.65 hours, and the approximate space occupied by 120 cerium nodules prepared in this period was 50 cubic inches. The total space available for collecting cerium nodules was 67 cubic inches. Possibly the nodules did not coalesce into a single mass under the bottom ends of the vertical cathodes because the temperature gradient was too steep in this area due to the restricted space and the need for maintaining a frozen protective layer of the electrolyte above the graphite bottom of the cell. (See fig. 1, p. 15.) The temperature in the end of the graphite anode in test run CE-41 ranged from 752° to 822° C. and averaged 785° C. during electrolysis. The temperatures were higher on the cathode surfaces than at the anode, as the respective current densities were 10.0 and 4.1 a. per sq. cm. Anode density is based on the size and shape of anodes before electrolysis. In test run CE-41 the temperature in the graphite cell bottom was 630° to 728° C. and averaged 675° C. The coalescence of the molten metal droplets at the same temperature depends upon surface tension, viscosity, and relative density of metal and electrolyte. The molten cerium metal deposits on the round cathode and slips down to the end of the rod, where it sinks into the electrolyte and solidifies into irregular, rounded nodules approximately 1/4 by 1/2 by 3/4 inch in size.

The other important difference in the 6-inch-diameter, graphite, pilot cerium cell and the commercial aluminum cell is in the geometry of the electrode arrangement and its effect on the cathode products.

The aluminum cell has vertical carbon anodes and a molten horizontal aluminum cathode. This arrangement of electrodes gives the anode gas more freedom to exit without contacting the molten aluminum, compared with the 6-inch-diameter cerium pilot cell where both the anodes and cathodes are parallel and vertical. Moreover, as soon as a molten droplet of cerium metal leaves the surface of the cathode, it sinks into a zone of decreasing temperatures and is prevented from coalescing with the nearest neighboring nodule. The molten aluminum cathode layer, being horizontal and above the melting point of aluminum, does not have this temperature gradient problem.

Other electrodes and electrode arrangements for cerium electrowinning cells are to be investigated in the future.

Electrical-conductivity data are the result of the initial 6 months' work in the Physics of Metals unit and show only the progress made to establish the relationship between the several grades of cerium metal and electrical conductivity.

FUTURE WORK PLANS

The next major phase in the development of a process for electrowinning cerium ingot from its oxide is to improve the molten, steady-state or equilibrium conditions. Although the operations in the next phase will be semi-continuous, the volume of bath will be large enough to permit runs five times as long as any reported in this paper. Thus, it will be possible to predict what to expect in a continuous cell, and the investigations will yield data that can be translated into conditions approaching commercial possibilities. Present plans are to use a cell 12 inches in diameter by 12 inches deep. The cell will be enclosed in a larger cell box, designed for closer control of the composition, temperature, and pressure of the atmosphere in the box and for closer control of the temperature of the cell and molten bath. The cell will be equipped with a continuous, mechanical oxide feeder. This feeder will be an important step forward, because a uniform and controlled rate of feeding the oxide is essential to maintaining equilibrium in the molten bath.

Eventually, a method of casting ingot cerium in an inert-atmosphere chamber connected to this cell box will be developed, thus permitting more continuous cell runs.

The longer runs and steadier conditions in the 12-inch cell and associated equipment will provide better control for selective refining of electrolyte and will yield data on aspects of the process that could not be developed with the smaller cell, such as watt-hours per pound of ingot, current efficiencies, and current densities. Furthermore, improved coalescence of the metal might be achieved in the larger bath unit. This improvement, together with the larger quantities of metal product, would result in metal that is more homogeneous and uniform in quality. Confidence that conditions necessary for coalescence can be obtained was encouraged when about 50-percent coalescence of 1,055 grams of metal product was achieved in one run, No. CE-46.

Several months will elapse before the projected cell is in operation. Meanwhile, plans are being made to investigate certain other process variables. Among these variables are oxide feed rate, amount of carbon dioxide that can be tolerated in the box atmosphere, higher purity carbon anodes, and helium cooling of cell accessories.

Ultimately, it is desired to determine the maximum possible rate of feed. Subsequent operations have shown that feed rates higher than those used in the runs described in this report are feasible. A rate of 5.2 grams of ceric oxide per minute at an amperage of 276 has been used successfully for a 3-1/2-hour test run.

Future electrolyte studies will continue the efforts to measure molten-state properties of the currently used electrolyte, such as solubilities of CeO_2 , and will continue research on the nature of the phenomena that occur during electrolysis of ceric oxide.

Electrical-conductivity studies on higher purity cerium ingot will be continued to establish more precise data on the relation of purity to specific contamination and to develop data on the true resistivity of higher purity cerium. Investigations will be initiated on the coalescence of individual nodules of cerium using ultrasonics. Methods will be developed for helium cooling the electrowinning cell boxes and accessories.

BIBLIOGRAPHY^{8/}

1. AHMANN, D. H. Metallurgy of the Rare Earths With Particular Emphasis on Cerium. Ames Lab., Iowa State College, Ames, Iowa. AECD-3205, Feb. 14, 1950, pp. 3-79.
2. FEIGL, F. Qualitative Analysis by Spot Tests. Nordemann Pub. Co., Inc., New York, N. Y., 1939, pp. 170-171.
3. FOSTER, L. S. The Preparation of Crucibles From Nitrides. AECD-2942, July 1945, 60 pp.
4. GRAY, P. M. J. The Production of Pure Cerium Metal By Electrolytic and Thermal-Reduction Processes. Trans. Inst. Min. Met. (London), vol. 61, 1951-52, pp. 141-170.
5. HENRY, J. L., AND HOLLIDAY, R. D. Mass Spectrometric Examination of Anode Gases From Aluminum Reduction Cells. Jour. Metals, vol. 9, October 1957, pp. 1384-85.
6. HIRSCH, A. The Preparation and Properties of Metallic Cerium. Trans. Am. Electrochem. Soc., vol. 20, 1912, pp. 57-102.
7. HONIG, J. M. Literature Review on Properties of Praseodymium and Cerium Oxides. Dept. Chem., Purdue Univ., Lafayette, Ind., January 1958, 49 pp. (ASTIA Rept. AD148098).
8. JAMES, N. R., LEGVOLD, S., AND SPEDDING, F. H. The Resistivity of Lanthanum, Cerium, Praseodymium and Neodymium at Low Temperature. Phys. Rev., vol. 88, Dec. 1, 1952, p. 1092.
9. JUKKOLA, E. E., AUDRIETH, L. F., AND HOPKINS, B. S. Observations on the Rare Earths. XLI. Electrolytic Preparation of Rare Earth Amalgams. 3. Amalgams of Lanthanum, Neodymium, Cerium, Samarium, and Yttrium. Metallic Lanthanum, Neodymium, and Cerium by Thermal Decomposition of Their Amalgams. Jour. Am. Chem. Soc., vol. 56, 1934, pp. 303-304.
10. KROLL, W. J. Anhydrous Fluorides in Metallurgy. Metal Ind. (London), vol. 83, Aug. 21, 1953, pp. 141-143.
11. KUNZLER, J. E., AND SCAFF, J. H. Use of Resistivity of Copper at Low Temperatures to Evaluate Purity in Relation to Performance of Copper-Oxide Varistors. Trans. Met. Soc. AIME, vol. 212, No. 5, October 1958, pp. 635-637.
12. LA BLANCHETAIS, C. H. (Magnetic Properties of Iron-Free Cerium). Compt. rend., vol. 220, 1945, pp. 392-394.

^{8/} Titles in parentheses are translations from the language in which the item was published.

13. LAWSON, A. W., AND TANG, Y. T., Concerning the High-Pressure Allotropic Modification of Cerium. *Phys. Rev.* vol. 76, 1949, pp. 301-302.
14. MEGGERS, W. F., ed. *Key to Periodic Chart of the Atoms.* W. M. Welch Scientific Co., Chicago, Ill., 1954, 48 pp.
15. NEIDRACH, L. W., AND DEARING, B. E. Electrowinning of Uranium From Its Oxides. KAPL-1761, General Electric Co., Knolls Atomic Power Lab., Schenectady, N.Y., Apr. 30, 1957, 53 pp.
16. PEARSON, T. G., AND WADDINGTON, J. Electrode Reactions in the Aluminum Reduction Cell. *Disc. Faraday Soc.*, vol. 1, 1947, pp. 307-320.
17. PETAR, A. V. *The Rare Earths.* Bureau of Mines Inf. Circ. 6847, 1935, 46 pp.
18. POPOV, A. I., AND KNUDSON, G. E. Preparation and Properties of the Rare Earth Fluorides and Oxyfluorides. *Jour. Am. Chem. Soc.*, vol. 76, Aug. 5, 1954, pp. 3921-3922.
19. SPEDDING, F. H., AND DAANE, A. H. Production of Rare Earth Metals in Quantity Allows Testing of Physical Properties. *Jour. Metals*, vol. 6, May 1954, pp. 504-510.
20. STERN, H., AND HOLMES, G. T. Mechanism of Anode Thermal Reactions in Aluminum Reduction Cells. *Jour. Electrochem. Soc.*, vol. 105, August 1958, pp. 478-483.
21. TROMBE, FÉLIX. Préparation et propriétés des métaux des terres rares. (Preparation and Properties of the Rare Earth Metals.) *Chim. et ind. Technol.*, vol. 77, No. 2, February 1957, pp. 277-288.
22. _____. Les Métaux des terres rares. (The Rare Earth Metals.) *Revue de métallurgie*, January 1956, pp. 1-36.
23. TROMBE, F. AND FOEX, M. (The Action of Impurities on Different Varieties of Metallic Cerium). *Compt. rend.*, vol. 223, 1946, pp. 949-950.
24. VON WARTENBERG, H. Über einige höhere Fluoride (PbF_4 , CeF_4 , BiF_5). (Some Higher Fluorides: PbF_4 , CeF_4 , BiF_5) *Ztschr. anorg. allgem. Chem.*, vol. 244, August 1940, pp. 337-347.
25. YIM, E. W., AND FEINLEIB, M. Electrical Conductivity of Molten Fluorides. 1. Apparatus and Method. *Jour. Electrochem. Soc.*, vol. 104, October 1957, pp. 622-626.
26. ZADRA, J. B., ENGEL, A. L., AND SHEDD, E. S. Concentration of Bastnaesite and Other Cerium Ores. Bureau of Mines Rept. of Investigations 4919, 1952, 15 pp.

RI bureau of mines
report of investigations **5868**

ELECTROWINNING CERIUM-GROUP AND YTTRIUM-GROUP METALS

By E. Morrice, B. Porter, E. A. Brown, C. Wyche,
and R. G. Knickerbocker



UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

1961

ELECTROWINNING CERIUM-GROUP AND YTTRIUM-GROUP METALS

By E. Morrice, B. Porter, E. A. Brown, C. Wyche,
and R. G. Knickerbocker

* * * * * report of investigations 5868



UNITED STATES DEPARTMENT OF THE INTERIOR
Stewart L. Udall, Secretary

BUREAU OF MINES
Marling J. Ankeny, Director

This publication has been cataloged as follows:

Morrice, Edward

Electrowinning cerium-group and yttrium-group metals, by
E. Morrice [and others. Washington] U. S. Dept. of the Interior,
Bureau of Mines [1961]

ii, 39 p. illus., tables. 27 cm. (U. S. Bureau of Mines. Report
of investigations, 5868)

Bibliography: p. 36-39

1. Cerium group—Electrometallurgy. 2. Yttrium group—Electrometallurgy. I. Title. II. Title: Electrowinning yttrium-group metals. (Series)

TN23.U7 no. 5868 622.06173

U. S. Dept. of the Int. Library

CONTENTS

	<u>Page</u>
Summary and introduction.....	1
Acknowledgments.....	1
Historical review.....	1
Electrowinning liquid metal deposits.....	2
Electrowinning liquid alloy deposits.....	6
Electrowinning solid metal deposits.....	7
Electrowinning at room temperature.....	7
Electrowinning as practiced commercially.....	8
Misch metal.....	8
Cerium, lanthanum, and didymium metals.....	10
Electrowinning cerium.....	11
Cell design.....	11
Cell operation.....	13
Electrolyte studies on cerium systems.....	15
Capsule design.....	16
Composition of the cerium electrowinning bath.....	18
Oxide solubility in cerium electrowinning bath.....	19
Oxide depletion electrolyses.....	22
Decomposition voltage curve.....	24
Valence of cerium reduced to form the metal.....	26
Molecular oxygen in cell gas.....	26
Radioactive cerium metal.....	28
"Reactivity" of cerium metal with molten electrowinning bath.....	29
Discussion.....	29
Fusion of the cerium electrowinning bath.....	29
Solution of ceric oxide.....	32
"Normal" electrowinning of liquid cerium metal.....	33
Electrowinning in an oxide-depleted bath.....	33
Addition of oxide to an oxide-depleted bath.....	34
Interruption of the direct current while electro- winning ingot cerium in an oxide-depleted bath.....	34
Formation of "moly blue" on addition of CeO_2 to an oxide-depleted bath.....	35
Bibliography.....	36

ILLUSTRATIONS

<u>Fig.</u>		<u>Page</u>
1.	Portion of metallurgical laboratory for electro-winning higher purity rare-earth and other ingot metals.....	12
2.	C.A.T.P. capsule used for electrolyte studies.....	17
3.	Schematic cross section of cerium electrowinning cell.....	23
4.	Decomposition voltage curve.....	24

TABLES

1.	Analyses of three commercial samples of misch metal.	8
2.	Analysis of one commercial hydrated rare-earth chloride.....	9
3.	Manufacturers' analyses of commercial cerium metal samples.....	10
4.	Manufacturers' analyses of commercial lanthanum and didymium metal samples.....	11
5.	Data obtained from electrowinning cerium metal in run CE-55.....	13
6.	Analyses of cerium nodules from runs CE-55 and CE-49.....	14
7.	Neutron activation analyses of cerium nodules from run CE-55.....	14
8.	Mass spectrometric analysis of cell gas from run CE-55.....	15
9.	Solubility of oxide in standard, clear cerium electrowinning bath.....	21
10.	Mass spectrometric analyses of gas taken from area above the cell during electrowinning in C.A.T.P. capsule.....	27
11.	Speculative representation of reactions that may take place in the molten bath from which cerium metal is electrowon.....	30
12.	Estimated free energies and electrode potentials of reactions similar to those presented in table 11, calculated from data in table 13.....	31
13.	Free energy values used in calculation of free energies and potentials of reaction reported in table 12 and their sources.....	32

ELECTROWINNING CERIUM-GROUP AND YTTRIUM-GROUP METALS¹

by

E. Morrice,² B. Porter,³ E. A. Brown,³ C. Wyche,³ and R. G. Knickerbocker⁴

SUMMARY AND INTRODUCTION

This report of the Federal Bureau of Mines presents a laboratory procedure, with the requisite equipment, for electrowinning ingot (liquid) cerium metal from a fused-fluoride bath, the metal purity being about 99.9 percent. Physicochemical studies, including bath properties and electrochemistry, are included, with a speculative model of the mechanisms involved.

An historical review of the methods used for electrowinning misch metals and yttrium-group metals, as well as individual rare-earth metals, is presented. The electrolytic preparation of metal from fused salt and nonaqueous media is summarized, along with the unsuccessful attempts at depositing the metals from aqueous solutions.

ACKNOWLEDGMENTS

The cooperation of the following manufacturers of rare-earth products in furnishing information on commercial practices is gratefully acknowledged:

American Metallurgical Products Co., Inc., Pittsburgh, Pa.; General Cerium Corp., Edgewater, N. J.; Lindsay Chemical Division, American Potash and Chemical Corp., West Chicago, Illinois; Mallinckrodt Chemical Works, St. Louis, Mo.; Michigan Chemical Corp., Saint Louis, Mich.; Ronson Metals Corp., Cerium Metals and Alloys Division, Newark, N. J.; and Vitro Chemical Co., New York, N. Y.

The analytical assistance on cerium electrowinning bath samples by the Ames Laboratory, Iowa State University, Ames, Iowa, and Mallinckrodt Chemical Works is gratefully acknowledged.

HISTORICAL REVIEW

Electrowinning cells associated with rare-earth technology generally fall into two types. One type depends solely on the electrolytic current to supply

¹Work on manuscript completed March 1961.

²Metallurgist, Reno Metallurgy Research Center, Bureau of Mines, Reno, Nev.

³Chemist, Reno Metallurgy Research Center, Bureau of Mines, Reno, Nev.

⁴Former Bureau of Mines supervisory metallurgist, Reno, Nev.

the heat necessary to keep the bath molten; the other requires supplemental thermal energy. Except where specified in the following discussion, all cells were heated internally by the passage of electrolytic current.

Electrowinning Liquid Metal Deposits

The first comprehensive report on the electrolytic preparation of the rare-earth metals was that by Hillebrand and Norton (13)⁵ in 1875. They used a two-compartment cell constructed from two porcelain crucibles, one of which was porous. Cerium, lanthanum, or didymium chlorides were melted separately in the porous crucible, which then was plunged into the second crucible containing the NaCl-KCl eutectic. They prepared cerium, lanthanum, and didymium on an iron cathode. Six grams of cerium was prepared in a single operation.

In 1876, Frey (10) reported that he had prepared rare-earth metals in the laboratory of Dr. Schuchardt in Gorlitz, Germany, using the fused-salt technique developed by Bunsen.

In 1902, Muthmann and his associates (34) published the first of a series of articles on the electrowinning of misch metal, cerium, lanthanum, neodymium, praseodymium, and samarium from fused salts. They used a water-jacketed copper container, which was not part of the electrical circuit, to hold the fused-chloride or fused-fluoride bath. The cathode, a carbon rod, projected into the cell through the bottom of the copper vessel and was electrically insulated by porcelain rings. A vertical carbon anode was introduced into the bath from the top of the cell, completing the electrical circuit. In one experiment, several pounds of 99.92 percent cerium was produced (34). The melting point of this cerium was stated to be 623° C. Muthmann and Weiss (36) continued their efforts to prepare rare-earth metals from the fused chlorides, using the cell described herein (often called the Muthmann-type cell in the early literature). Large cerium and lanthanum nodules were obtained, but neodymium was recovered only in the form of very small nodules. Attempts to prepare praseodymium using the same type of apparatus were not successful; the authors attributed the failure to the formation of oxychlorides. In a bath composed of $\text{SmCl}_3\text{-BaCl}_2$, a thin deposit of samarium metal was formed on the carbon cathode, and the authors noted the formation of samarium carbides.

Muthmann and Scheidemandel (35) prepared cerium by electrolysis of $\text{CeF}_3\text{-CeO}_2$, using a modification of the cell previously described. The CeF_3 was made by precipitation with hydrofluoric acid and was contaminated with silicates. The cerium metal prepared in this fluoride bath was reported to contain: 12.49 percent SiO_2 , 86.48 percent Ce, and 0.87 percent Fe.

In 1912, Hirsch (14) reported numerous experiments on the electrolysis of fused cerium and other rare-earth chlorides, using cells similar to the one developed by Muthmann, but with the container fabricated from graphite. To quote Hirsch regarding his experiments: "One of the principal difficulties in all of the previous electrolyses has been the formation of carbides, which made the bath viscous and unfit for electrolysis."

⁵Underlined numbers in parentheses refer to items in the bibliography at the end of this report.

To eliminate this difficulty, Hirsch replaced the graphite container with a wrought iron crucible in which he electrolyzed a molten mixture containing 90 percent of anhydrous CeCl_3 and 10 percent NaCl . Five hundred and eighty grams of cerium was prepared in 4 hours, using 12 to 14 volts and an average current of 200 amperes. A typical metal analyzed 97.8 percent cerium; the major impurity was iron.

When electrolyzing rare-earth oxyfluoride baths using graphite or carbon electrodes, Hirsch had only limited success in several attempts to prepare misch metal. He attributed the difficulties to the formation of carbides, as in his previous chloride experiments, and to the high melting point of the electrolyte (about $1,400^\circ \text{C}$). To obtain a lower melting electrolyte, Hirsch used a bath of the same composition and added KF . Electrolysis resulted in violent explosions, ejecting large portions of the bath.

Attempts to prepare coherent "yttrium mixed metals," presumably the higher melting rare-earth metals with yttrium, were reported by Hicks (12) in 1918. When electrolyzing either a fused yttrium-earth chloride bath or a solution of yttrium-earth oxides in cryolite, he was able to prepare deposits only in the form of black powders. His cell consisted of a graphite container which served as the cathode, a graphite anode, and a molten bath which was operated at temperatures up to $1,300^\circ \text{C}$.

Publications since 1923 on the laboratory preparation of the rare-earth metals by fused-salt electrolysis have been, for the most part, descriptions of techniques for making only small quantities of high-purity metals. The small scale of the work was primarily due to the unavailability of large quantities of individual rare-earth compounds and to the difficulty of finding cell materials resistant to attack by the molten metals and baths.

Starting in 1923, Kremers with different coworkers (20, 22, 23, 45, 46) published a series of papers on the electrowinning of cerium-free misch metal, neodymium, lanthanum, cerium, and yttrium metals from molten chlorides. In most of his work, Kremers used a graphite or iron crucible as the bath container and cathode, and a carbon anode. The crucible was set in a resistance-type muffle furnace to supply extra heat as necessary. The lanthanum and cerium metals contained up to 32 percent iron, and the neodymium metal contained up to 6.5 percent iron. Lanthanum carbide was found when graphite rather than iron was used as the crucible material.

Kremers, using a cell with a tungsten cathode and a carbon anode, prepared lanthanum metal containing 0.77 percent iron and no tungsten. In this cell the electrolyte was a mixture of LaCl_3 - NaCl and KF .

Following the general procedure that they had developed for preparation of the rare-earth metals, Kremers, Thompson, and Holten deposited yttrium powder and 4 grams of coherent yttrium metal from a YCl_3 - NaCl electrolyte. The bath temperature was maintained below the melting point of yttrium during the electrolysis and then raised to $1,450^\circ \text{C}$ to $1,500^\circ \text{C}$ at the conclusion of the run. Their attempts to duplicate this run were unsuccessful. They were unable to fuse the powdery yttrium even by heating to $1,500^\circ \text{C}$ under vacuum.

Schumacher and Lucas (39) used a cell consisting of a cathodic graphite crucible, a graphite anode, and fused anhydrous rare-earth chlorides. They noted from an examination of the frozen bath that much of the metal was disseminated throughout the bath in the form of small particles. To permit the metal particles to coalesce at the bottom of the crucible in liquid form, the temperature was raised at the end of each run by increasing the direct-current amperage. The product was remelted in a magnesia crucible. These authors attempted to prepare cerium pure enough to permit study of the crystal structure of the metal. Their analysis of the metal was 0.03 percent carbon, 0.03 percent iron, and 99.9 percent cerium.

In 1926, Schumacher and Harris (38), using the above procedure, reported the preparation of small amounts of cerium, lanthanum, praseodymium, neodymium, and samarium metals. In the case of samarium, external heating was necessary at the end of the electrolysis to produce a temperature high enough to collect the metal in a coherent mass. The metals, after remelting in the magnesia crucible, were reported to contain not more than 0.03 percent carbon and 0.02 percent iron, but the magnesium content was not given.

Billy and Trombe (3) designed an externally heated cell for preparation of high-purity rare-earth metals. The anode was a carbon crucible, and a rotating molybdenum rod served as the cathode. To collect the product, a fluorspar crucible was placed in the melt below the cathode. Fluorspar was chosen as the material for this crucible after many others (graphite, quartz, and ceramics) were tested and rejected because they seriously contaminated the product. However, fluorspar introduced a difficulty in the cell operation because its solubility in the chloride-fluoride melts increased their viscosity.

In one experiment, using 25 grams of CeCl_3 and 16 grams of CaF_2 at 850°C ., Billy and Trombe prepared 9 grams of cerium in 1-1/2 hours. Analysis of the cerium showed only a slight amount of molybdenum and no calcium.

Trombe (47) then prepared lanthanum from a LaCl_3 - KCl - CaF_2 bath. The lanthanum metal analyzed 0.05 percent silicon and 0.006 percent iron. Trombe also electrolyzed a mixture of NdCl_3 , KCl , and CaF_2 at $1,040^\circ$ to $1,060^\circ \text{C}$. in the same cell arrangement (48). The neodymium metal analyzed less than 0.05 percent silicon with 0.02 percent iron and a trace of calcium. When a quartz crucible was substituted for the fluorspar crucible, the metal contained 0.6 percent silicon.

Modifications of the cell designed by Trombe have been used by several investigators. The preparation of massive lanthanum metal of 99.86-percent purity by the electrolysis of a fused mixture of LaCl_3 , KCl , and CaF_2 was reported by Weibke (53). The molten lanthanum metal was collected in an alumina crucible below the cathode.

Gray's work (11) with cerous chloride was essentially a repetition of the earlier work by Trombe. Gray tried beryllia, stabilized zirconia, and fluorspar crucibles below the molybdenum cathode to collect the molten cerium metal. When a beryllia crucible was used, Gray stated that the pickup of beryllium in

the cerium varied between 0.01 and 1.0 percent. The calcium, iron, and magnesium oxides present in stabilized zirconia reacted with the molten cerium metal. The fluorspar crucible dissolved in the molten chloride, increasing the viscosity of the bath so as to make the electrolytic process unworkable in about 30 minutes.

Gray's most successful experiments employed CeO_2 dissolved in a CeF_3 - LiF - BaF_2 electrolyte within an externally heated, 2-1/2-inch-inside-diameter, carbon container. A graphite anode rod and a molybdenum cathode rod were immersed in the melt. Argon gas was passed continuously over the top of the molten bath to protect the electrode, cell materials, and cerium metal from reaction with the atmosphere. The molten cerium metal collected in a molybdenum crucible below the cathode. Gray selected a molybdenum container because he found that only after oxidation would it dissolve in the cerium metal. He reported that the cerium contained 0.1 to 0.6 percent calcium and up to 0.3 percent magnesium as the major impurities.

Gray's report represents one of the first attempts to operate these electrowinning cells in an atmosphere free from air and moisture. While atmosphere problems, that is, air oxidation of electrodes, were mentioned by early workers, no particular efforts to exclude air appear to have been made.

In 1954, Kojima and Sato (19) purified their starting bath materials to eliminate anything containing oxygen. They electrolyzed a fused mixture of 108 grams of rare-earth chlorides and 99 grams of potassium chloride, taking precautions to prevent the surface of the melt from contacting air. In 3-1/4 hours they prepared 22 grams of misch metal and reported current efficiencies as high as 77 percent.

Lanthanum containing iron, 0.053 percent; silicon, 0.041 percent; aluminum, 0.034 percent; and potassium, 0.13 percent was prepared by T. Kuroda (24) from a LaCl_3 - KCl system at 900°C . with a reported current efficiency of 91.7 percent. The effects on current efficiency of cathode current density, bath temperature, time of electrolysis, addition of KCl , and distance between electrodes were discussed.

Eastman and associates (8) have reported preparation of electrocerium from several fused-salt mixtures. In one case, the LiCl - KCl eutectic containing either CeCl_3 or CeF_3 was used at a temperature of 850°C . A second eutectic of CeF_3 - LiF , in which CeCl_3 was dissolved, was electrolyzed at $1,000^\circ\text{C}$. Their best results were obtained by electrolyzing the CeCl_3 - KCl - LiCl system from which 15 to 100 grams of ingot cerium was prepared in each run, representing up to 80 percent current efficiency. When a CeF_3 - CaF_2 - LiF melt was electrolyzed, metal was produced in a finely dispersed form.

Eastman ran chloride electrolyses both in air and with air excluded. In the former, his metal recovery amounted to 82 percent of the theoretical yield whereas under the latter condition, he obtained as much as 98 percent. It did not, however, seem to decrease the formation of finely dispersed cerium metal in the bath.

The apparatus used by Eastman was very similar in principle to that used by Billy and Trombe (3). Eastman placed a beryllia or zirconia crucible below the tungsten cathode to collect the molten cerium metal and reported that the beryllia crucible was not attacked in the chloride systems but was in the fluoride system. Analyses of his cerium metal were not given.

A novel method of introducing the rare-earth feed into a fused-chloride electrolytic cell is described in a patent (31). The oxide is briquetted with carbon and placed in the hollow graphite anode. By passing chlorine gas through this mixture in the anode, the oxide is converted to the chloride which then diffuses into the molten bath to be electrolyzed.

Electrowinning Liquid Alloy Deposits

Considerable work was done by Trombe in the laboratories of Georges Urbain in Paris on the electrowinning of the rare-earth metals from their molten chlorides, using a liquid cadmium or zinc cathode to form an alloy with the rare-earth metal. The principal advantage of the alloy technique is the ease with which the alloy can be separated from the electrolyte. This technique employs low-melting, fused-salt baths.

Using the liquid cathode technique in a cell arrangement similar to the one used for deposition of pure liquid metals, Trombe (49-51) prepared gadolinium, europium, and dysprosium in alloys with cadmium. The rare-earth metals were then recovered by vacuum-distilling off the cadmium.

To illustrate the scale of these experiments, the following details are included. Trombe used a total of 4 grams of electrolyte, composed of 44 percent $GdCl_3$, 44 percent KCl , and 12 percent $LiCl$. The electrolytic current was maintained for 15 minutes with the bath temperature held between 625° and 725° C. This run produced an alloy containing 6 percent gadolinium. After removal of the cadmium by vacuum distillation, the gadolinium was melted in a molybdenum crucible at $1,240^\circ$ C., forming a semicoalesced mass. Analysis of the metal following these treatments was reported as 98.4 percent gadolinium, 0.7 percent silicon, and no cadmium.

Trombe and Mahn (52) used a molten alkali chloride bath in their cells at 750° C., to which praseodymium, yttrium, or samarium chlorides were added. A liquid alloy of Mg-Cd served as the cathode, in which up to 35 percent of the rare-earth metal was deposited. The magnesium and cadmium were vacuum-distilled from the alloy, leaving the rare-earth regulus which was then coalesced by melting. In the case of samarium, difficulty was encountered, since samarium tended to distill together with the magnesium.

Fischer and others (9) prepared metallic scandium, using a variation of Trombe's alloy cathode cell arrangement, in which they employed zinc as the molten cathode. They used the eutectic of $KCl-LiCl$, in which the scandium chloride was dissolved.

Electrowinning Solid Metal Deposits

To minimize inherent problems in formation of liquid deposits, a few investigators operated fused-salt baths below the melting points of the metals.

In 1932, Canneri and Rossi (6) described a method for preparing praseodymium sponge from a mixture of PrCl_3 , NaCl , and KCl (melting point 535°C .). During electrolysis the temperature of the molten bath was kept below 600°C . to avoid polarization and the formation of PrO_2 . An Acheson⁶ graphite anode and a tungsten cathode were used. The praseodymium sponge later was melted down in a magnesia crucible.

In 1938, Mazza (28), using a technique similar to that used by Canneri and Rossi, electrowon solid lanthanum, cerium, and praseodymium at 700° and 750°C . from their chlorides dissolved in a molten mixture of NaCl and KCl . Mazza stated that it was necessary to exclude oxygen to avoid the formation of oxychlorides. Purities of his metals were reported as follows: Lanthanum, 99.7 percent; cerium, 99.8 to 99.9 percent; and praseodymium, 99.6 percent.

Electrowinning at Room Temperature

The possibility of preparing rare-earth metals at ambient temperatures from both aqueous and nonaqueous media has long intrigued many investigators. Electrolysis in water solutions is complicated by hydrogen formation, even when the cathode displays a high hydrogen overvoltage, as in the case of mercury. Most efforts in aqueous solutions, alcohols, ethylene-diamine, pyridine, and other organic solvents, have been unrewarding, although McCoy (29) has reported preparation of europium and ytterbium amalgams from potassium citrate solutions.

Audrieth and others (1, 15, 17, 30) starting in 1931, published a series of reports on the preparation of neodymium, lanthanum, cerium, samarium, and yttrium amalgams from their respective salts in aqueous solution, as well as in organic solvents, using a mercury cathode. Their best results were obtained by electrolyzing concentrated solutions of the anhydrous chlorides dissolved in absolute ethyl alcohol. The various amalgams were then vacuum-distilled to remove the mercury. By subsequently heating the rare-earth powders in crucibles lined with the respective rare-earth oxides, they were able to make small pellets of lanthanum, neodymium, and cerium (17).

Amalgams reported to contain 0.5 to 1.2 weight-percent cerium were prepared by Sklyarenko and Sakharov (41) by electrolysis of solutions of CeCl_3 in absolute ethyl alcohol, in methyl alcohol, and in methyl-ethyl alcohol mixtures.

In 1954, Moeller and Zimmerman (32) reported qualitative indications of yttrium, neodymium, and lanthanum metals from the electrolysis of anhydrous

⁶Reference to specific makes or models of equipment is made to facilitate understanding and does not imply endorsement of such brands by the Bureau of Mines.

ethylenediamine solutions of $Y(OAc)_3$, $NdBr_3$, and $La(NO_3)_3$, using platinum electrodes.

Electrowinning as Practiced Commercially

Information received from several rare-earth producers in the United States indicates that rare-earth metals and alloys, prepared commercially by electrowinning, can be divided arbitrarily into the following groups: Misch metal, cerium and lanthanum metals, and didymium metal. With the exception of cerium and lanthanum, the preparation of individual rare-earth and yttrium metals is largely by metallothermic reduction. Many of these reductions closely parallel the techniques developed by Spedding and Daane (42, 43).

From the standpoint of the amounts utilized in industry, misch metal is the most important of the rare-earth metals. Approximately one-quarter of the rare-earth compounds produced in the United States goes into the manufacture of misch metal and cerium (25).

One of the largest European producers of misch metal in 1939, according to a British Intelligence Report (40), was the Treibach Chemical Works in Austria, reputed to have produced 61.4 metric tons in that year.

Misch Metal

Misch metal is a mixture of the cerium group rare-earth metals and varies in composition, depending on the raw material, and is available for purchase in the form of pig, rod, pellet, turnings, and powder. Commercial producers furnished analyses of three of their products, as shown in table 1.

TABLE 1. - Analyses of three commercial samples of misch metal

Element	Weight-percent		
	Sample 1	Sample 2	Sample 3
Cerium.....	52-56	48-52	53
Lanthanum.....	24-25	23-27	26
Neodymium.....	14-15	15-17	16
Praseodymium.....	5-6	5-7	5
Samarium.....	2-3	(¹)	.1
Iron.....	0.2-0.5	0.2-0.5	.05
Aluminum, carbon, oxygen, nitrogen, etc.....	(²)	0.3-0.5	(³)

¹Not detected.

²Trace.

³Not reported.

Large-scale commercial production of misch metal is presently limited to the electrolysis of fused anhydrous chlorides (21). The analysis of a hydrated chloride supplied to this industry by a commercial manufacturer is given in table 2.

The requisite dehydration of rare-earth chlorides prior to electrowinning normally is accomplished by one of two methods. In the first method, the

chloride is melted in cast iron, steel, or ceramic vessels from which air is largely excluded (21). Heating is continued until a porous, solid, nearly anhydrous product is obtained, which contains up to 10 percent water-insoluble basic chlorides.

The second method for drying these chlorides is in a vacuum chamber. One supplier to the German misch metal industry dried the hydrated chloride at 370° C. under a vacuum of 700 millimeters of mercury (26). The anhydrous chloride was reported to contain 1.5 percent oxychlorides.

TABLE 2. - Analysis of one commercial hydrated rare-earth chloride¹

Compound	Weight-percent	Compound	Weight-percent
CeO ₂	21.1	P ₂ O ₅	0.05
La ₂ O ₃	10.5	Na ₂ O.....	2.0
Nd ₂ O ₃	7.5	CaO + MgO.....	2.0
Pr ₆ O ₁₁	2.2	Fe ₂ O ₃ + Al ₂ O ₃5
Sm ₂ O ₃	1.3	Silica.....	.5
Gd ₂ O ₃9	Fluoride.....	(²)
Y ₂ O ₃1	Acid-insoluble.....	.5
Other rare-earth oxides.....	.4	Water-insoluble.....	.5-1.0
Thorium oxide (maximum).....	.05	Pb.....	.01
SO ₂05	Fe ₂ O ₃005

¹The values are reported as oxides by the manufacturer, although they are present as chlorides.

²Not reported.

Most cells for electrowinning misch metal have an iron, carbon, graphite, or refractory-lined steel vessel to contain the molten bath. The bath container, or an iron or carbon block at the bottom of the container, serves as the cathode. One or more carbon or graphite rods extend vertically into the cell through its top and serve as anodes. A cell of this type, used in Germany in the 1940's, has been described in the literature (26).

A mixture of anhydrous rare-earth chloride and NaCl, KCl, or CaCl₂ is charged into the pot, and in one procedure, the charge is melted by external burners. In another procedure, the anodes are lowered until they contact broken pieces of cerium metal placed at the bottom of the pot. Solid bath is packed around the bottom of the anodes, and the direct current is turned on to melt the electrolyte. The anodes are then raised to their operating positions.

Some producers use steel covers on their electrowinning cells, while others prefer to leave them uncovered. In each case the chloride bath is raised to a temperature between 800° and 900° C. by passage of the direct current. External heating normally is not required during electrolysis.

The electrolytic action is continued until the current efficiency or the metal quality declines. The product is removed from the cell at fixed intervals determined by such factors as the size of the cell and the amperage. Comparison of this metal with that obtained in the previously operated cells permits the operator to decide whether to continue operating or to shut down. If the cell is to continue to operate, additional chloride is introduced as needed to replace that used in the electrolysis.

The misch metal product can be collected in various ways. One procedure is to remove the liquid metal by ladling. Other manufacturers prefer to pour the entire contents of the cell, bath included, into molds. Once the misch metal has settled to the bottom of the mold, the liquid bath is returned to the cell, and electrolysis is recommenced.

One example of electrolytic cell operation data is given in the British Intelligence Report, previously mentioned (40). Two rows of five cells each were installed. The cells within each row were connected in series and the rows in parallel. Each cell required 14 direct-current volts at a current of 2,300 amperes. Individual cell production was 40 to 50 kilograms per day of misch metal, which corresponded to an energy consumption of 15.6 kilowatt-hours per kilogram of metal and a current efficiency of 45.1 percent.

Cerium, Lanthanum, and Didymium Metals

Cerium, lanthanum, and didymium metals are electrowon commercially from their anhydrous chlorides, using essentially the same procedure as that previously described for misch metal. Didymium metal is an alloy of the rare-earth metals, consisting of neodymium and praseodymium, with minor amounts of lanthanum and the other rare earths. Three commercial producers of cerium, lanthanum, and didymium metals have furnished analyses of their products as shown in tables 3 and 4.

TABLE 3. - Manufacturers' analyses of commercial cerium metal samples

Element	Weight-percent		
	Sample 1	Sample 2	Sample 3
Rare-earth elements other than cerium.....	0.08	0.70	0.10
Iron.....	.07	.70	.19
Silicon.....	.02	.02	.002
Calcium.....	(¹)	(¹)	.02
Magnesium.....	(¹)	(¹)	.02
Aluminum.....	(²)	(²)	0
Manganese.....	(¹)	(¹)	.02
Barium.....	(¹)	(¹)	(²)
Lead.....	(¹)	(¹)	(²)
Thorium.....	(²)	(²)	(¹)
Phosphorus.....	(¹)	(¹)	.001
Carbon.....	.03	.03	.05
Oxygen.....	(²)	(²)	(¹)
Nitrogen.....	(²)	(²)	(¹)

¹Not reported.

²Trace.

TABLE 4. - Manufacturers' analyses of commercial lanthanum and didymium metal samples

Element	Weight-percent	
	Lanthanum metal sample	Didymium metal sample
Lanthanum.....	99.6	0.95
Cerium.....	.09	.20
Neodymium.....	.04	72.1
Praseodymium.....	.05	27.2
Samarium.....	.03	.3
Other rare-earth elements.....	(¹)	(¹)
Aluminum.....	.01	.10
Calcium.....	.01	.10
Iron.....	.11	.05
Magnesium.....	.10	.10
Silicon.....	.04	.07

¹Not detected.

ELECTROWINNING CERIUM

Previous work on electrolytic preparation of higher purity cerium metal at these laboratories was reported (33). Data from this and more recent work have resulted in the design of a 6-inch-diameter graphite cell with a controlled atmosphere-temperature-pressure (C.A.T.P.) gloved cell box and accessories. Figure 1 shows a portion of the metallurgical laboratory for electro-winning higher purity rare-earth and other ingot metals.

Cell Design

The present 6-inch-diameter electrowinning cell yields higher purity cerium metal than generally available, at the rate of 0.8 pound per hour. It is similar in design to cell type No. 5 previously described (33). It has three 0.4-inch-diameter molybdenum cathodes and three 1.0-inch-diameter carbon anodes extending down into a 6-inch-diameter graphite container through its cover. This electrode arrangement is used with alternating current to melt the bath, and later with direct current for the electrolysis. Cell type No. 6 is located within a C.A.T.P. steel box, and all necessary manipulations, such as raising and lowering of electrodes, are made by a gloved operator.

The main difference between cell types is that in the No. 6 the CeO_2 is fed continuously into the bath by a mechanical feeder, while in the No. 5 the feed was introduced intermittently.

Ceric oxide powder is fed into the molten electrolyte in the 6-inch cell by a vibrating horizontal stainless steel helical screw enclosed in a stainless steel pipe. The screw is operated by a variable-speed Graham drive and can be set to deliver from 1 to 40 grams of CeO_2 powder per minute.

The feeder and hopper are mounted outside the cell box, but are connected with the cell box so that they operate in the same controlled atmosphere.

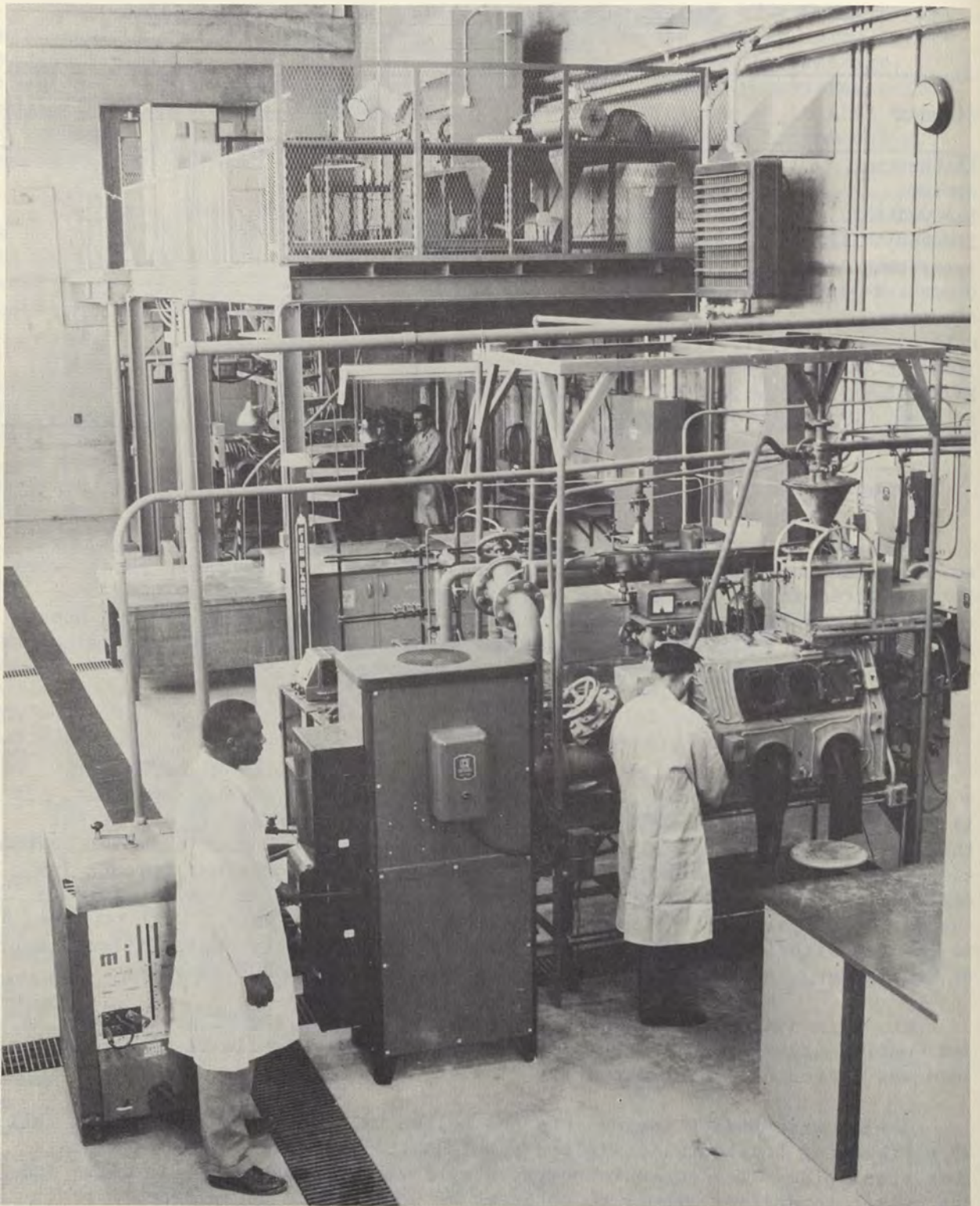


FIGURE 1. - Portion of Metallurgical Laboratory for Electrowinning Higher Purity Rare-Earth and Other Ingot Metals.

Cell Operation

The solvent-phase electrolyte, 73 percent CeF_3 , 15 percent LiF , and 12 percent BaF_2 , was vacuum-dried in Pyrex glass flasks at approximately $280^\circ C.$, then transferred to the cell chamber. The chamber was repeatedly pumped down and back-filled with helium to assure an inert atmosphere. Cerium ingot has been electrowon from CeO_2 both in high-purity argon and in helium atmospheres, with no difference noted in electrolytic conditions or in the purity of the metal prepared.

The dried electrolyte was packed into the graphite container by a gloved operator. A graphite resistor ring was placed on top of the powder, and the electrodes were lowered to make contact. Alternating current was used to melt the powder. When sufficient melt was obtained to carry the current, the graphite ring was removed and alternating-current melting continued until the bath reached a temperature of 810° to $830^\circ C.$

The vibrating-screw feeder was turned on and 10 to 20 grams of previously vacuum-dried CeO_2 powder was added to the bath. At this point the alternating current was disconnected, and direct current was turned on. During the electrolysis, CeO_2 powder was fed continuously into the molten bath at a rate of about 7 grams per minute.

Samples of cell gases taken during the electrolysis contained carbon monoxide and dioxide, oxygen, traces of moisture, and fluorocarbons.

Electrolysis was continued, usually for about 2 hours, until massive cerium nodules bridged the gaps between anodes and cathodes, necessitating that cell operation be terminated. The bath was allowed to solidify within the cell atmosphere and, once cold, was removed from the cell box. The bath then was broken up to recover the cerium nodules.

The data obtained in a typical run (CE-55) are presented in table 5. Continuous controlled feeding of the CeO_2 powder into this cell resulted in a marked decrease in the number of interruptions to the direct current used to electrowin the metal. This is believed to be one of the reasons for the recovery of massive cerium nodules weighing up to 1.6 pounds. The small size of this cell makes it unwise, however, to compare its operating data with those from cells of commercial size.

TABLE 5. - Data obtained from electrowinning cerium metal in run CE-55

Average direct-current voltage.....volts	11
Average direct-current amperage.....amperes	249
Initial cathode current density.....amperes per square inch	66.0
Initial anode current density.....do.....	26.4
Duration of electrolysis.....minutes	132
Electrocerium recovered.....pounds	1.76
Direct current power consumed, per pound of cerium.....kilowatt-hours	3.4

Table 6 shows the values obtained by analysis of a 750-gram nodule of cerium prepared in run CE-55. For comparison, the values obtained by analysis of a nodule from another run are included.

TABLE 6. - Analyses of cerium nodules from runs CE-55 and CE-49

Element	Element in cerium nodule, ¹ weight-percent	
	Run CE-55	Run CE-49
Fe.....	0.02	(²)
Al.....	<.01	<0.01
Ca + Mg.....	<.004	< .004
Li.....	.002	.001
C.....	.016	.004
O ³036	.006
H ³0003	.0003
N ³	(⁴)	.0006
Mo.....	(²)	<.005
Total rare-earth elements other than cerium.....	(²)	(²)
Si.....	(²)	(²)
Ba.....	(²)	(²)
Cr.....	(²)	(²)
Mn.....	(²)	(²)

¹Spectrochemical analysis.

²Not detected.

³Vacuum-fusion analysis.

⁴Not analyzed.

Several cerium nodules from run CE-55 were submitted to the Oak Ridge National Laboratory for neutron activation analysis. The results are given in table 7.

TABLE 7. - Neutron activation analyses of cerium nodules from run CE-55

Nodule No.	Element, weight-percent				
	Fe	Si	Al	Cr	Mn
1.....	0.0102	(¹)	<0.0100	(¹)	(¹)
1.....	.0055	(¹)	(¹)	(¹)	(¹)
2.....	(¹)	<0.0010	(¹)	<0.0007	(¹)
3.....	(¹)	(¹)	(¹)	(¹)	0.0003
3.....	(¹)	(¹)	(¹)	(¹)	.0001

¹Not analyzed.

Electrical resistivity measurements made at 27° C. showed that cerium metal prepared at Reno had a resistivity approximately seven microhm-centimeters lower than that of commercial metal, indicating the former to be of higher purity.

A gas sample was taken from the area immediately above the cell in run CE-55 after 30 minutes of electrolysis and submitted for mass spectrometric analysis (table 8).

TABLE 8. - Mass spectrometric analysis of cell gas from run CE-55

Gas	Mole-percent
Helium.....	83.32
Carbon dioxide.....	13.58
Oxygen.....	1.24
Carbon monoxide.....	.43
Nitrogen.....	.78
Silicon tetrafluoride.....	.25
Hexafluoroethane.....	.20
Carbon tetrafluoride.....	.13
Hydrogen.....	.07

In order to study the formation of gases at the anode, two electrodes were placed in a small laboratory cell so that they could be observed during an electrolysis to prepare cerium metal. Bubbles were observed to form at discrete locations on the surface of the anode during the electrolysis, grow, and break away. A new bubble appeared to form immediately at the identical site. High-speed (750 frames per second) motion pictures taken at the beginning of a run confirmed visual observations. The meaning of "anode current density" is therefore doubtful because of the impossibility of determining the active anode surface area. A consideration of the term "cathode current density" leads to a similar conclusion. It is understood, however, that such descriptive terms will continue to be used until more concise ones can be defined, but the limited meaning of such terms should constantly be kept in mind.

ELECTROLYTE STUDIES ON CERIUM SYSTEMS

Studies were carried out to obtain necessary chemical and physical data to promote the electrowinning efforts for preparation of higher purity, reactive metals. Both a rapid, possibly less thorough, search for these data and a long-range investigation were carried out simultaneously.

The quality of the metal which can be prepared in an inert-atmosphere chamber depends, in large measure, on the purity of the atmosphere itself. Control is only as good as the methods used to evaluate it. The instruments described, some of which were mentioned in a previous report (33), are used with all controlled-atmosphere equipment.

The moisture content of the gaseous atmosphere is determined by use of a commercial moisture monitor that can detect as little as 1 part per million water in a gas. The instrument is based on a quantitative electrolysis of the water in the gas passing through a special tube at a controlled flow rate. This tube was described by Keidel (18).

Several instruments are used for determination of CO, CO₂, and O₂, based on absorption of the component into a reactive solution whose volume or titer is then measured. Precision gas analysis equipment of the Orsat type, with a minimum reading of 0.1 percent, is employed when sufficient time is available. When a quicker analysis is desired, a Kwik-Chek instrument, calibrated for a minimum reading of 0.25 percent, is employed.

To allow an overall test of the quality of the atmosphere, the thermal conductivity of the gas in the chamber is compared to that of pure reference gas (either argon or helium) by a gas master.

By careful use of the above instruments, the quality of the atmosphere in any of the controlled-atmosphere chambers can be determined. Replacement of the atmosphere a sufficient number of times to obtain minimum readings on these instruments prior to electrolysis creates the proper environment for initiation of electrowinning of higher purity, reactive metals like cerium.

Capsule Design

A controlled atmosphere-temperature-pressure capsule was designed in which it is possible to obtain rapidly the inert atmospheres essential to higher-purity-metal investigations (fig. 2).

The capsule is a steel cylindrical work chamber 24 inches in diameter by 34 inches high, with a steel plate welded in place for the bottom. Top closure of the capsule is made by means of a hemispherical dome forced against an O-ring. Domes constructed of Plexiglas and steel are available for particular experiments. Each capsule is provided with the following:

1. Two glove ports which permit manipulations inside the work area without loss of the inert atmosphere.
2. Vacuum valves for taking gas samples and for evacuation and refilling of the inert atmosphere chamber.
3. Thermocouple leadthroughs to permit temperature measurements.
4. Power leadthroughs for both induction and resistance furnaces.
5. Additional power leadthroughs to permit electrolyses inside the controlled-atmosphere work chamber.
6. A combination of mechanical and diffusion pumps, together with required manifolds, cold traps, and valves for evacuation of the chamber.
7. Thermocouple and cold-cathode ionization tubes and gages with which the vacuum inside the capsules can be measured.
8. Safety blowout disk to prevent accidental overpressures building up in the work chamber.

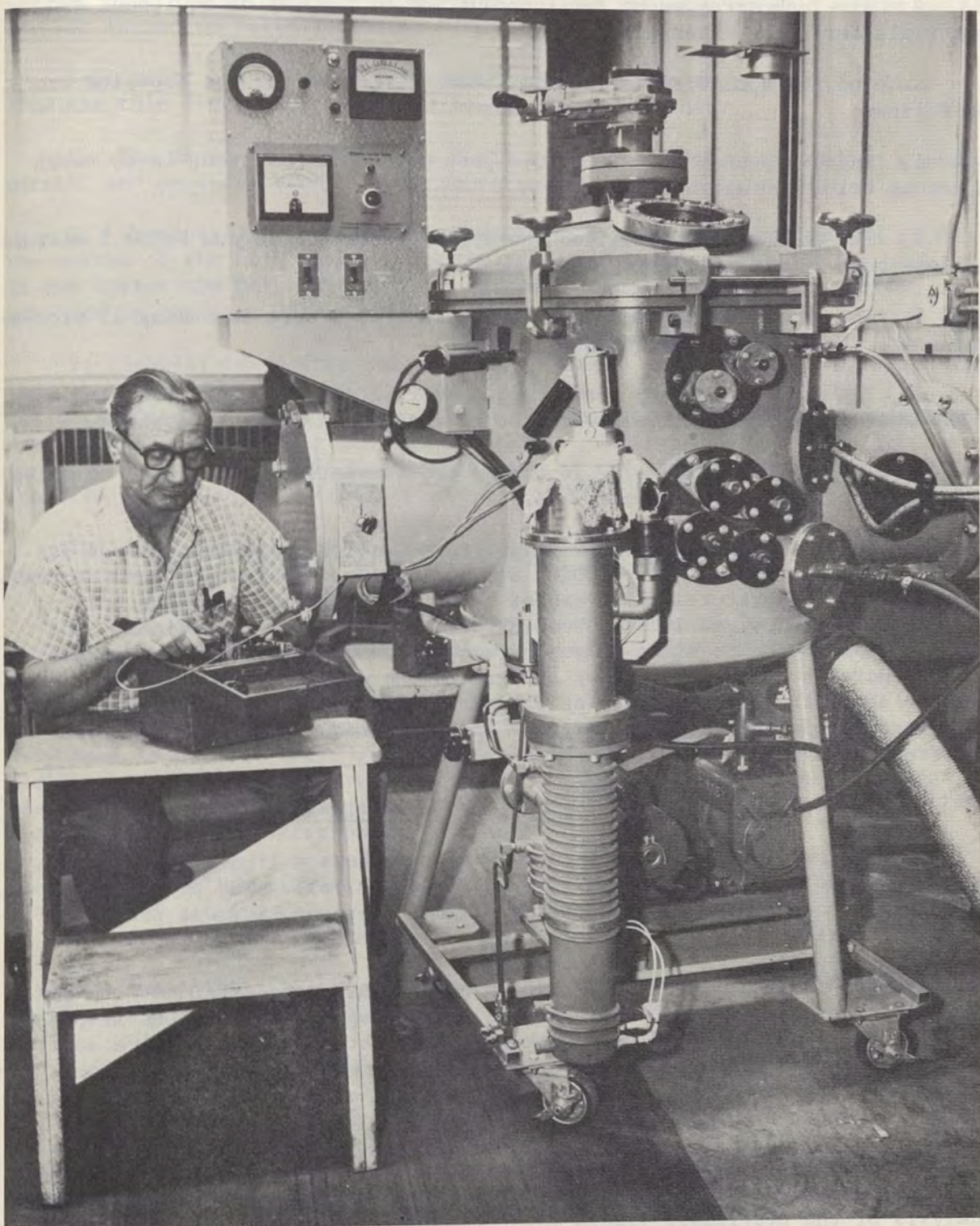


FIGURE 2. - C. A. T. P. Capsule Used for Electrolyte Studies.

9. Air-lock arrangement for introduction or removal of equipment and materials during an experiment.

Some of the specified performance characteristics for the capsules are as follows:

1. The empty chamber, with glove port covers in position, is to reach a vacuum below 0.5 micron.

2. The chamber (as specified above) is to reach a vacuum below 5 microns in less than 20 minutes, using the pump system provided.

3. The empty chamber must not lose vacuum at a rate exceeding 15 microns per hour, the test to commence at 15 microns.

4. The induction power leadthroughs must be capable of maintaining a 6-kilowatt induction furnace inside the chamber in an argon atmosphere.

The capsule, shown in figure 2, is one of two currently in use, both of which meet the specified requirements.

One unit, designated the low-temperature C.A.T.P. capsule, is used for studies at temperatures below 1,000° C. Resistance furnaces are used to reach the required temperatures. The use of a resistance furnace permits holding temperatures at desired levels, but introduces several complications. One problem is the time required to reach reaction temperatures. A second problem is the increase in temperature of the gas in the working chamber. Little can be done about the first problem at present, but the second problem has been minimized by cooling the shell of the capsule and equipping the tools with heat reflectors.

Composition of the Cerium Electrowinning Bath

The cerium electrowinning bath was known to have a liquid phase, and a more dense, solid phase, serving as a skull in the cell. The powder mixture, 73 weight-percent CeF_3 , 12 percent BaF_2 , and 15 percent LiF , was prepared, dried, and melted in the capsule.

Samples of the clear liquid portion of the bath were obtained with small graphite scoops and ladles. By removing as much as possible of the liquid layer, samples of the solid skull material were obtained. These were analyzed by spectrographic, X-ray, and wet chemical techniques. Additional samples were obtained by freezing the bath in situ without agitation, and then removing samples from the top and bottom of the solidified bath.

X-ray analysis showed that the skull was largely cerium fluoride grains in a matrix similar in composition to the liquid portion of the bath. X-ray analysis of the previously liquid layer indicated that there was an unidentified phase present which could not be found when checking binary melts such as LiF-BaF_2 or LiF-CeF_3 . Identification of this phase, however, was not undertaken because it would be impossible to determine whether this phase, so

obvious when examining the solidified bath, was actually present in the molten bath or formed on solidification.

Solidified bath samples were submitted for petrographic examination. From the thin sections it was possible to determine that:

1. The skull layer is mainly small crystals of CeF_3 embedded in a glassy matrix, and on a megascopic basis appears to be grayish in color.
2. There is a sharp dividing line between the skull area, which is on the bottom of the bath sample, and the previously molten area of the bath. In the latter the CeF_3 crystals are larger and better defined, but also embedded in the same glassy matrix.
3. Samples taken from baths to which excess ceric dioxide was added show that the bluish material on the bottom of these baths is CeO_2 . From this and the X-ray data, it would appear that the ceric oxide never dissolved in the saturated melt but merely passed through it. This checks the visual observations but needs some qualification because of the radioactive tracer work reported in the oxide solubility section of this report.

The specific gravity of the skull layer was determined to be 5.55, and the solidified clear layer was determined to be 5.21.

Cooling curves were run on the cerium electrowinning bath to determine the initial freezing temperature of the liquid mixture. The data and results can be summarized as follows:

1. The original mixture of powders (73 weight-percent CeF_3 , 12 percent BaF_2 , and 15 percent LiF), when heated to $800^\circ C.$, forms a liquid whose composition is 63, 16, and 21 weight-percent, respectively, of the compounds based on quantitative analysis for the elements. This composition is called the standard, clear, transparent cerium electrowinning bath.
2. The solid material at the bottom of the molten standard electrowinning bath is largely CeF_3 . It is found interspersed in the liquid but settled to the bottom of the container.
3. The initial freezing point of the liquid is $699^\circ C.$, while the solidus temperature is $660^\circ C.$; both temperatures are reported to $\pm 5^\circ C.$

Oxide Solubility in Cerium Electrowinning Bath

One important operating variable for electrowinning procedures is the amount of feed that will dissolve in the melt, because only that material is presumed to be available for reaction at the electrode surface. Gray (11), using a visual determination of the endpoint, reported the solubility of ceric oxide to be 3 to 5 weight-percent in his bath at $850^\circ C.$

Attempts to repeat Gray's work were unsuccessful because even the first grains of oxide added to the molten bath would not dissolve. The pinkish

oxide changed to golden-yellow when it touched the surface of the molten bath so that it was comparatively easy to follow its path. The apparent insolubility of the oxide indicated that the bath, once molten, was saturated or nearly saturated, with the oxide.

Oxide could have been introduced into the molten bath in two ways:

1. Being present in the original powders.
2. Formation due to hydrolysis of the powders during the melting process.

In an attempt to remove both of these sources of oxide from the electro-winning bath, the individual powders were repeatedly fluorinated with ammonium bifluoride at a temperature of 500° to 600° C., then vacuum-dried at 400° C. to remove residual gases. In some cases these powders were dried, weighed, mixed, and melted, all operations taking place in an argon atmosphere to minimize contamination by water or air. On melting the powder to form bath, it was found that these treatments for removal of oxide had not been successful.

Powders were mixed to give the standard, clear bath composition, then vacuum-dried at 400° C. for several hours. During the drying, the container was evacuated and then refilled with dry argon, pump and refill cycles being repeated to minimize water retention. When placed in the capsule and melted, these bath mixtures behaved as did those previously tested. In some experiments the molten bath was dropped in temperature to 600° C.; then the entire capsule was evacuated to remove the water locked out of the chilled bath. The melt, chill, pump, and refill cycle was repeated and eventually reduced the amount of water detected in the gas above the molten bath. This procedure, however, defeated the original purpose of the experiments, for in melting, some of the powders were hydrolyzed by reaction with water. It appeared to be virtually impossible to prepare a molten bath that did not contain some oxide. Published work (27) indicated that the existence of molecular water in fused salts at elevated temperatures was more prevalent than previously believed.

Another approach to measurement of the oxide solubility in the bath was to use radioactive CeO_2 , the oxide containing Ce^{141} . Visually, addition of the oxide to the bath caused no reaction, the added oxide dropping to the bottom of the bath container. Samples taken from the melt, however, indicated that in the time it took for the added oxide to break through the surface of the bath and drop to the bottom of the container, and for sample removal, complete exchange had taken place. The distribution of the radiolabeled cerium ions throughout the melt and the remaining oxide at the bottom of the container was in the proportion fixed by the relative amount of cerium in each. This approach was not capable of giving the oxide solubility in the melt but gave instead an indication of the rapid rate of exchange between solid cerium oxide and the bath. This would seem to indicate that in a bath not saturated with cerium oxide, the rate of oxide solution would be extremely rapid, approaching instantaneous solution.

Bath samples were melted in the argon atmosphere in a C.A.T.P. capsule, a large quantity of CeO_2 was added, and the mixture was stirred and then held

at 850° C. for several hours to complete saturation of the bath. Samples of the clear liquid layer, not containing suspended oxide, were taken for analysis of the oxide-ion content. Identical samples were analyzed by the Ames, Mallinckrodt, and Reno laboratories. The results of these analyses are reported in table 9. Three samples were analyzed in the first series:

1. The standard, clear bath mixture prior to fusion.
2. The bath, once molten but before oxide was added.
3. The bath, after saturation with the oxide.

Converting the reported oxide-ion contents of the bath to CeO_2 or Ce_2O_3 gave a solubility range of 1.0 to 2.0 percent. The same oxide ion content, when calculated as $CeOF$, gave a solubility of approximately 2 percent.

Bath samples were electrolyzed with the intention of depleting the oxide contents. It was expected that once the bath had been depleted in oxide content, weighed amounts of oxide could be added to the bath and a solubility value obtained. Table 9 includes the value which was measured in this fashion, the end point being taken as that value where the first grain of oxide was seen not to dissolve.

TABLE 9. - Solubility of oxide in standard, clear cerium electrowinning bath

Sample, type	Oxide ion, by oxygen analysis, percent	CeO_2 , percent ¹	Ce_2O_3 , percent ¹	$CeOF$, percent ¹	Analysis, source
Cerium electrowinning bath, no added oxide.	² 0.11	0.6	0.7	1.2	Ames. ³
	² .09	.5	.6	1.0	Mallinckrodt. ⁴
	² .11	.6	.7	1.2	Reno. ³
	.19	1.0	1.3	2.1	Do.
Cerium electrowinning bath, saturated with oxide.	² .20	1.1	1.4	2.2	Ames.
	² .11	.6	.7	1.2	Mallinckrodt.
	² .24	1.3	1.6	2.6	Reno.
	.15	.8	1.0	1.6	Do.
	.32	1.7	2.2	3.5	Do.
Depleted cerium electrowinning bath brought to saturation.		.6			Visual observation in laboratory during addition of CeO_2 to the molten bath.
		.7			

¹Each value calculated from same oxygen analysis.

²Identical sample.

³By inert-gas fusion, at atmospheric pressure.

⁴By vacuum fusion.

The valence of the added oxide, once dissolved into the bath, became important. Adding ceric oxide (containing +4 ions) to the bath might have introduced ions of the same valence into the bath, or they might have been converted to the +3 valence state during solution. Quenched bath samples were dissolved into a water medium, then titrated to measure the amount of ceric ions in the water solution. It was necessary, naturally, to assume that the quenched solid samples were representative of the melt. The following conclusions were reached within the limit of the analytical method:

1. Molten bath, prior to oxide additions, contained only +3 cerium ions.
2. Bath saturated with CeO_2 contained only +3 cerium ions.
3. The oxide at the bottom of a solidified, saturated bath (shown to be approximately CeO_2) did contain +4 cerium ions.
4. During oxide depletion electrolyses, +4 cerium ions were being produced in the molten electrolyte. This will be further amplified in the section on oxide depletion in this report.

An attempt was made to see whether there was a surface effect that restricted the solubility of the added oxide. A definite surface tension could be observed on the molten bath because the oxide would float for finite times before entering the bath proper. Oxide was treated with molten LiF in an experiment intended to alter its surface character. The oxide solubility rate was not altered by this pretreatment.

Oxide Depletion Electrolyses

The standard, clear cerium electrowinning bath was electrolyzed with and without skull in a crucible with a molybdenum cathode and a carbon anode, oxide not being added during the experiment. To observe the cell at operating temperatures, a strong spotlight was used which minimized the reddish glow associated with elevated temperatures. After several hours of electrolysis the melt was solidified, removed from the container, and broken apart to remove the metallic cerium produced. The metal was collected, and the solid bath was returned to the crucible, remelted, and reelectrolyzed. It was noted that gas appeared to form at the anode only for about the first hour of electrolysis and then ceased. Metal was still produced, but no anode gas was observed. As the electrolysis progressed, the bath changed from a clear, transparent state to a ruby-red, translucent condition, passing through various shades of brown. The bath quivered like a bowl of ruby-red gelatin and had a convex appearance except near the molybdenum cathode (fig. 3). Only the cathode appeared to be wet by freshly melted bath as well as by oxide-depleted bath. In some of these oxide-depletion runs, all operations, starting with drying the bath components, mixing, fusing, and electrolyzing, through final recovery steps, were done inside the capsule to minimize air and moisture contact.

As the electrolyses proceeded, less and less metal was produced, finally reaching a point at which the metal was not recoverable. Possibly, a cyclic

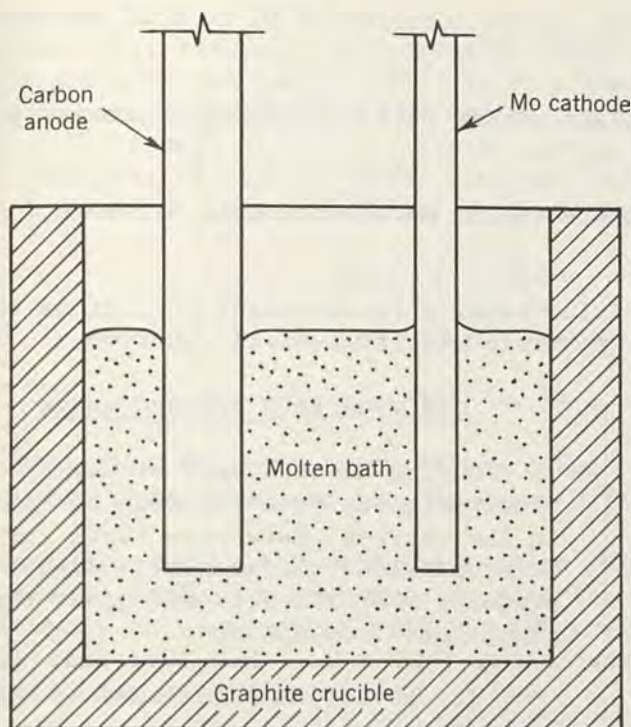


FIGURE 3. - Schematic Cross Section of Cerium Electrowinning Cell.

oxidation-reduction steady state was reached at this time, metal forming at the cathode and being redissolved at the anode.

Addition of CeO_2 to the oxide-depleted baths after the cessation of electrolysis changed the color of the baths from ruby red to the original clear, transparent state. Foaming of the bath occurred at the same time. The foaming always appeared when ceric oxide was fed to oxide-depleted bath, regardless of the previous treatment of the oxide. Baths not depleted in oxide content did not foam under the identical test conditions regardless of the previous history of the oxide. This addition of oxide to the bath to discharge the color permitted the visual measurement of the solubility of the oxide, as earlier indicated.

Some characteristic voltages were measured:

1. The voltage between molybdenum-carbon and molybdenum-graphite in cerium electrowinning melts prior to electrolysis was 0.2 volt, while for carbon-graphite no measurable voltages were observed.

2. After oxide-depletion electrolysis of a bath, the back electromotive force measured across the molybdenum-carbon electrode couple was approximately 0.9 volt. If the electrodes were connected to a voltmeter for a period of 6 hours, the voltage decayed from 0.9 to 0 volt, accompanied by a color reversal of the molten bath from ruby red to colorless.

3. If after electrolysis the molybdenum electrode contacted cerium metal in the bath, the measured voltage was 3.5 volts. If the molybdenum rod separated from the cerium metal, this voltage fell immediately to 0.9 volt.

4. Measurement of molybdenum-carbon and molybdenum-graphite pairs to determine the thermoelectric electromotive force at the same temperature gave readings of the order of 0.010 volt.

It was obvious that competing reactions were occurring simultaneously at the electrodes in the cerium bath. As indicated, electrolysis to deplete the oxide contents of molten baths was discontinued every few hours and the bath was frozen to allow removal of the metal prepared during the run. This metal was analyzed for molybdenum content with the following results:

1. After 1 hour of electrolysis cerium contained 0.01 to 0.02 percent molybdenum.

2. After 12 hours of electrolysis cerium metal contained approximately 0.2 percent molybdenum.

3. After 16 hours of electrolysis cerium metal contained 0.2 to 0.7 percent molybdenum.

The presence of molybdenum in the cerium metal when the oxide content of the bath is very low represents another possible electrochemical reaction.

Decomposition Voltage Curve

During electrolyses of cerium electrowinning baths at 800° to 850° C. in the capsule, data were taken for a decomposition voltage plot. Figure 4 presents the data obtained under three experimental conditions:

1. No cerium oxide added to the bath (run EC-5).
2. Cerium oxide added to the bath as the electrolysis proceeds (run EC-7).
3. No cerium oxide added, oxide content depleted by previous electrolysis of the bath (run EC-3).

All three sets of data fall on a single curve, within experimental reproducibility. This suggests that the electrode reactions should be the same under the three sets of experimental conditions.

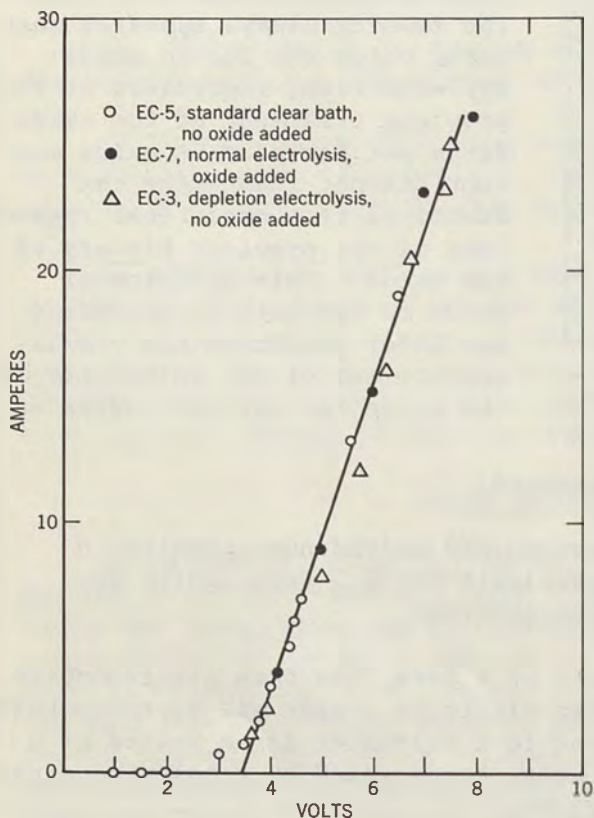
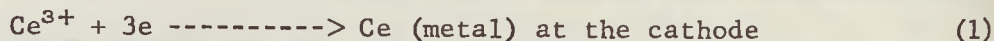
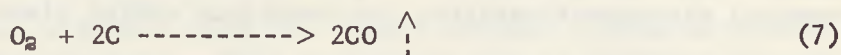


FIGURE 4. - Decomposition Voltage Curve.

During "normal" electrolysis, in which sufficient oxide was dissolved in the melt, the electrode reactions can be represented schematically as follows:



Equations (2), (3), and (4) represent simultaneous reactions that can be taking place at the anode, each reaction competing with the others for the available reactive sites on the immersed anode surface. Gases formed at the anode pass through the bath and then escape from the surface. Secondary chemical reactions of the hot gases with the carbonaceous anode then take place above the bath. These reactions could be represented schematically as follows:

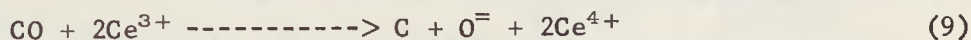
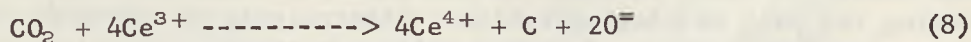


Equations (5), (6), and (7) represent the "air-burn" type of reaction found just above the melt line in fused-salt electrowinning cells.

Equations (2), (3), and (4) require sufficient oxide ion to be in solution and to arrive at the anode surface for the reactions to proceed. In the cases where this amount of oxide is not available in the bath, it would be anticipated that some other anode reaction will take place. Experimentally, the following was observed:

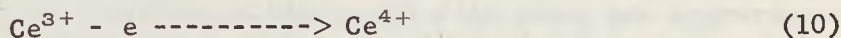
1. Under "normal" electrolytic conditions: Large amounts of gas leave the bath, some ruby-red color is observed in the molten bath, and the bath is under violent agitation.

2. Electrolyzing oxide-depleted bath: No visible gas escapes from the bath, no anode "air-burn," the ruby-red color in the bath covers a larger area, total lack of bath agitation, and black scum in bath. A plausible explanation for the observations would be to postulate a secondary, spontaneous chemical reaction that takes place in the body of the bath, but not at the anode surface, after equations (2), (3), or (4). For example:



Either reaction, (8) or (9), would explain the single decomposition curve in figure 4, the observation of when there is and is not gas coming out of the bath, the appearance of a black scum (carbon) in and on the bath, and the formation of ruby-red colors in the bath. From a thermodynamic analysis, neither equation (8) nor (9) is spontaneous.

Since ceric ions are found in larger quantities during electrolysis of oxide-depleted baths, the following occurs at the anode:



Because the voltage of the cerium electrowinning cell does not change when the oxide content is depleted, when gas formation appears to stop at the anode, and when the bath turns ruby-red, it follows that equation (10) must

also be competing with equations (2), (3), and (4) during the "normal" electrolysis. With sufficient oxide ion in the bath for equations (2), (3), and (4), there are still some ceric ions produced, as suggested in equation (10). In support of this explanation is the fact that even with baths saturated with oxide, a small amount of ruby-red color is observed in the immediate vicinity of the anode during "normal" electrowinning.

Under oxide-depleted conditions, therefore, it is suggested that the electrode reactions are (1), that is, cerous ions in the bath being reduced to metallic cerium, and (10), cerous ions being oxidized to the ceric state. Because this change cannot be spontaneous, the process has been called electrochemical disproportionation, the reactions taking place at the electrodes.

Valence of Cerium Reduced To Form the Metal

As previously indicated, the valence of cerium ion reduced to form the metal was uncertain because both cerous and ceric ions were present in the molten electrowinning bath. Evidence was obtained to show that the number of ceric ions in the bath was markedly limited and that the CeO_2 feed dissolved with formation of trivalent ions.

The data in table 5 were used to calculate the current efficiency. With an average direct current of 249 amperes passed through the cell for 132 minutes, and with 791 grams of cerium metal recovered, the current efficiency was 83 percent. This figure compared well with other electrochemical cells used for preparation of liquid metals, such as an aluminum reduction cell.

Molecular Oxygen in Cell Gas

During some electrolyses the anode was badly eroded at and above the melt line of the fused salt. Prior to electrolysis the atmosphere in the cell box was changed often enough to obtain a zero reading on the previously described control instruments, which indicated total removal of O_2 , CO, and CO_2 . A minimum amount of water remained in the atmosphere but was removed if it increased during the bath melting operation. Electrolysis of the melt was then initiated in an inert atmosphere of either helium or argon.

Routine monitoring of the cell gas during electrolysis indicated that some molecular oxygen was present. This could have come from many places, including leaks in the cell box, so that a series of experiments was conducted to determine the source of the oxygen, as follows:

1. A Vycor container was placed in a helium atmosphere, and vacuum-dried CeO_2 was fed into the container to determine whether the oxide contained air that would be released in an inert atmosphere.

2. Experiment 1 was repeated first with a graphite container at room temperature and later with the graphite container held at $835^\circ C$. The vacuum-dried oxide was fed by hand and also by a mechanical vibrating screw feeder. These tests were to determine whether the feeder mechanism was the source of oxygen and whether the oxide would decompose to form oxygen upon contact with carbon.

3. The undried CeO_2 was placed in a graphite crucible, introduced into an inert atmosphere, and then heated to temperatures over 800°C . to determine whether the oxide, prior to drying, would produce oxygen as it was heated in contact with carbon.

4. The cerium electrowinning bath was placed into a graphite container and then melted in an inert atmosphere. Vacuum-dried ceric oxide was fed into the molten electrolyte, but the direct current source was not activated. This test was to determine whether contact with the molten salt, in the presence of carbon, would liberate oxygen.

5. Experiment 4 was repeated with the direct current source activated to produce cerium metal from the bath. This experiment was to indicate whether the oxygen was made as part of the electrode reactions.

Gas samples were withdrawn from the controlled atmosphere and analyzed for CO , CO_2 , and O_2 . Only in the experiments of type 5 was molecular oxygen detected. In experiment types 2, 3, and 4, small amounts of CO and CO_2 were found but not O_2 . To provide an additional check on the analyses, samples were analyzed by mass spectrometer (table 10).

TABLE 10. - Mass spectrometric analyses of gas taken from area above the cell during electro-winning in C.A.T.P. capsule

Identity	Mole-percent	
	Sample A ¹	Sample B ²
Hydrogen.....	0.04	0.06
Carbon monoxide.....	0	.42
Nitrogen.....	.07	.20
Oxygen.....	.02	.31
Argon.....	99.87	89.63
Carbon dioxide.....	0	9.35
Carbon tetrafluoride ³	0	.03
Total.....	100.00	100.00
H_2O	⁴ (.10)	⁴ (.15)

¹Bath molten, instruments show absence of impurities prior to start of electrolysis.

²During electrolysis, note N to O ratio less than unity.

³Tentatively identified only.

⁴Estimated.

The results confirmed the presence of molecular oxygen in the cell gas and also discounted the possibility of an air leak because the ratio of nitrogen to oxygen was not that of air. Data in table 8 also support this conclusion.

A recent critique on rare-earth metals (2) indicated the necessity for identification of the source of oxygen found in the cell box. Anode corrosion

above the bath level by an oxidizing atmosphere cannot be minimized unless its source is known. Corrosion of the anode is expected when CO_2 , likewise O_2 , is formed, and the electrode behavior pattern is similar to that experienced in other electrochemical cells, such as aluminum reduction cells. While inconvenient, it does not prevent production of large quantities of aluminum or cerium.

Once the source was identified, the second phase of the problem was to find means of minimizing the effect. Several possible solutions were projected, all with one common basis--testing must be done on a continuously operating electrowinning cell. It may be possible to protect the anode by shielding with frozen bath or some other material that does not contaminate the electrowinning medium. An alternate method of protection would involve removal of the anode gases as they formed. It is possible that a change in anode current density would affect this corrosion, although this factor is, to some extent, determined by the necessity for production of higher purity metal.

The need for continuous operation has been indicated by the formation of small ingots or nodules rather than a large single one when the current is interrupted for any reason, such as, anode failure or "anode effect," so that anode corrosion may also play a part in this phenomenon. It may be necessary to accept the corrosion by CO_2 and O_2 as an inherent part of the electrowinning scheme and make adjustments accordingly, such as, the use of continuous anodes.

Radioactive Cerium Metal

The question was raised whether it would be feasible to prepare radioactive cerium metal by the procedure now under development. To answer the question, a standard cerium electrowinning run was prepared, the sole difference being that radioactive cerium oxide, containing Ce^{141} , was used as the feed material.

During a 3-hour electrolysis the oxide was fed by hand into the cell at a rate of approximately 1.5 grams of oxide every 5 minutes. Addition of the oxide to the electrowinning bath was accompanied by foaming, and the bath appeared ruby red in color, indicating that the electrolysis was taking place in a bath not saturated with oxide. At the end of the electrolysis the carbon anode and molybdenum cathode were removed, and the contents of the cell were allowed to solidify. Once frozen, the cell container and contents were examined, and the following data were obtained:

1. Radioactive cerium metal nodules were prepared. The activity of the nodules was proportional to the amount of isotopic oxide added to the cell.
2. The cerium metal that remained attached to the cathode at the end of the run exhibited the highest radioactivity, comparable to that of the bath layer in contact with it.

3. The skull material showed a minimum amount of exchange between the CeF_3 and the labeled cerium oxide added to the bath, notwithstanding the rapid exchange between labeled CeO_2 and cerium ions in the bath shown in earlier experiments.

The electrowinning procedure, therefore, was shown to be applicable to preparation of radioactive cerium metal by using radioactive oxide as the feed material.

"Reactivity" of Cerium Metal With Molten Electrowinning Bath

Radioactive cerium metal was added in two pieces to a bath at $850^\circ C.$; the additions were separated by a period of 1 hour. Analyses of appropriate bath samples showed that cerium metal "reacted" with the bath to the extent of approximately 0.1 percent. This low value made it unnecessary to elucidate the reaction mechanism.

As part of the experimental sequence the metal was analyzed for carbon and oxygen contents before and after immersion in the fused-cerium electrowinning bath. Analyses showed both interstitial impurities to be decreased by immersion in the bath; the oxygen decreased from 0.06 to 0.01 percent, while the carbon decreased from 0.04 to 0.01 percent. These results suggest a possible approach to upgrading metal prepared in a cerium electrowinning operation which would not involve remelting the product.

DISCUSSION

To aid in electrowinning larger quantities of cerium metal, as well as metal of higher purity, a model of what may be taking place in the cerium electrowinning cell was constructed. While speculative, such an explanation affords a chance to examine the procedure and its boundary conditions.

Table 11 presents the results of one such attempt at speculation. The equations are shown in ionic form with no implication that these ions actually exist, as such, in the molten bath because it is probable that most ions are present in some form of complexes. To aid in evaluation of the equations presented in table 11, the estimated free energies and electrode potentials of similar molecular reactions are presented in tables 12 and 13.

Fusion of the Cerium Electrowinning Bath

Fusion of cerium electrowinning bath takes place with some hydrolysis in spite of strenuous efforts to remove moisture prior to heating. Equations (1a) and (1b) in table 11 show two possible mechanisms by which the hydrolysis could take place, both effectively introducing oxide into the molten bath.

TABLE 11. - Speculative representation of reactions that may take place in the molten bath from which cerium metal is electrowon¹

No.	Equation ²
1a.....	$2F^- + H_2O \text{ -----} > 2HF \overset{\wedge}{\underset{ }{\downarrow}} + O^{2-}$
1b.....	$3F^- + H_2O \text{ -----} > 2HF \overset{\wedge}{\underset{ }{\downarrow}} + OF^{3-}$
2.....	$2CeO_2 + C \text{ -----} > 2Ce^{3+} + 3O^= + CO \overset{\wedge}{\underset{ }{\downarrow}}$
3a.....	$Ce^{3+} + 3e \text{ -----} > Ce \text{ (cathode)}$
3b.....	$O^{2-} + C - 2e \text{ -----} > CO \overset{\wedge}{\underset{ }{\downarrow}}$
3c.....	$2O^{2-} + C - 4e \text{ -----} > CO_2 \overset{\wedge}{\underset{ }{\downarrow}} \text{ (anode)}$
3d.....	$2O^{2-} - 4e \text{ -----} > O_2 \overset{\wedge}{\underset{ }{\downarrow}}$
4a.....	$Ce^{3+} + 3e \text{ -----} > Ce \text{ (cathode)}$
4b.....	$3Ce^{3+} - 3e \text{ -----} > 3Ce^{4+} \text{ (anode)}$
5a.....	$2Ce^{4+} + \underline{CeO_2} \text{ -----} > 3/4O_2 \overset{\wedge}{\underset{ }{\downarrow}} + 3Ce^{3+} + 1/2O^{2-}$
5b.....	$^3 2Ce^{4+} + \underline{SiO_2} \text{ -----} > 1/2O_2 \overset{\wedge}{\underset{ }{\downarrow}} + 2Ce^{3+} + Si^{4+} + O^{2-}$
6a.....	$Ce^{4+} + e \text{ -----} > Ce^{3+} \text{ (cathode)}$
6b.....	$^4 \underline{Mo} + xe \text{ -----} > Mo^{x+} \text{ (anode)}$
7a.....	$Ce^{4+} + e \text{ -----} > Ce^{3+} \text{ (cathode)}$
7b.....	$Ce - 3e \text{ -----} > Ce^{3+} \text{ (anode)}$
8a.....	$^4 \ ^5 \underline{5CeO_2} + 4Mo^{x+} + (4x-15)e \text{ -----} > 2(MoO_2 + MoO_3) \overset{\wedge}{\underset{ }{\downarrow}} + 5Ce^{3+}$
8b.....	$\underline{10CeO_2} + \underline{2Mo} \text{ -----} > (MoO_2 + MoO_3) \overset{\wedge}{\underset{ }{\downarrow}} + 10Ce^{3+} + 15O^{2-}$

¹Equations are presented in ionic form with no implication that these ions exist in the melts.

²Underlined compounds or elements are in the solid state.

³SiO₂ added to the bath to test the effect of an oxide other than cerium.

⁴Valence of Mo, from the Mo electrode rod, given as (x) because exact valence in the melt not known.

⁵(MoO₂ + MoO₃) used to represent "moly blue," exact composition unknown.

TABLE 12. - Estimated free energies and electrode potentials of reactions similar to those presented in table 11, calculated from data in table 13

[Temperature equals 1,130° K. (857° C.)]

Reaction designation	Equation	Thermodynamic quantities ¹	Comparison equation, table 11
A.....	$2\text{CeO}_2(\text{c}) + \text{C}(\text{graphite}) = \text{Ce}_2\text{O}_3(\text{in bath}) + \text{CO}(\text{g})$	² $\Delta F < 0$	2
B.....	$2\text{CeO}_2(\text{c}) + \text{C}(\text{graphite}) = \text{Ce}_2\text{O}_3(\text{l}) + \text{CO}(\text{g})$	$\Delta F = + 19 \text{ kcal.}$	None
C.....	$\text{Ce}_2\text{O}_3(\text{l}) = \text{Ce}_2\text{O}_3(\text{in bath})$ (from reactions A + B)	$\Delta F^\circ < - 19 \text{ kcal.}$	Do.
D.....	$\text{Ce}_2\text{O}_3(\text{in bath}) + 3\text{C}(\text{graphite}) = 2\text{Ce}(\text{l}) + 3\text{CO}(\text{g})$	$\Delta F^\circ > + 197 \text{ kcal.};$ $E^\circ < - 1.4 \text{ volts.}$	3a + 3b
E.....	$\text{Ce}_2\text{O}_3(\text{in bath}) + 3/2\text{C}(\text{graphite}) = 2\text{Ce}(\text{l}) + 3/2\text{CO}_2(\text{g})$	$\Delta F^\circ > + 208 \text{ kcal.};$ $E^\circ < - 1.5 \text{ volts.}$	3a + 3c
F.....	$\text{Ce}_2\text{O}_3(\text{in bath}) = 2\text{Ce}(\text{l}) + 3/2\text{O}_2(\text{g})$	$\Delta F^\circ > + 350 \text{ kcal.};$ $E^\circ < - 2.5 \text{ volts.}$	3a + 3d
G.....	$2\text{Ce}_2\text{O}_3(\text{in bath}) = 3\text{CeO}_2(\text{l}) + \text{Ce}(\text{l})$	$\Delta F^\circ > + 112 \text{ kcal.};$ $E^\circ < - 1.6 \text{ volts.}$	4
H.....	$4\text{CeF}_3(\text{l}) = 3\text{CeF}_4(\text{l}) + \text{Ce}(\text{l})$	$\Delta F^\circ = + 277 \text{ kcal.};$ $E^\circ = - 4.0 \text{ volts.}$	4
I.....	$2\text{CeF}_4(\text{l}) + \text{CeO}_2(\text{c}) = 1/6\text{Ce}_2\text{O}_3(\text{in bath}) + 8/3\text{CeF}_3(\text{l}) + 3/4\text{O}_2(\text{g})$	$\Delta F^\circ < - 40 \text{ kcal.}$	5a
J.....	$2\text{CeF}_4(\text{l}) + \text{SiO}_2(\text{quartz}) = \text{SiF}_4(\text{g}) + 1/3\text{Ce}_2\text{O}_3(\text{in bath})$ $+ 1/2\text{O}_2(\text{g}) + 4/3\text{CeF}_3(\text{l})$	$\Delta F^\circ < - 13 \text{ kcal.}$	5b
K.....	$6\text{CeO}_2(\text{c}) + \text{Mo}(\text{c}) = \text{MoO}_3(\text{l}) + 3\text{Ce}_2\text{O}_3(\text{in bath})$	$\Delta F^\circ < + 54 \text{ kcal.};$ $E^\circ > - 0.4 \text{ volts.}$	8b, 6a + 6b
L.....	$4\text{CeO}_2(\text{c}) + \text{Mo}(\text{c}) = \text{MoO}_2(\text{c}) + 2\text{Ce}_2\text{O}_3(\text{in bath})$	$\Delta F^\circ < + 19 \text{ kcal.};$ $E^\circ > - 0.2 \text{ volts.}$	8b, 6a + 6b
M.....	$2\text{Ce}_2\text{O}_3(\text{in bath}) + \text{CO}_2(\text{g}) = 4\text{CeO}_2(\text{l}) + \text{C}(\text{graphite})$	$\Delta F^\circ > + 11 \text{ kcal.}$	(³)
N.....	$4\text{CeF}_3(\text{l}) + \text{CO}_2(\text{g}) = 3\text{CeF}_4(\text{l}) + \text{CeO}_2(\text{l}) + \text{C}(\text{graphite})$	$\Delta F^\circ > + 176 \text{ kcal.}$	(³)

¹Standard thermodynamic nomenclature is used throughout. A positive (+) ΔF and a negative (-) E mean that the reaction is not spontaneous, as written.

²This reaction was observed to be spontaneous in the experiments, therefore $\Delta F < 0$. The partial pressure of CO in equations (A) and (B) is of the order of 0.1 atmosphere.

³No comparative equation included in table 11. See section on Decomposition Voltage Curve, equations (8) and (9).

TABLE 13. - Free energy values used in calculation of free energies and potentials of reaction reported in table 12 and their sources

Compound	ΔF° 1,130° K. kcal./mole	Sources ¹
CeO ₂ (c).....	-203	Huber and Holley (16); Coughlin (7).
CeO ₂ (1).....	-196	Estimated values: m.p. 2,873° K.; ΔS_m 6 cal./mole-deg. at 2,873° K.; ΔC_{p_m} 5 cal./mole-deg. from 1,130° - 2,873° K.
Ce ₂ O ₃ (c).....	-338	Coughlin (7).
Ce ₂ O ₃ (1).....	-331	Rossini (37); m.p. 1,960° K.; estimated values: ΔS_m 10 cal./mole-deg. at 1,960° K.; ΔC_{p_m} 7 cal./mole-deg. from 1,130° - 1,960° K.
Ce ₂ O ₃ (in bath)....	<-350	Reaction (A), table 12, is spontaneous.
CeF ₃ (1).....	-337	Brewer (5, 4); Spedding (44).
CeF ₄ (1).....	-357	Do.
SiO ₂ (quartz).....	-161	Coughlin (7).
SiF ₄ (g).....	-322	Brewer (5).
MoO ₃ (1).....	-114	Coughlin (7).
MoO ₂ (c).....	- 93	Do.
CO(g).....	- 51	Do.
CO ₂ (g).....	- 95	Do.

¹Underlined numbers in parentheses refer to items in the bibliography at the end of this report.

Solution of Ceric Oxide

The addition of ceric oxide to a molten bath already containing some dissolved oxide, could be represented by equation (2), table 11. This is a reaction type of solution rather than solubility as such, for the ceric ion in the oxide converts to a cerous ion in the melt. Solution of the oxide was observed to be spontaneous and has been so indicated in equation (A), table 12, in which the free energy of the reaction is stated to be less than zero. The exact mechanism of the solution reaction is unknown, but some information can be obtained from a consideration of the data in table 13. The free energies of formation of the oxides and fluorides show that at 1,130° K.:

1. Crystalline CeO_2 is more stable than crystalline Ce_2O_3 .
2. Liquid CeO_2 is more stable than liquid Ce_2O_3 .
3. Liquid CeF_4 is more stable than liquid CeF_3 .

Thus, quadrivalent cerium ions would be more stable than trivalent in the pure compounds. This is not true in the molten bath. It would appear that there is a driving force at work in the molten bath which takes cerium ions, as the oxide dissolves, into some form of stabilized complex, at the same time making unlikely the existence in the bath of the quadrivalent form of the ion. Equation (C), table 12, gives an estimate of the free energy of formation of the complex, the value being of the order of 19 kilocalories per mole and negative. This picture appears correct so long as sufficient oxide ion is present in the melt.

"Normal" Electrowinning of Liquid Cerium Metal

Equation (3a), table 11, represents the formation of cerium metal from the ion at the cathode. Equations (3b), (3c), and (3d) are anode reactions which most likely occur simultaneously, competing for the reactive sites at the anode surface. All show a removal of oxide ion from the melt, thus precluding an exact reversal of these electrode reactions should the direct current be interrupted. Equations (D), (E), and (F), table 12, show that of the indicated anode reactions, formation of gaseous CO is most favored thermodynamically. It follows that both O_2 and CO_2 , which have been identified in the gases coming off the electrowinning cell, must have been primary anode products because they cannot be made spontaneously from CO at these temperatures. The presence of these gases likewise indicates polarization of the anode because under equilibrium conditions neither O_2 nor CO_2 would be formed. Kinetically, therefore, it appears that the anode is controlling the rate and route of reaction in the cerium electrowinning cell.

Electrowinning in an Oxide-Depleted Bath

Equations (4a) and (4b), table 11, represent the electrode reactions that may be occurring in a molten cerium electrowinning bath whose oxide content has been depleted but not totally removed. Equation (4a) indicates the cathode product to be cerium metal, whereas equation (4b) implies that three cerous ions have to be oxidized to the ceric state at the anode for each cerous ion reduced to the metal in an oxide-depleted bath. Under oxide-depleted conditions, equations (3b), (3c), and (3d) are not plausible because of lack of sufficient dissolved oxide in the bath. Equations (G) and (H), table 12, are comparable to equations (4a) and (4b), table 11, and are not thermodynamically spontaneous, and therefore these electrode reactions have to be forced electrochemically. Note that equation (4b) shows ceric ions to be present in the melt. This is in contrast to their known instability in similar melts containing sufficient oxide ions to stabilize the trivalent state. These facts strongly suggest that the oxide ion concentration plays a most important role in the formation of complex ions in the cerium electrowinning bath, the complex in some way including cerous ions.

As an alternate explanation to that indicated in equations (G) and (H), equations (M) and (N) have been included in table 12. In the section on decomposition voltage curve, a possible explanation of electrowinning reactions in an oxide-depleted bath was developed, based on the formation of CO_2 at the anode, followed by a spontaneous secondary chemical reaction in the body of the melt. Equations (M) and (N), table 12, would have to be spontaneous for this explanation to be valid, but their estimated, standard free energies are shown to be positive. This explanation of the electrode reactions, involving the spontaneous secondary reaction in the melt, cannot, therefore, be considered feasible.

In the section on decomposition voltage curve, it was noted that there was no increase in voltage when the oxide content of the bath was depleted by electrolytic action. For example, when the anode product changed from mixtures of carbon oxides and oxygen gases to a nongaseous product (Ce^{4+}), the voltage requirement for continued electrolysis was not increased. An examination of equations (D), (E), and (G), table 12, shows a relatively small difference in electrode potential between the three reactions, which would agree with the proposed explanation of the experimentally determined facts.

Addition of Oxide to an Oxide-Depleted Bath

Equation (5a), table 11, suggests a reaction which might take place when ceric oxide is added to a molten oxide-depleted bath, the oxide depletion being indicated by the presence of ceric ions in the melt. This equation suggests discharge of the ceric ions, with solution of a large amount of ceric oxide. Equation (I), table 12, is indicated as being spontaneous, since its free energy of reaction is negative. It was found experimentally that under these conditions, that is, discharge of the ceric ions from an oxide-depleted bath, the addition of ceric oxide caused the bath to foam. A similar spontaneous discharge of the ceric ions is indicated in table 11, equation (5b), and table 12, equation (J), the added oxide being silica. Again, the addition of this oxide to the oxide-depleted bath caused foaming, and in each case the previously described changes took place--a bath color reversal from ruby red to colorless, accompanied by a discharge of any voltage shown by measurement across the molybdenum-carbon electrodes immersed in the molten bath.

These facts once again suggest that the ceric ion cannot be present to any extent in a cerium electrowinning bath containing sufficient oxide ion. When oxide ion is added to a depleted bath (as in the form of CeO_2), any ceric ions are converted to the cerous form, the latter being stabilized by inclusion in some form of complex ion in the melt.

Interruption of the Direct Current While Electrowinning Ingot Cerium in an Oxide-Depleted Bath

If, at the time of this interruption, the liquid cerium metal had lost contact with the molybdenum rod that serves as the cathode, the reactions that occur in the oxide-depleted bath might be represented by equations (6a) and (6b), table 11. Some ceric ions would be present in the bath, and the bath itself would be ruby red in color at the time of the interruption. As

previously indicated, measurement of the voltage between the molybdenum-carbon rods gave a value of 0.9 volt. As the reaction proceeded, the bath color reversed from ruby red to colorless, the voltage across the cell fell from 0.9 to the zero area, and molybdenum ions appeared in the melt, their presence in quenched bath samples having been demonstrated by analysis. A lack of information about molybdenum fluorides at elevated temperatures prevented estimation of reaction free energies comparable to equations (6a) and (6b), table 11, on the basis of fluoride anions. If the calculation is made on the basis of oxide anions, and a valence of +6 is assigned to the molybdenum ion, then equation (8b), table 11 and equation (K), table 12, apply. On the other hand, assigning a valence of +4 to the molybdenum ion leads to equation (L), table 12. Both equations (K) and (L), table 12, indicate that formation of molybdenum oxides at unit activity would not be spontaneous. If the activity of the products was less than unity, equilibrium would shift to the right in each of these equations and change the free energy of the reaction toward a negative value. Some such effect must take place since "moly blue" is found experimentally.

If the direct current were interrupted in an oxide-depleted bath while liquid cerium metal was in contact with the molybdenum cathode rod, the reactions might be represented by equations (7a) and (7b), table 11. This is the reversal of the electrochemical disproportionation illustrated in equations (4a) and (4b), table 11. Ceric ions would be reduced to the cerous form, and simultaneously cerium metal would be reentering the bath as the cerous ion. Again, there would be the expected color reversal as the reactions in equations (7a) and (7b), table 11, took place. A measurement of the voltage across the electrodes immediately after interruption of the direct current gave 3.5 volts, compared with the reverse of the electrode potentials estimated in equations (G) and (H), table 12, which suggests a voltage range of +1.6 to +4.0 volts for the spontaneous reactions.

Formation of "Moly Blue" on Addition of CeO_2 to
an Oxide-Depleted Bath

Equations (8a) and (8b), table 11, are suggested as possible explanations of the formation of "moly blue," quite often encountered in electrowinning of liquid cerium from oxide-depleted baths. In equation (8a), the valence of the molybdenum ion has been given as (x) because it was not specifically determined, its exact valence being of little importance. In a similar manner the composition of "moly blue" has been indicated as $(MoO_2 + MoO_3)$, although not specifically determined. Note that equation (8a) calls for molybdenum ions in the melt, while equation (8b) suggests a reaction which could take place with the molybdenum metal itself. As the CeO_2 powder was fed into an oxide-depleted electrowinning bath, it could have reacted at the surface of the molybdenum cathode rod, or with molybdenum ions, and so forth. Equations (K) and (L), table 12, give estimated free energies of reaction for an equation similar to (8b), table 11, which being positive, suggest that the reaction would not be spontaneous, as written (see the discussion in the preceding section of this report).

BIBLIOGRAPHY⁷

1. AUDRIETH, L. F., JUKKOLA, E. E., MEINTS, R. E., AND HOPKINS, B. S. Observations on the Rare-Earths XXXVII. Electrolytic Preparation of Rare-Earth Amalgams. 1. Preparation of Amalgams of Lanthanum and Neodymium. Jour. Am. Chem. Soc., vol. 53, 1931, pp. 1805-1809.
2. BAROCH, C. T. Rare-Earth Metals. Bureau of Mines Bull. 585, 1960, pp. 679-690.
3. BILLY, M., AND TROMBE, F. (Preparation of Pure Cerium.) Compt. rend., vol. 193, September 1931, pp. 421-423.
4. BREWER, L. The Fusion and Vaporization Data of the Halides. Nat. Nuclear Energy Ser., Div. 4, McGraw-Hill Book Co., Inc., New York, N.Y., vol. 19B, 1950, pp. 193-275.
5. BREWER, L., BROMLEY, L. A., GILLES, P. W., AND LOFGREN, N. L. The Thermodynamic Properties of the Halides. Nat. Nuclear Energy Ser., Div. 4, McGraw-Hill Book Co., Inc., New York, N.Y., vol. 19B, 1950, pp. 76-192.
6. CANNERI, G., AND ROSSI, A. (On the Preparation of Metallic Praseodymium.) Gazz. chim. ital., vol. 62, 1932, pp. 1160-1163.
7. COUGHLIN, J. P. Contributions to the Data on Theoretical Metallurgy. XII. Heats and Free Energies of Formation of Inorganic Oxides. Bureau of Mines Bull. 542, 1954, 80 pp.
8. EASTMAN, E. D., FONTANA, B. J., THURMOND, C. D., AND WILMARTH, W. K. The Preparation of Cerium by Electrolysis of Molten Salts. U.S. Atomic Energy Commission, TID-5212, 1955, pp. 14-24.
9. FISCHER, W., BRÜNGER, K., AND GRIENEISEN, H. (On Metallic Scandium.) Ztschr. anorg. allgem. Chem., vol. 231, 1937, pp. 54-62.
10. FREY, E. (Notice of the Preparation of the Earth Metals in the Chemical Plant of Dr. Schuchardt in Gorlitz.) Ann. Chem. Liebigs, vol. 183, 1876, pp. 367-368.
11. GRAY, P. M. J. The Production of Pure Cerium Metal by Electrolytic and Thermal-Reduction Processes. Trans. Inst. Min. Met. (London), vol. 61, 1951-52, pp. 141-170.
12. HICKS, J. F. G. The Preparation and Properties of Yttrium Mixed Metal. Jour. Am. Chem. Soc., vol. 40, 1918, pp. 1619-1626.

⁷Titles in parentheses are translations from the language in which the item was published.

13. HILLEBRAND, W., AND NORTON, T. (Electrolytic Deposition of Cerium, Lanthanum, and Didymium.) *Ann. Phys. Chem., Sechste Reihe, von J. C. Poggendorff*, vol. 155, 1875, pp. 633-639.
14. HIRSCH, A. The Preparation and Properties of Metallic Cerium. *Trans. Am. Electrochem. Soc.*, vol. 20, 1912, pp. 57-102.
15. HOPKINS, B. S., AND AUDRIETH, L. F. The Electrolysis of Rare-Earth Metal Salts in Non-Aqueous Solvents. *Trans. Am. Electrochem. Soc.*, vol. 66, 1934, pp. 135-142.
16. HUBER, E. J., AND HOLLEY, C. E. The Heat of Combustion of Cerium. *Jour. Am. Chem. Soc.*, vol. 75, 1953, pp. 5645-5647.
17. JUKKOLA, E. E., AUDRIETH, L. F., AND HOPKINS, B. S. Observations on the Rare-Earths. XLI. Electrolytic Preparation of Rare-earth Amalgams. 3. Amalgams of Lanthanum, Neodymium, Cerium, Samarium, and Yttrium. Metallic Lanthanum, Neodymium and Cerium by Thermal Decomposition of Their Amalgams. *Jour. Am. Chem. Soc.*, vol. 56, 1934, pp. 303-304.
18. KEIDEL, F. A. Determination of Water by Direct Amperometric Measurement. *Anal. Chem.*, vol. 31, No. 12, 1959, pp. 2043-2048.
19. KOJIMA, T., AND SATO, M. (Metallurgical Research on Cerium Metal (Part 10), Application: On the Fused Salt Electrolysis of $\text{CeCl}_3 \cdot 2\text{KCl} - \text{KCl}$ Eutectic Mixture.) *Jour. Electrochem. Soc. Japan*, vol. 22, 1954, pp. 303-306.
20. KREMERS, H. C. The Preparation and Some Properties of Metallic Neodymium. *Trans. Am. Electrochem. Soc.*, vol. 47, 1925, pp. 365-371.
21. _____. Rare-Earth Metals. *Rare Metals Handbook*, Reinhold Pub. Corp., New York, N.Y., 1954, pp. 329-346.
22. KREMERS, H. C., AND BEUKER, H. The Preparation and Some Properties of Metallic Cerium. *Trans. Am. Electrochem. Soc.*, vol. 47, 1925, pp. 353-364.
23. KREMERS, H. C., AND STEVENS, R. Observations on the Preparation and Properties of Metallic Lanthanum. *Jour. Am. Chem. Soc.*, vol. 45, 1923, pp. 614-617.
24. KURODA, T. (The Preparation of Lanthanum by Fused Salt Electrolysis and Its Application.) *Denki Shikenjo Kenkyu Hokoku*, No. 561, 1957, p. 103.
25. LINDSAY CHEMICAL DIVISION. American Potash and Chemical Corp. Rare-Earth and Yttrium Metals. Report, December 1958, pp. 1-20.
26. LIVINGSTON, J., AND KENT, H. The Cerium Metal and Lighter Flint Industry in Germany and Austria. Office of Military Government for Germany (US), Field Information Agency, Technical, Final Report No. 909, Sept. 30, 1946, pp. 5-18.

27. MARICLE, D. L., AND HUME, D. N. A New Method for Preparing Hydroxide-Free Alkali Chloride Melts. *Jour. Electrochem. Soc.*, vol. 107, No. 4, April 1960, pp. 354-356.
28. MAZZA, L. (On the Electrometallurgy of Lanthanum, Cerium, and Praseodymium.) *Atti cong. intern. chim.*, vol. 3, 1938, pp. 604-609.
29. McCOY, H. N. Europium and Ytterbium Amalgams. *Jour. Am. Chem. Soc.*, vol. 63, 1941, pp. 1622-1624.
30. MEINTS, R. E., HOPKINS, B. S., AND AUDRIETH, L. F. (Electrolytic Preparation of Rare-Earth Amalgams. II. Decomposition of Lanthanum Amalgam for the Preparation of the Free Metal.) *Ztschr. anorg. allgem. Chem.*, vol. 231, 1937, pp. 54-62.
31. MERLUB-SOBEL, M. Preparation of Fused Salt Electrolytes. U.S. Patent 2,870,072, Jan. 20, 1959.
32. MOELLER, T., AND ZIMMERMAN, P. A. Electrolyses of Rare-Earth Metal Salts in Basic Solvents. *Science*, vol. 120, 1954, pp. 539-540.
33. MORRICE, E., DARRAH, J., BROWN, E., WYCHE, C., HEADRICK, W., WILLIAMS, R., AND KNICKERBOCKER, R. G. Metallurgical Laboratory Data on Reduction and Refining of Ceric Oxide and Cerous Fluoride to Cerium Ingot. Bureau of Mines Rept. of Investigations 5549, 1960, 36 pp.
34. MUTHMANN, W., HOFER, W., AND WEISS, L. (On the Preparation of the Metals of the Cerium Group by Molten Electrolysis.) *Ann. Chem. Liebigs*, vol. 320, 1902, pp. 231-269.
35. MUTHMANN, W., AND SCHEIDEMANDEL, J. (III. On the Extraction of the Rare-Earth Metals by Electrolysis of the Fluorides.) *Ann. Chem. Liebigs*, vol. 355, 1907, pp. 116-136.
36. MUTHMANN, W., AND WEISS, L. (I. Investigations on Metals of the Cerium Group.) *Ann. Chem. Liebigs*, vol. 331, 1904, pp. 1-46.
37. ROSSINI, R. D., WAGMAN, D. D., EVANS, W. H., LEVINE, S., AND JAFFE, I. Selected Values of Chemical Thermodynamic Properties. *Nat. Bureau of Standards Circ.* 500, 1952, 1268 pp.
38. SCHUMACHER, E., AND HARRIS, J. Investigations of the Thermionic Properties of the Rare-Earth Elements. *Jour. Am. Chem. Soc.*, vol. 48, 1926, pp. 3108-3114.
39. SCHUMACHER, E., AND LUCAS, F. Photomicrographic Evidence of the Crystal Structure of Pure Cerium. *Jour. Am. Chem. Soc.*, vol. 46, 1924, pp. 1167-1169.

40. SINGER, R., AIREY, H., GRIMMETT, L., LEECH, H., AND BENNETT, R. The Cerium Industry in German Territory Including Reports on Radium and Mesothorium. British Intelligence Sub-Committee, Final Report No. 400, Item No. 21, September 1945, pp. 1-118.
41. SKLYARENKO, S. I., AND SAKHAROV, B. A. (The Electrochemical Preparation of Cerium Amalgam.) Jour. Appl. Chem. (U.S.S.R.), vol. 13, 1940, pp. 841-845.
42. SPEDDING, F. H., AND DAANE, A. H. Production of Rare-Earth Metals in Quantity Allows Testing of Physical Properties. Jour. Metals, vol. 6, May 1954, pp. 504-510.
43. _____. The Preparation and Properties of Rare-Earth Metals. Progress in Nuclear Energy, Series 5, Metallurgy and Fuels. McGraw-Hill Book Co., Inc., New York, N.Y., 1956, pp. 413-432.
44. SPEDDING, F. H., AND MILLER, C. Thermochemistry of the Rare Earths. I. Cerium and Neodymium. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 4195-4198.
45. THOMPSON, A. P., HOLTEN, W. B., AND KREMERS, H. C. The Preparation and Some Properties of Metallic Yttrium. Trans. Am. Electrochem. Soc., vol. 49, 1926, pp. 277-289.
46. THOMPSON, A. P., AND KREMERS, H. C. The Preparation and Properties of Cerium-Free Misch Metal. Trans. Am. Electrochem. Soc., vol. 47, 1925, pp. 345-352.
47. TROMBE, F. (Preparation of Metallic Lanthanum Free From Iron and Silicon.) Compt. rend., vol. 194, May 1932, pp. 1653-1655.
48. _____. (Preparation of Metallic Neodymium Free From Iron and Silicon.) Compt. rend., vol. 196, March 1933, pp. 704-706.
49. _____. (The Isolation of Gadolinium.) Compt. rend., vol. 200, February 1935, pp. 459-461.
50. _____. (On the Isolation of Metallic Europium.) Compt. rend., vol. 206, May 1938, pp. 1380-1383.
51. _____. (On the Isolation of Metallic Dysprosium.) Compt. rend., vol. 220, April 1945, pp. 603-604.
52. TROMBE, F., AND MAHN, F. (Electrolytic Preparation and Thermal Dissociation of Magnesium-Cadmium-Praseodymium, Magnesium-Cadmium-Samarium, and Magnesium-Cadmium-Yttrium Alloys.) Compt. rend., vol. 220, May 1945, pp. 778-779.
53. WEIBKE, F. (Preparation of Lanthanum by Electrolysis of Its Fused Chloride.) Ztschr. Elektrochem., vol. 45, 1939, pp. 518-520.

ELECTROWINNING MOLTEN LANTHANUM FROM LANTHANUM OXIDE

By E. Morrice, C. Wyche, and T. A. Henrie

* * * * * report of investigations 6075



UNITED STATES DEPARTMENT OF THE INTERIOR
Stewart L. Udall, Secretary

BUREAU OF MINES
Marling J. Ankeny, Director

This publication has been cataloged as follows:

Morrice, E

Electrowinning molten lanthanum from lanthanum oxide, by
E. Morrice, C. Wyche, and T. A. Henrie. [Washington] U. S.
Dept. of the Interior, Bureau of Mines [1962]

9 p. illus., tables. 27 cm. (U. S. Bureau of Mines. Report of
investigations, 6075)

Bibliography: p. 9

1. Lanthanum—Electrometallurgy. 2. Lanthanum oxide. I. Title.
(Series)

TN23.U7 no. 6075 622.06173

U. S. Dept. of the Int. Library

CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	1
Laboratory cell development.....	2
Equipment.....	2
Cell construction materials.....	2
Electrolyte.....	2
Cell operation.....	4
Lanthanum metal analyses.....	5
Discussion of results.....	6
Conclusions.....	8
References.....	9

ILLUSTRATIONS

Fig.

1. Lanthanum electrowinning cell box.....	3
2. Imposed alternating current cell for electrowinning lanthanum.....	6

TABLES

1. Composition of the frozen electrolyte from lanthanum electrowinning run LE-19.....	4
2. Operational data of a typical run with imposed alternating current.....	7
3. Analyses of lanthanum metal nodules.....	7

ELECTROWINNING MOLTEN LANTHANUM FROM LANTHANUM OXIDE

by

E. Morrice,¹ C. Wyche,² and T. A. Henrie³

ABSTRACT

High-purity lanthanum metal was prepared by electrolysis of La_2O_3 in a $\text{LaF}_3\text{-LiF-BaF}_2$ bath at 950°C . The requisite bath temperature for the deposition of molten metal was maintained by supplying the heat as current directly to the electrodes. A current efficiency of about 60 percent was obtained. The lanthanum nodules contained carbon and oxygen as major impurities. The total impurity content was from about 0.1 to 0.2 percent.

INTRODUCTION

Lanthanum and cerium are the most abundant of the rare-earth elements. The earth's crust is estimated to contain 19 grams of lanthanum (1)⁴ and 44 grams of cerium per ton. Bastnasite and monazite are the principal minerals of these two elements. Lanthanum is associated with the rare-earth or lanthanide group of elements in nature and is considered to be a member of this group. Lanthanum metal has a density of 6.2 grams per cubic centimeter and a melting point of 920°C . It is one of the more reactive of the rare-earth metals with respect to moisture and oxygen.

Lanthanum metal has been prepared on a laboratory scale by metallothermic reduction of the fluoride with calcium (5). Tantalum was found to be the best material to contain the reaction. This technique is a batch process, and vacuum melting of the metal product is required to remove contained calcium. Tantalum was the chief metallic impurity, and is generally present to the extent of 0.03 to 0.04 weight-percent. Oxygen, nitrogen, and carbon were readily picked up by the lanthanum from the reactants and from the atmosphere during the reaction. Unless extreme precautions were taken, the lanthanum metal prepared by metallothermic reduction contained as much as 0.3 weight-percent oxygen.

¹ Supervisory extractive metallurgist, Reno Metallurgy Research Center, Bureau of Mines, Reno, Nev.

² Chemist, Reno Metallurgy Research Center, Bureau of Mines, Reno, Nev.

³ Supervising research metallurgist, Reno Metallurgy Research Center, Bureau of Mines, Reno, Nev.

⁴ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

The published data on the electrolytic preparation of lanthanum from molten halides were recently summarized (3). The possibility of preparing lanthanum, free from the impurities found in metal produced by the calcium reduction technique, and the ready availability of high-purity La_2O_3 led to an investigation on electrowinning lanthanum from its oxide. Experience in the electrowinning of cerium from cerium oxide in a fluoride electrolyte guided the selection of cell design and operating procedures (2). The low vapor pressure, melting points, conductivities, and thermodynamic stability of LaF_3 , LiF , and BaF_2 , as well as the solubility of La_2O_3 , were the determining factors in the selection of these materials for the electrolyte components.

LABORATORY CELL DEVELOPMENT

Equipment

The electrowinning experiments were conducted in an inert-atmosphere steel chamber with gloveports and mechanical facilities for manipulations, such as raising and lowering of electrodes. Figure 1 shows the principal features of the chamber or cell box.

The direct-current power source for electrolytic reduction was a silicon rectifier unit capable of supplying 0 to 40X volts and 0 to 300 amperes. The alternating current power source for meltdown and auxiliary heating of the bath was a 300-ampere, single-phase, 40-volt, alternating current arc-welding unit.

Lanthanum oxide was fed into the molten electrolyte from a hopper by a vibrating, stainless-steel helical screw enclosed in a stainless-steel pipe. The screw was operated by a variable speed drive.

Cell Construction Materials

Carbon rod (AUC-grade) anodes and high-purity molybdenum rod cathodes were used in all electrowinning experiments.

The crucibles, holding the molten electrolyte, were AGX-grade graphite and had an inside diameter of 6 to 6½ inches, insulated with slabs of foamed silica. The crucible cover was a 3-inch-thick slab of foamed silica drilled to accommodate the electrodes. A graphite thermocouple protection tube and an alumina tube for feeding lanthanum oxide into the molten bath were also inserted through the cover.

Electrolyte

The electrolyte constituents were reagent-grade lithium fluoride and barium fluoride powders and pulverized 99.9-percent lanthanum fluoride crystals. The La_2O_3 cell feed contained less than 0.1 percent total impurities. Spectrographic analysis showed less than 0.01 percent rare earths other than lanthanum. Microscopic examination of the lanthanum oxide indicated the following particle size distribution: 1 to 2 microns, 60 percent; 2 to 3 microns, 20 percent; 3 to 4 microns, 10 percent; and 4 to 8 microns, 10 percent.

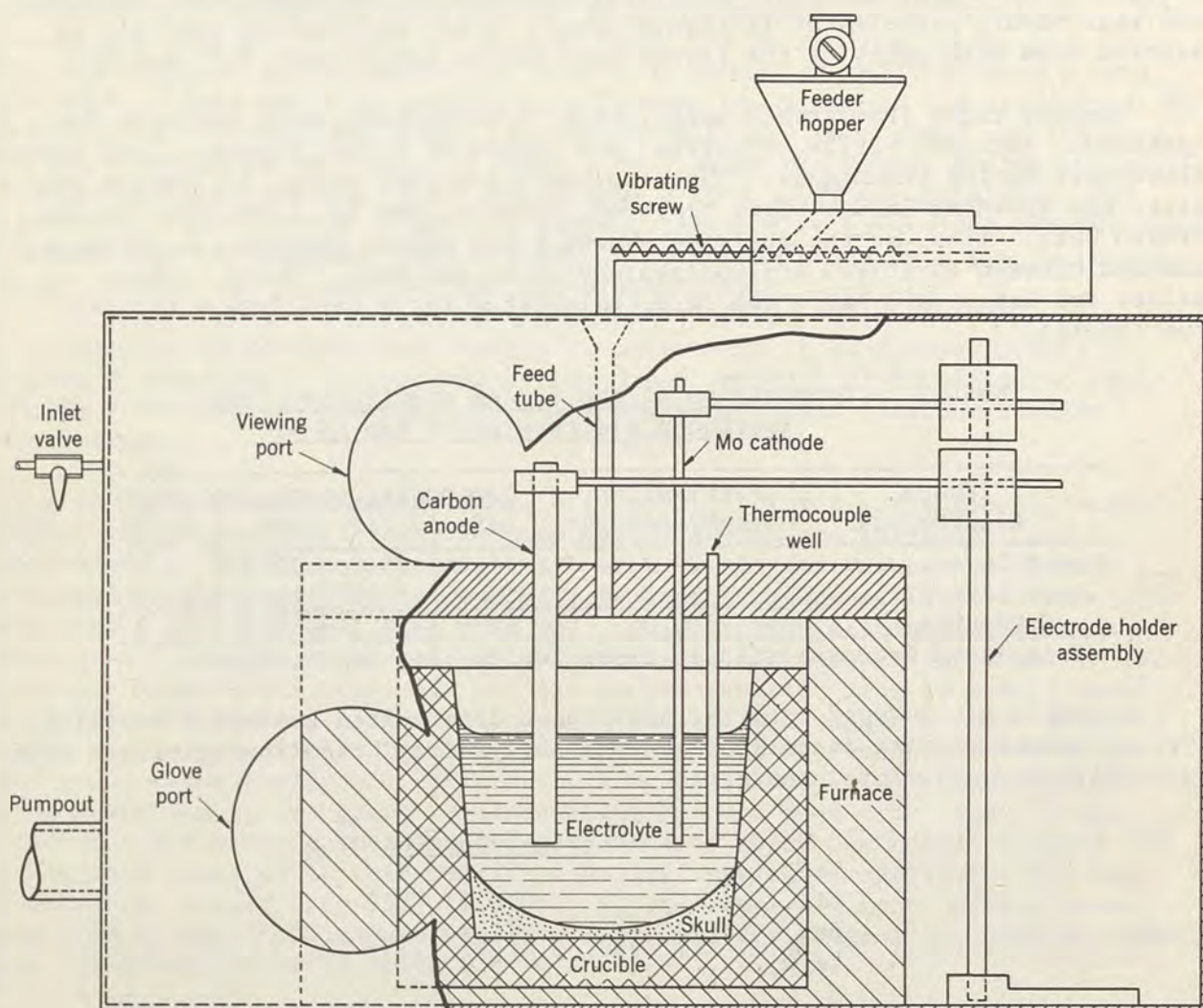


FIGURE 1. - Lanthanum Electrowinning Cell Box.

The electrolyte constituents and La_2O_3 were thoroughly dried by heating at 600°C and by purging with helium gas prior to charging the cell.

The 60-weight-percent LaF_3 , 27-percent LiF , and 13-percent BaF_2 solvent-phase electrolyte had a melting point of 750°C , a specific gravity of 3.2 from 950° to $1,050^\circ\text{C}$, and dissolved 2.3 percent La_2O_3 in the operating temperature range (4).

Examination of frozen electrolyte, after completion of electrowinning runs, indicated the presence of two distinct layers. A sharp dividing line between the two layers was located about one-fourth inch below the ends of the electrodes. The lanthanum metal nodules were contained in the lower layer; the bottom part of this layer served as a skull, thus preventing molten lanthanum from contacting the graphite bath container or crucible. The upper layer of the frozen bath was a white, vesicular material. The lower layer was

a light to dark-gray material containing numerous yellow translucent crystals and some minute globules of lanthanum metal. X-ray diffraction analysis of samples from both parts of the frozen bath showed LaF_3 , LaOF , LiF , and BaF_2 .

Samples taken from frozen baths, after electrolysis, were analyzed for lanthanum, lithium, barium, fluorine, and oxygen by X-ray, chemical, and inert-atmosphere fusion techniques. The reported analytical values for oxygen contents are given as La_2O_3 . This compound, however, was not identified in the frozen bath. Also, as the analyses showed total oxygen content, no differentiation between dissolved and undissolved La_2O_3 was made. Table 1 shows values for LaF_3 , LiF , BaF_2 , and La_2O_3 calculated for a bath from a typical run (LE-19).

TABLE 1. - Composition of the frozen electrolyte from lanthanum electrowinning run LE-19

Frozen electrolyte	Distribution, weight-percent	Compounds, weight-percent ¹			
		LaF_3	LiF	BaF_2	La_2O_3
Upper layer.....	33.2	56.4	25.0	12.3	6.4
Lower layer.....	66.8	53.7	16.0	8.2	21.0
Composite.....	100.0	55.0	19.1	9.6	16.3

¹ Calculated from analytical values for La, Li, Ba, O, and F.

A sample was scooped from the upper part of a molten electrolyte during typical electrowinning conditions and was analyzed. The following values were calculated from elemental analyses:

	<u>Weight-percent</u>
LaF_3	52.1
LiF	28.9
BaF_2	14.3
La_2O_3	5.0

Because only 2.3 percent La_2O_3 is soluble in the electrolyte, the analytical data indicate that some of the La_2O_3 is in suspension even in the upper layer and also that the excess tends to settle to the bottom and becomes part of the skull.

Cell Operation

An inert atmosphere was obtained in the cell box by pumping and filling with helium gas prior to loading the bath into the graphite cell and meltdown. The quality of the atmosphere was assured by using a gas master to compare the thermal conductivity of the cell atmosphere to that of high-purity tank helium.

Melting of the electrolyte was accomplished by passing alternating current through a graphite resistor submerged between the anodes in the powdered electrolyte. When sufficient electrolyte was melted to carry the current, the graphite resistor was removed and alternating-current melting continued until the temperature of the molten electrolyte was 950° to 960° C. When meltdown was completed, sufficient La_2O_3 powder was added and stirred into the

electrolyte to bring the bath content to approximately 15 percent La_2O_3 . Even though this amount of La_2O_3 is several times the solubility of the oxide in the electrolyte, it was necessary to have an excess of oxide to form a skull and also to have material available to prevent depletion of the oxide from the bath during the anode reaction. Lanthanum oxide was then added continuously to the electrolyte at a rate of about 3 to 5 grams per minute during the electrolysis. After the run which lasted from 3 to 5 hours was completed, the electrolyte was allowed to cool to ambient temperature before the crucible was removed from the chamber. The contents were broken to recover the lanthanum metal nodules and to examine the frozen electrolyte.

Samples of the cell-box atmosphere were taken at 20-minute intervals during electrolysis for analysis by the Orsat method. Electrolyte and cell-bottom temperatures were taken by using platinum versus platinum-rhodium thermocouples.

In the initial investigations, triangular electrode arrangements consisting of three vertical 1-inch-diameter carbon anodes and three vertical 0.2-inch-diameter molybdenum cathodes were used. This was the same electrode arrangement that was used successfully for electrowinning liquid cerium (2). The direct current power that this cell would carry was insufficient to maintain an electrolyte temperature high enough for the deposition of molten lanthanum. Experiments were made using a carbon-resistor ring to supply auxiliary internal heating. The best results with this arrangement were obtained using one 1-inch-diameter carbon rod anode and one 0.4-inch-diameter molybdenum rod cathode inside a 0.25-inch-thick by 0.875-inch-wide carbon-resistor ring suspended by two graphite alternating-current conductor rods. Three hundred and seventy grams of lanthanum metal, of which one nodule weighed 170 grams, were prepared in this cell in 4 hours. During electrolysis, the bath temperature ranged from 960° to $1,060^\circ$ C, the average direct current power was 0.40 kilowatt (80 amperes and 5 volts), and the alternating current power was 3.5 kilowatts at 11 volts.

Marked improvement in the operation of the electrowinning cells was obtained by using alternating current across the anodes, which served as the auxiliary source of heat to maintain the requisite temperature. A typical cell, shown in figure 2, was used successfully to prepare high-purity liquid lanthanum metal.

The data in table 2 were obtained from a typical lanthanum electrowinning run in which alternating current was imposed across the anodes. As compared with the previous runs, these data show a marked increase in the amount of direct current that could be passed through the cell without creating anode effect.

LANTHANUM METAL ANALYSES

A high degree of coalescence of the metal product was attained in the imposed alternating current cell, and in most runs individual nodules, weighing 200 to 400 grams, represented over 90 percent of the lanthanum prepared.

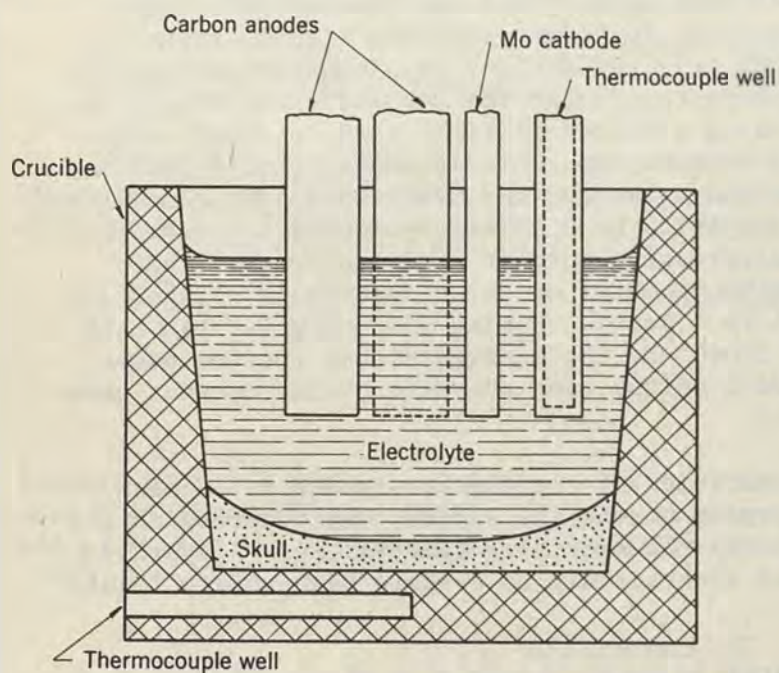
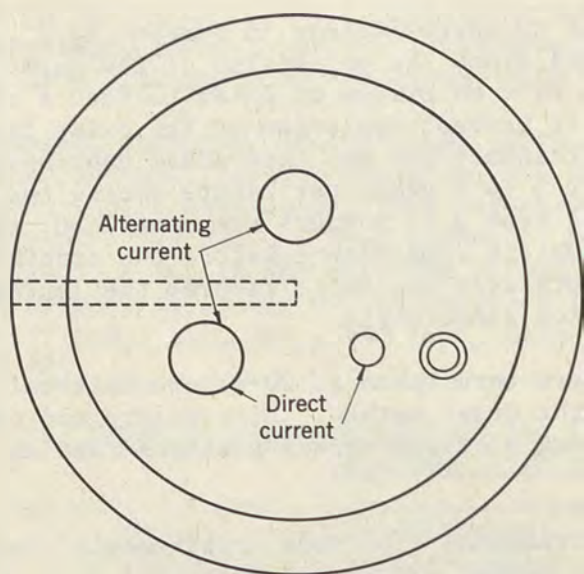


FIGURE 2. - Imposed Alternating Current Cell for Electrowinning Lanthanum.

Table 3 shows the values obtained by analysis of various lanthanum metal nodules. Spectrochemical, polarographic, inert-atmosphere fusion, and wet chemical analytical techniques were used.

Carbon and oxygen were the major impurities of the deposited metal. Nodules surrounded by bath contained as little as 0.003 percent carbon, whereas those nodules that contacted the graphite crucible had from 1 to 3 percent carbon.

Molybdenum, silicon, and lithium impurities were each usually less than 0.01 percent. The molybdenum cathode was the source of molybdenum contamination; the silicon impurity was from the foamed silica crucible cover. Microscopic examination showed that most lanthanum nodules contained small amounts of interspersed bath, a possible source of the lithium impurity.

DISCUSSION OF RESULTS

A lanthanum electrowinning cell was operated in which alternating current was imposed to the two anodes, and direct current was imposed to one anode and the cathode. With this

arrangement 150 to 160 direct-current amperes were sustained. When a carbon resistor arrangement was used to supply auxiliary heat, direct currents of 75 to 80 amperes were the highest that could be obtained without anode effect.

In electrowinning experiments with imposed alternating current, small arcs were noted between the electrolyte and the anodes. Corresponding with this arcing were momentary conditions of high voltage and low amperage on

direct current and alternating current. These conditions increased in intensity and duration with the depletion of the La_2O_3 content of the electrolyte. At higher La_2O_3 concentrations the rate of production of lanthanum metal was increased. Cathode current efficiencies, however, did not appear to be affected by the amount of La_2O_3 present.

TABLE 2. - Operational data of a typical run with imposed alternating current

Operational parameter	Numerical value
La_2O_3 added to fluoride bath prior to electrolysis.....g	1,320
La_2O_3 added during electrolysis.....g	886
Average direct-current amperes.....amp	159
Average direct-current volts.....v	12
Average alternating current amperes.....amp	149
Average alternating current volts.....v	17
Initial anode current density (direct current) ¹amp/cm ²	6.2
Cathode current density (direct current).....do.	1.5
Initial anode current density (alternating current).....do.	1.4
Average electrolyte temperature.....°C	946
Average cell bottom temperature.....°C	711
Duration of electrolysis.....hr	3
Lanthanum metal recovered ²g	451
Current efficiency.....pct	57
Metal recovery ³pct	60
Direct current power consumed.....kw-hr/lb of lanthanum	5.8
Alternating current power consumed.....do.	7.6
CO in cell box at end of run.....mole-pct	1.4
CO ₂ in cell box at end of run.....do.	7.6

¹ Calculated using the average amperage for the run and the starting electrode surface area.

² One nodule weighed 410 grams.

³ Metal recovery based on La_2O_3 added during electrolysis.

TABLE 3. - Analyses of lanthanum metal nodules

Run	Total rare earths other than La	Elements, weight-percent						
		Al	Ba	Ca	Cu	Fe	Li	Mg
LE-9....	0.04	0.007	<0.01	<0.0009	0.002	0.0017	0.010	0.015
LE-10...	.04	.001	< .01	.0009	.0004	.004	.016	.015
LE-13...	.004	.0007	< .01	.007	.001	.004	.030	.001
LE-15...	.04	.0007	< .01	.001	.0003	.0038	.014	.002
LE-17...	.01	.001	.005	.002	.005	.002	.001	.001

Run	Total rare earths other than La	Elements, weight-percent						Total impurities
		Mn	Mo	Si	C	O	N	
LE-9....	0.04	<0.0008	0.006	0.03	0.01	0.04	<0.002	0.18
LE-10...	.04	< .0008	.019	.01	.03	.04	< .002	.19
LE-13...	.004	.002	.008	.003	.016	.02	< .002	.11
LE-15...	.04	.001	.0010	.01	.06	.008	< .002	.15
LE-17...	.01	.001	.005	.01	.003	.015	< .002	.06

In individual electrowinning runs, approximately equal and even corrosion was noted on the parts of both carbon anodes that had been immersed in the molten electrolyte. No anode corrosion above the molten electrolyte level was evident. The graphite thermocouple protection tube was not corroded.

The role played by the alternating current in overcoming anode effect as well as the optimum direct current to alternating current ratio for this purpose have not been determined. A study of this effect is projected in a larger cell with sufficient direct current wattage to maintain the requisite bath temperature.

CONCLUSIONS

Molten lanthanum metal, 99.8 percent, was electrowon from lanthanum oxide dissolved in a fluoride electrolyte in an internally heated cell. Requisite auxiliary heat was supplied to this cell and anode effect was minimized by imposing alternating current on the anodes.

REFERENCES

1. Himes, Richard C. Where Are the Rare-Earths Today? Battelle Tech. Rev., v. 7, June 1958, pp. 3-8.
2. Morrice, E., J. Darrah, E. Brown, C. Wyche, W. Headrick, R. Williams, and R. G. Knickerbocker. Metallurgical Laboratory Data on Reduction and Refining of Ceric Oxide and Cerous Fluoride to Cerium Ingot. BuMines Rept. of Inv. 5549, 1960, 36 pp.
3. Morrice, E., B. Porter, E. A. Brown, C. Wyche, and R. G. Knickerbocker. Electrowinning Cerium-Group and Yttrium-Group Metals. BuMines Rept. of Inv. 5868, 1961, 39 pp.
4. Porter, B., and E. A. Brown. Determination of Oxide Solubility in Molten Fluorides. BuMines Rept. of Inv. 5878, 1961, 8 pp.
5. Spedding, F. H., and A. H. Daane. Metallothermic Preparation of Rare-Earth Metals. Ch. in The Rare Earths. John Wiley and Sons, Inc., New York, N.Y., 1961, pp. 102-112.