502

K-1761

MASTER

ELECTRODEPOSITION OF THORIUM,
NEPTUNIUM, AND TECHNETIUM

AUTHORS:

G. S. Petit
J. D. Griffin
C. A. Kienberger

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE GASEOUS DIFFUSION PLANT

operated for the ATOMIC ENERGY COMMISSION under U. S. GOVERNMENT Contract W-7405 eng 26

UNION
CARBIDE

OAK RIDGE GASEOUS DIFFUSION PLANT
P. O. Box P
Oak Ridge, Tennessee 37830

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America. Available from Clearinghouse for Federal
Scientific and Technical Information, National Bureau of Standards,
U.S. Department of Commerce, Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

— LEGAL NOTICE —

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Date of Issue: October 17, 1968

Report Number: K-1761

Subject Category: CHEMISTRY

ELECTRODEPOSITION OF THORIUM,
NEPTUNIUM, AND TECHNETIUM

G. S. Petit
J. D. Griffin
C. A. Kienberger

Laboratory Division

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
Oak Ridge Gaseous Diffusion Plant
Oak Ridge, Tennessee

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

Report Number: K-1761

Subject Category: CHEMISTRY

Title: ELECTRODEPOSITION OF THORIUM,
NEPTUNIUM, AND TECHNETIUM

Authors: G. S. Petit, J. D. Griffin,
and C. A. Kienberger

A B S T R A C T

Electrodeposition methods have been developed for applying very thin films of thorium oxide, neptunium oxide, and technetium metal on metal surfaces. Recovery of these materials from solution ranges from 96 to 100%. The adherent uniform films range in thickness from 0.0037 to 0.8 mg/cm². The materials are deposited from an ammonium oxalate or ammonium acetate solution with current densities ranging from 200 to 400 ma/cm². Thorium oxide and technetium metal have been deposited on several hundred disks; neptunium oxide has been deposited on several thousand.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ELECTRODEPOSITION OF THORIUM,
NEPTUNIUM, AND TECHNETIUM

CONTENTS

INTRODUCTION	7
SUMMARY	8
EXPERIMENTS AND RESULTS	8
Thorium Oxide	8
Results	9
Neptunium Oxide	9
Thin Films	9
Thicker Films	9
Technetium	13
Application	13
ELECTROPLATING DETAILS	14
Electroplating Equipment	14
For Disks	14
For Cylinders or Tubes	14
General Plating Procedure	14
Electrodeposition of Thorium Oxide	18
Determining Thorium on Plated Disk	18
Electroplating of Neptunium Oxide	19
Electroplating of Technetium	19
BIBLIOGRAPHY	19

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ELECTRODEPOSITION OF THORIUM,
NEPTUNIUM, AND TECHNETIUM

Methods have been needed for the electrodeposition of thin films of thorium, neptunium, and technetium on metal surfaces, for preparing alpha and beta sources, for measuring neutron capture cross sections, and for radiochemical analyses. The methods must give nearly quantitative recovery; the deposits must be adherent, uniform and smooth.

Graves and Froman (5) developed a method for the electrodeposition of thorium by precipitating thorium ferrocyanide on a metal foil from thorium ferricyanide solution. The thorium ferrocyanide on the foil was ignited to thorium oxide; the iron was removed by leaching with hydrochloric acid, which also removed some of the thorium oxide. Since the completion of the present authors' work, Cerrai, Dugnani, and Gazzarrini (3) reported a method for the electrolytic deposition of thorium on metal disks. The reported degree of recovery from solution ranged from 77 to 96%. Also recently, Kim, et al., (6), electrodeposited thorium, uranium, and protactinium from an ethanol solvent system.

Seaborg and Gofman (10) electrodeposited neptunium from an aqueous solution containing a neptunium salt and an alkali acetate buffer; the electroplating efficiency of the neptunium ranged from 8.8 to 85%. Subsequent to the present authors' work, Rajagopalan and Ramaniah (8) reported a method for electroplating neptunium; however, recovery was only 90%.

Motta, Larson, and Boyd (7) and Eakins and Humphries (4) were able to plate metallic technetium from sulfuric acid solutions, but with yields of less than 75%. Box (1) reported the electrodeposition of films of technetium metal with thicknesses up to 18 mg/cm². His method employed oxalate ion, recommended by Petit (2), in combination with sulfuric acid; recoveries above 99% were achieved.

The techniques for electrodepositing thorium, neptunium and technetium, developed by the present authors employ an approach adapted from the method for electroplating uranium, reported by Cohen and Hull (9). Preparation requirements and actual plating conditions were determined empirically for each element. This report describes, in separate sections, methods for electrodepositing very thin films of these three elements on metal surfaces. Special electroplating equipment is described, the general plating procedure is presented, and the specific method for electrodepositing each of the materials is detailed. Special techniques are given for preparing thorium and neptunium solutions used for the deposition of thicker films. The thickness of films that can be plated of each material and the degree of recovery of the metal from solution are discussed.

SUMMARY

Methods have been developed for electrodepositing very thin films of thorium oxide, neptunium oxide, and technetium metal on metal surfaces. Plated films of these materials are smooth, uniform, and adherent. Recovery of thorium oxide from a solution is approximately 98%. For neptunium oxide, it varies from 99.2%, when thin films are plated, down to 96.4% for thicker films. The plating efficiency for technetium is 100%. The thorium oxide and the technetium metal are plated on nickel disks from an ammonium oxalate solution. Thin films of neptunium oxide are applied from an ammonium oxalate or acetate solution; thicker films of neptunium oxide are plated only from an ammonium acetate solution. The deposits range in thickness from 0.001 mg/cm² for technetium to approximately 0.8 mg/cm² for both thorium and neptunium oxides. Thorium oxide and technetium metal have been deposited on several hundred disks; neptunium oxide has been deposited on several thousand.

EXPERIMENTS AND RESULTS

This section discusses the innovative aspects of the work and presents the results obtained. While plating hundreds of disks, many were prepared in identical fashion, from identical solutions. One criterion of the technique was the efficiency, that is the degree of recovery from solution (defined generally, in this report, for an electroplating time of 90 minutes). Detailed plating procedures are given later in the Electroplating Details section.

Thorium Oxide

Thorium normally exists in the tetravalent state in aqueous solution and cannot readily be reduced electrically to a lower valence state or to the metal. The mechanism for the electrodeposition of thorium oxide from an aqueous solution departs from that of conventional electrodeposition; it is a controlled pH precipitation of the hydrated oxide at the cathode, rather than reduction to the metal or, as in the case of uranium or neptunium, reduction to a lower valence state.

Deposition of thorium was attempted from ethyl alcohol, alcohol and water, and acetone solutions. Good adherence was obtained only from the acetone solution, but the deposition was neither quantitative nor reproducible.

Ammonium oxalate proved to be a satisfactory electrolyte. Ammonium oxalate forms a complex with thorium and decomposes to form hydroxyl ions, thereby producing the conditions for controlled deposition of the hydrated oxide at the cathode. Hydrogen peroxide is added to prevent the precipitation of thorium oxalate, to lower the acidity around the cathode, and to decrease formation of hydrogen gas at the cathode.

The best plating efficiency is achieved at pH 8; some plating is obtained at pH as low as 6. If the pH decreases to 4.5, or less, thorium oxalate is precipitated; if the pH exceeds 9, thorium hydroxide is precipitated.

Results. Thorium oxide films, in thicknesses up to 0.8 mg Th/cm², were deposited on several hundred metal disks. The amounts of thorium electro-deposited on a group of nickel disks selected at random are shown in table I. The films were adherent, uniform, and smooth. The plating efficiency for thin (approx. 0.04 mg/cm²) films, table I, was 98.3 ± 1.3% for a 60-minute electrodeposition; for the thicker films (0.8 mg/cm²), it was 97.5 ± 1.9% for a 90-minute electrodeposition.

Neptunium Oxide

Deposition of neptunium from an ammonium nitrate solution was fairly quantitative (> 90%) but the deposit was very powdery and nonadherent. A better approach was needed.

Using ammonium oxalate as the electrolyte, neptunium, like uranium, is deposited on the cathode of a dc electrical system by reduction to a lower valence state (from Np⁺⁶ to Np⁺⁴). This is achieved by limiting the concentration of neptunium in the plating solution (content ≤ 0.04 mg Np/cm² of deposition area) and using the proper current density and pH.

Ammonium oxalate is a satisfactory electrolyte, table II, for plating neptunium from solutions with contents of 0.04 mg, or less, of neptunium per cm² of deposition area. With higher concentrations of neptunium, the ammonium oxalate causes a black precipitate of neptunium to form on the anode when the solution becomes slightly basic during electrolysis. Ammonium acetate was found to be a satisfactory electrolyte for electroplating neptunium from solutions containing a maximum concentration of 0.1 mg Np/cm² of deposition area.

Thin Films. Neptunium oxide has been deposited on several thousand metal disks or foils for radiochemical determination of neptunium. The film thickness and percentage of neptunium electroplated from solutions containing only enough for a deposit thickness of 0.04 mg Np/cm² are shown in table II. The plating efficiency from such solutions is about 99%.

Thicker Films. Thicker films of neptunium oxide were electroplated using acetate as the electrolyte. Adherent and smooth films of neptunium oxide were obtained by limiting the amount of neptunium in the acetate plating solution at any one time. The concentration was limited to a maximum of 0.1 mg Np/cm² of deposition area (0.5 mg Np/disk of 1-inch diameter). Typical results of plating neptunium oxide on disks of 1-inch diameter are given in table III. The electroplating efficiency is 96.4 ± 1.4%.

TABLE I
AMOUNT OF THORIUM OXIDE DEPOSITED ON NICKEL DISKS

<u>Disk Number</u>	<u>Deposited Thickness, mg/cm²</u>	<u>Plating Efficiency, %</u>
1	0.0389	96.9
2	0.0393	97.9
3	0.0394	98.1
4	0.0400	99.6
5	0.0399	99.4
6	0.0386	96.1
7	0.0398	99.1
8	0.0399	99.4
	Mean	
	0.0394*	98.3 ± 1.3***
9	0.797	99.6
10	0.785	98.1
11	0.786	98.3
12	0.769	96.1
13	0.774	96.8
14	0.794	99.3
15	0.754	94.3
	Mean	
	0.780**	97.5 ± 1.9***

* 100% = 0.04015 mg/cm²

** 100% = 0.800 mg/cm²

*** All precisions are standard deviations (absolute) for single determinations.

TABLE II

THIN FILMS OF NEPTUNIUM OXIDE ELECTROPLATED ON NICKEL DISKS

<u>Disk Number</u>	<u>Electrolyte</u>	<u>Deposited Thickness, mg/cm²</u>	<u>Plating Efficiency, %*</u>
1	Ammonium Oxalate	0.0387	97.4
2	" "	0.0393	98.9
3	" "	0.0397	99.9
	Mean	<u>0.0392</u>	<u>98.7±1.3**</u>
4	Ammonium Acetate	0.0397	99.9
5	" "	0.0397	99.9
6	" "	0.0393	98.9
	Mean	<u>0.0396</u>	<u>99.6±0.6**</u>

* 100% = 0.03974 mg/cm².

** Precisions are standard deviations (absolute) for single determinations.

TABLE III
THICKER FILMS OF NEPTUNIUM OXIDE PLATED
ON 1-INCH METAL DISKS

<u>Disk Number</u>	<u>Deposited Thickness, mg/cm²</u>	<u>Plating Efficiency, %*</u>
1	0.776	94.5
2	0.796	97.0
3	0.780	95.0
4	0.803	97.8
5	0.801	97.6
6	0.793	96.6
Mean	0.792	96.4±1.4**

* 100% = 0.821 mg/cm²

** The precision is standard deviation (absolute) for a single measurement.

Technetium

Technetium in an ammonium oxalate electrolyte is quantitatively (100.0%) deposited on nickel disks in 90 minutes. Electroplating efficiency was determined by electrolyzing solutions containing 3.7 and 18.5 μg of Tc for periods of 15, 30, 60, and 90 minutes. Results, obtained by beta counting, are given in table IV. The concentration of technetium at this low level had little effect on the time required for quantitative electroplating.

TABLE IV
TECHNETIUM DEPOSITED ON NICKEL DISKS 1 INCH IN DIAMETER

<u>Plating Time,</u> <u>Minutes</u>	<u>Deposited Amount,</u> <u>micrograms</u>	<u>Plating</u> <u>Efficiency, %</u>
15	3.57	96.5
30	3.56	96.1
30	3.57	96.5
60	3.64	98.3
60	3.66	98.9
90	3.70	100.0
30	18.22	98.5
60	18.44	99.7
90	18.50	100.0

Application. Several hundred disks have been plated for determining trace amounts of technetium by beta counting. The plated deposit or film is very adherent, uniform, and metallic (silvery) in appearance.

For this work approximately 500 ml of a technetium solution was obtained from the Oak Ridge National Laboratory. The concentration of 1.85 μg Tc/ml was determined by beta counting an aliquot of the solution. A portion of this technetium solution was used for control purposes in a radiochemical analysis program.

Electroplated films thicker than 0.0037 mg Tc/cm² were not attempted, because the amount of available technetium was limited at the time of

this work. The ease of reduction and the rapid quantitative deposition of technetium indicated that thicker films are feasible. This has been demonstrated by Box (1).

ELECTROPLATING DETAILS

Electroplating Equipment

For Disks. The basic equipment, figure 1, used for electrodeposition on one side of a flat disk was developed by Cohen and Hull (9). The primary components of each plating unit are a platinum anode and a cell which has as its base (and cathode) the metal disk on which the film is to be deposited.

For Cylinders or Tubes. To plate the inside surface of a metallic cylinder or tube, the cylinder is used as the cathode of the plating cell, figure 2. A stopcock is attached at the bottom for draining the plating solution. The anode consists of a platinum rod rotated by an electric stirring motor, and the current is supplied by a dc rectifier which has a capacity of 35 amperes. Electric heating coils supply the necessary heat.

In plating the outside surface of a cylinder, the cylinder is placed in the center of the cell as the cathode. It is rotated with a stirring motor, figure 3. A platinum ribbon anode is wound around the inside surface of the glass cell.

General Plating Procedure

Nickel is a convenient base metal for receiving the electrodeposit; it is easily cleaned and maintained free of troublesome oxide films. The nickel disk is degreased in trichloroethylene or acetone; the glass parts of the plating cell and the anode are cleaned with chromic acid and rinsed with distilled water. The cell is then assembled, figure 1.

The prepared plating solution is heated to 80°C. and transferred into the cell. An approximately equal volume of 0.4 M ammonium oxalate or of 1 M ammonium acetate is added to the cell for each volume of plating solution. The cell is placed in a water bath that is maintained at 95 to 100°C. The electrolyte is maintained at a depth sufficient to cover the anode at all times, by periodic additions of water. The solution is electrolyzed with the plating equipment for the desired period of time and designated amperage, as specified for each material.

At the end of the deposition period, the spent solution is immediately poured out of the cell into a beaker. The inside of the cell is washed with distilled water; it is then dried by washing with alcohol or acetone, to prevent water marks on the deposit. The disk with its deposit is promptly removed by disassembling the cell.

ELECTRODEPOSITION CELL FOR FLAT DISKS

Figure 1

CELL FOR ELECTROPLATING THE
INSIDE SURFACE OF A CYLINDER

Figure 2

CELL FOR ELECTROPLATING THE
OUTSIDE SURFACE OF A CYLINDER

Figure 3

The amount of material remaining in the spent plating solution is determined by evaporating the solution to dryness and counting the alpha or beta activity. The amount of material plated is then calculated from a direct radiation measurement or by subtracting the amount in the spent plating solution from the amount taken for plating.

Electrodeposition of Thorium Oxide

A weighed amount of thorium oxide is dissolved in concentrated nitric acid containing a trace of hydrofluoric acid. The hydrofluoric acid is then removed by repeatedly (2 or 3 times) evaporating to dryness in platinumware and redissolving in concentrated nitric acid. The thorium nitrate is finally dissolved in a few drops of nitric acid and diluted to about 1 mg Th/ml.

For film thicknesses up to 0.35 mg Th/cm^2 , the total amount of thorium needed is transferred directly to the plating cell. Ammonium oxalate is added and the solution is electrolyzed for 1 hour at 130 ma/cm^2 .

For thicker films (up to 0.8 mg Th/cm^2) the required amount of the 1 mg/ml thorium solution is placed in a beaker and an equal volume of 0.4 M ammonium oxalate is added. The solution is made slightly basic with dilute ammonium hydroxide, and 1 drop of 15% hydrogen peroxide is added for each 7.5 ml of thorium solution. This precipitates thorium peroxide, which is redissolved by adding a few drops of 0.08 M oxalic acid. The solution is poured into the cell and electrolyzed for 90 minutes. During the first 60 minutes the current density is 200 ma/cm^2 ; this is increased to 400 ma/cm^2 for the final 30 minutes. A pH of 8 is maintained by adding 0.08 M oxalic acid dropwise during the first period, and adding ammonium hydroxide during the final period as the pH tends to decrease.

Determining Thorium on Plated Disk. The amount of thorium deposited is determined by measuring the alpha radiation from the plated disk. The amount remaining in the spent solution is also determined, to account for all the thorium taken for deposition.

In one procedure, the alpha radiation from the plated deposit is measured when the radiation has reached equilibrium, which is 30 days, or more, after plating. This period of time permits the ingrowth of the thorium daughters, replacing those that were separated from the thorium in the electroplating process.

In a second method, thorium-230 is added in an amount equal to 0.12% of the thorium present, prior to plating, to increase the alpha radiation from the thorium by a factor of over 100. The increased alpha radiation from the thorium to 52,000 d/m/mg is so large that the increase in radiation due to the ingrowth of the thorium daughters (500 d/m/mg) is insignificant (less than 1%). The radiation is measured promptly following the plating process; the amount of thorium deposited is calculated from the measured radiation. Plating efficiency is calculated from the amount of thorium in the deposit and the total thorium used.

Electroplating of Neptunium Oxide

A known amount of neptunium oxide is dissolved in a minimum amount of nitric acid and diluted to approximately 50 $\mu\text{g}/\text{ml}$. For a film with thickness up to 40 μg of Np/cm^2 , the total amount of neptunium required is transferred to the cell. Ammonium oxalate or ammonium acetate is added, as specified in the General Plating Procedure; the solution is electrolyzed for 90 minutes at 200 ma/cm^2 .

For thicker films, up to 0.8 $\text{mg Np}/\text{cm}^2$, a maximum of 0.1 mg of Np per square centimeter of deposition area (0.5 mg per disk of 1-inch diameter) is transferred to the cell. Ammonium acetate is added and the solution is electrolyzed for 60 minutes at 400 ma/cm^2 , after which the spent solution is removed. This process is repeated until a film of the desired thickness has been deposited. The spent solutions are consolidated for radiochemical determination of the neptunium; this value is subtracted from the amount used to obtain the amount deposited.

Electroplating of Technetium

In preparation for electroplating relatively thin films on small areas, 10 ml of solution containing the desired amount* of technetium is transferred to the cell; 10 ml of 0.4 M ammonium oxalate is added. The pH is then adjusted to the range between 5 and 7. The solution is electrolyzed at 200 ma/cm^2 for 90 minutes.

BIBLIOGRAPHY

1. Box, W. D., "Electrodeposition of Tc^{99} Metal," Nucl. Appl., 1, pp. 155-7 (April 1965).
2. Box, W. D. and Petit, G. S., Private Communication, Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory and Oak Ridge Gaseous Diffusion Plant, respectively (1963).
3. Cerrai, E. D., Dugnani, R., and Gazzarrine, F., "Preparation of Thorium Thin Layers through Electrolytical Deposition on Different Metallic Support," Energia Nucleare (Milan), 9, pp. 200-5 (April 1962).
4. Eakins, J. D. and Humphries, D. G., "Preparation of Technetium Metal," J. Inorg. Nucl. Chem., 25 (6), p. 737 (1963).
5. Graves, A. C. and Froman, D. K., Miscellaneous Physical and Chemical Techniques of the Los Alamos Project, 1st ed., New York, McGraw-Hill, 1952, Division V, Vol. 3.

* The authors applied a maximum of 18.5 μg to 1-inch disks, recognizing that larger amounts would be tolerable. After technetium became more available, Box (1) demonstrated excellent plating efficiency when plating films as thick as 18 mg/cm^2 , from 150 ml of solution.

6. Kim, S. M., Noakes, J. E. and Miller, W. W., "Electrodeposition Method for Counting Alpha and Beta Emitters," Nucleonics, 24, pp. 66-7 (March 1966).
7. Motta, E. E., Larson, Q. V. and Boyd, G. E., "Studies of the Tracer Chemistry of Element 43," Plutonium Project Record MonC-99, April 22, 1947.
8. Rajagopalan, M. and Ramaniah, M. V., "Electrodeposition of Neptunium," Radiochim. Acta, 5, p. 236 (July 1966).
9. Rodden, C. J., et al., Analytical Chemistry of the Manhattan Project, 1st ed., New York, McGraw-Hill, 1950, Division VIII, Vol. 1, pp. 523-529.
10. Seaborg, Glenn T. and Gofman, John W., Abstract of U. S. Patent Application Serial Number 25,076, Official Gazette, U. S. Patent Office, Vol. 655, No. 4, p. 1175, November 26, 1952.