142
2-1-78

AD. 1799

MLM-2490

MASTER

Recovery and Purification of Uranium-234 from Aged Plutonium-238

Perle L. Keister, Paul E. Figgins
and Ralph M. Watrous

January 20, 1978

Monsanto

MOUND FACILITY

Miamisburg, Ohio

operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company

for the

U. S. DEPARTMENT OF ENERGY

Contract No. EY-76-C-04-0053

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.

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or 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.

PRINTED IN THE UNITED STATES OF AMERICA

Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy \$4.00; Microfiche \$3.00

Recovery and Purification of Uranium-234 from Aged Plutonium-238

Perle L. Keister, Paul E. Figgins and Ralph M. Watrous

Issued: January 20, 1978

MOUND FACILITY

Miamisburg, Ohio 45342

operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company

for the

U. S. DEPARTMENT OF ENERGY

Contract No. EY-76-C-04-0053.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or 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.

Contents

	<u>Page</u>
ABSTRACT.	3
INTRODUCTION.	3
INITIAL SEPARATION.	5
INTERMEDIATE SEPARATION	7
FINAL SEPARATION.	9
PREPARATION AND ANALYSIS OF U_3O_8 PRODUCT.	12
APPENDIX: CONCENTRATION OF WASTE SOLUTIONS GENERATED BY PLUTONIUM RECOVERY.	15
REFERENCES.	16
DISTRIBUTION.	17

Abstract

The current production methods used to recover and purify uranium-234 from aged plutonium-238 at Mound Laboratory are presented. The three chemical separation steps are described in detail. In the initial separation step, the bulk of the plutonium is precipitated as the oxalate. Successively lower levels of plutonium are achieved by anion exchange in nitrate media and by anion exchange in chloride media. The procedures used to characterize and analyze the final U_3O_8 are given.

Introduction

High isotopic purity uranium-234 has been chemically separated from aged plutonium-238 for more than 10 yr at Mound Laboratory. The procedures presently in use for this separation differ significantly from those previously published. [1] This report will describe the current production methods used.

Plutonium-238, with a half-life of 87.404 yr, decays by alpha emission to uranium-234. One hundred grams of plutonium-238 will produce approximately 790 mg of uranium-234 in 1 yr. Until recently, the major source of uranium-234 has been the large volumes of waste solution generated during recovery of aged plutonium-238 from heat sources. Another source of uranium-234 is a series of plutonium-238 sources, referred to as "cows," which have been acquired and stored exclusively for the production of uranium-234. These "cows" are in the form of oxide, metal, or alloys in a variety of encapsulations. Since the waste solutions are not expected to be available in the future, production

will be totally dependent upon the plutonium "cows." A well managed "cow" of high chemical purity containing a minimum amount of uranium-238 is indispensable for producing a high purity uranium-234 product. To achieve this, an individual "cow" should be removed from storage every 10 to 15 yr to be "milked" of its uranium-234 content.

The procedure given in this report is for the processing of "cows" and is divided into three major chemical separation steps as shown in Figure 1. Each step achieves successively lower levels of plutonium and is done in a separate glovebox line. The initial separation step removes the bulk of plutonium by a homogeneous oxalate precipitation. The intermediate separation step is an anion exchange in nitrate media that reduces the plutonium-238 content to 1% or less. The final separation step is an anion exchange in chloride media that reduces the plutonium-238 content to less than 10 ppm in the uranium-234 product. This procedure normally reduces impurities, as detected by emission spectroscopy, to less than 1%.

FIGURE 1 - Chemical separation steps for recovery and purification of uranium-234.

To recover uranium from the large volumes of waste solution generated during recovery of aged plutonium-238, it was necessary to concentrate the uranium before it entered the "cow" processing procedure. The three concentration methods that were employed are described in the Appendix.

The uranium-234 product is shipped, as the oxide, to Isotope Sales at Oak Ridge National Laboratory on an inventory program sponsored by the DoE Division of Basic Energy Sciences. Uranium-234 is primarily used with uranium-235 in fission detectors to extend their useful life.

Initial Separation

The initial separation step (Figure 2) uses oxalic acid generated by the decomposition of dimethyloxalate in hot plutonium-nitrate solutions. This slowly introduced oxalic acid reacts with plutonium(IV) to produce a large particle size precipitate which is easily filtered. [2]

The plutonium "cow" is dissolved with hot 10M HNO_3 in a one-liter beaker on a hot plate or in a one-liter evaporator. The evaporator consists of a Friedrichs reflux condenser and distilling flask

heated in a hemispherical mantle. The addition of HF (0.05 - 0.10M) will speed the dissolution which, in some cases, may require several days to complete. Dissolutions are continued until the desired quantity of uranium-234 in the plutonium-238 has been dissolved.

Each dissolution is limited to a maximum of 75 g of plutonium-238 to minimize the hazards of gamma and neutron radiation. The most penetrating gamma radiation is that of thallium-208, one of the daughters of uranium-232 which is an always-present decay product of plutonium-236. Neutron radiation is probably from the oxygen-17

FIGURE 2 - Initial separation - oxalate precipitation of plutonium.

present and any fluoride used in the dissolution. Small, movable lead shields are used extensively throughout the glovebox lines to limit gamma radiation levels at glovebox surfaces.

An aliquot of the nitrate solution from the dissolutions, containing 25 g of plutonium-238, is concentrated to a minimum volume in the one-liter evaporator. The concentrated solution is transferred to a one-liter beaker and adjusted to an 800-ml volume of 2M HNO_3 . Ammonium hydroxide is used to make the adjustment, if necessary. Approximately 1 ml of 30% H_2O_2 is added to the solution to reduce the plutonium to plutonium (IV). The solution is magnetically stirred and heated to 50°C on a hot plate. Normally enough solid dimethyloxalate is added to precipitate the plutonium and provide a 0.1 M excess of oxalate. A much larger excess of oxalate is required if the plutonium solution contains large amounts of other metal impurities precipitated by the oxalate. Once precipitation has started (5-10 min), heating of the solution between 50 and 60°C, with stirring, is continued for 30 min. The beaker is then set aside to permit the precipitate to settle for at least 1 hr.

The precipitate is collected on a coarse-porosity glass filter by vacuum filtration. The beaker and precipitate are washed with 2M HNO_3 /0.1M $\text{H}_2\text{C}_2\text{O}_4$. The filtrate is returned to the beaker and held overnight to permit additional precipitation. Any additional precipitate is collected on a medium-porosity glass filter by vacuum filtration and washed with 2M HNO_3 /0.1M $\text{H}_2\text{C}_2\text{O}_4$.

Aliquots of the nitrate solution from the dissolutions are prepared, and the plutonium is precipitated until the dissolved "cow" has all been precipitated. After the oxalate precipitates have been allowed to dry on the glass filters, they are collected in a Vycor test tube. The test tube is placed in a vertical tube furnace and heated to 450 C to calcine the oxalate to a "low-fired" oxide. The packaged plutonium oxide "cow" is removed from the glovebox line and returned to storage.

The uranium-rich oxalate filtrates are fed to the one-liter evaporator to destroy the oxalate and concentrate to a minimum volume. Initially, the oxalate solution must be added slowly to hot HNO_3 to prevent violent decomposition of the oxalate. The concentrated uranyl nitrate solution is ready to be prepared for the intermediate separation step. Acid distillates are wasted or recovered depending on uranium and plutonium content.

During the initial separation step, analysis of solid plutonium is by direct calorimetric measurement. High levels of plutonium-238 in solution are measured by total alpha counting of aliquot samples mounted on stainless steel planchets. Uranium-234 content of product solutions is usually estimated from the age and quantity of the parent plutonium-238 but, if necessary, a mass spectroscopic isotope dilution method is available. Lower levels of plutonium-238 and uranium-234 in solution (i.e., distillate) are measured by total alpha count and alpha pulse height analysis of aliquot samples mounted on stainless steel planchets.

Intermediate Separation

The intermediate separation step (Figure 3) is made in dilute nitric acid media with a high concentration of aluminum nitrate, and both plutonium(IV) and uranium are adsorbed on the anion exchange resin. [3-6] The uranium is eluted first with 7M HNO_3 , followed by elution of the plutonium(IV) with dilute

HNO_3 . Addition of a reducing agent (hydroxylamine nitrate) speeds elution of the plutonium as plutonium(III).

The anion exchange resin bed for the intermediate separation step is approximately 3 cm in diameter and 14 to 19 cm deep, with a column volume of 100 to 135 ml. The nitrate form of Dowex 1 x 4 (80-100 mesh) resin is supported upon a coarse-porosity

FIGURE 3 - Intermediate separation - anion exchange in nitrate media.

glass frit, located near the bottom of a tube. Gravity flow through the column is controlled with an adjustable-bore, Teflon stopcock located below the frit. The effluent from the column is collected in a volume-calibrated bottle.

To prepare for the intermediate separation, the uranyl nitrate solution from the initial separation is salted to 1.6M with $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and adjusted to 0.3M HNO_3 with distilled water or NH_4OH as required.

The exchange is begun by backwashing the resin column with 0.35 M HNO_3 (storage condition between exchanges) to remove any entrapped gases and to settle the resin. Then the column is pretreated with two column volumes of 1.6M $\text{Al}(\text{NO}_3)_3$ /0.3M HNO_3 reagent. This pretreatment flows through the column at a rate of approximately 4 ml/min, a flow rate which is maintained throughout operation of the column. The first fractional cut is made, and the effluent is collected as the pretreatment fraction.

An aliquot of the salted uranyl nitrate feed solution, containing 5 to 7 g of uranium-234 and a maximum of 1.5 g plutonium-238 is added to the column, where both plutonium(IV) and uranium are loaded or adsorbed. A few milliliters of 1.2M hydroxylamine nitrate is added to this feed solution on the day before loading to reduce any plutonium(VI). When the addition of feed has been completed, the resin is washed with 1.6M $\text{Al}(\text{NO}_3)_3$ /0.3M HNO_3 until the effluent becomes clear and essentially colorless. Two to four column volumes of this wash are normally required. Next, addition of 7M HNO_3 to the column is started and continued until a

refractive phenomenon of two solutions of different densities mixing or subtle color change or density (deepening or lightening) change in the gray tones is observed in the effluent just under the glass frit. This requires about one column volume of 7M HNO_3 . The second fractional cut is made, and the effluent is collected as the raffinate/wash fraction.

Addition of 7M HNO_3 is resumed to elute the uranium, which is identified by the bright yellow color of the effluent. The addition of 7M HNO_3 is continued until the effluent becomes nearly colorless again. About 10 column volumes of 7M HNO_3 are required to elute the uranium. The third fractional cut is made, and the effluent is collected as the uranium fraction.

Next, the addition of 0.35M HNO_3 is started, at which time a narrow, green or brown band of plutonium(IV) is normally observed moving down the column. The addition of 0.35M HNO_3 is continued until the band approaches the glass frit, or a color change is observed in the effluent just under the frit. This normally requires about two column volumes of 0.35M HNO_3 . The fourth fractional cut is made, and the effluent is collected as a transition fraction.

Once the addition of 7M HNO_3 to the column has been started, the separation run is always completed to this point the same day. The resin is never left overnight in 7M HNO_3 because of the instability of the resin in higher acid concentrations.

The addition of 0.35M HNO_3 is resumed to elute the plutonium. A small quantity of 1.2M hydroxylamine nitrate is added to the 0.35M HNO_3 at this point to reduce the plutonium. The green or brown color

of plutonium(IV) eventually gives way to the blue color of plutonium(III) in the effluent. This addition is continued until the effluent becomes essentially colorless. Three to four column volumes of 0.35M HNO_3 with hydroxylamine nitrate is normally required to complete elution of the plutonium. One column volume of 0.35M HNO_3 is added to the column as a wash. The fifth and final fractional cut is made and collected as the plutonium fraction.

Intermediate separation runs are continued until all the prepared feed has been processed. The accumulated plutonium fractions are combined and concentrated to a minimum volume in a 500-ml evaporator. This plutonium concentrate is held for recycle to a "cow" or transferred to recovery. The uranium fractions and usually the transition fractions are combined and concentrated to a minimum volume in the 500-ml evaporator. This concentrated uranyl nitrate product is ready to be prepared for the final separation step. All other fractions and acid distillates are wasted or recovered depending on uranium and plutonium content.

During the intermediate separation step, the plutonium-238 and uranium-234 content in all fractions is determined by total alpha count and alpha pulse height analyses of aliquot samples mounted on stainless steel planchets.

Final Separation

In the final separation step (Figure 4), both plutonium(IV) or (VI) and uranium are adsorbed on anion exchange resin in 9M HCl . [3-6] The plutonium is eluted

as plutonium(III) with 9M HCl containing a reducing agent (NH_4I), followed by elution of the uranium with dilute HCl . An intermediate elution of neptunium-237 with 4M HCl is made also. Neptunium-237 can be present because of an incomplete separation in the production of the plutonium and by decay of plutonium-241.

To prepare for the final separation step, the uranyl nitrate solution from the intermediate separation must be converted to the chloride. This is accomplished with a double hydroxide precipitation of the uranium, with dissolution of the precipitates in HCl .

The uranyl nitrate solution is divided into aliquots containing 5 to 7 g of uranium-234. These aliquots are transferred to one-liter beakers. In turn, each beaker is placed on a magnetic stirring unit, and the solution is stirred while 10M NaOH is added slowly from a wash bottle until the precipitation is completed. Any aluminum present initially precipitates as the hydroxide but redissolves as the aluminate as the hydroxide concentration increases.

Agitation is continued for 15 to 20 min after the precipitation is completed, and then the beaker is set aside for several hours to allow the precipitate to settle.

The precipitate is collected on Whatman 41 filter paper by vacuum filtration using a porcelain filter funnel. The filtrate is passed through a medium-porosity glass frit to collect any mechanical losses. The beaker and precipitate are washed with dilute NaOH . After the precipitations have been completed for each of the aliquots, the precipitates are combined and dissolved in a minimum volume of 9M HCl .

FIGURE 4 - Final separation - anion exchange in chloride media.

The precipitations and dissolution are repeated as above with one exception: a dilute NH_4OH wash of precipitates is included after the dilute NaOH wash. After the final dissolution in 9M HCl , the uranyl chloride product solution is ready for the anion exchange.

The resin column for the final separation is identical to the one described for the intermediate separation with one exception: the chloride form of the Dowex 1 x 4 resin is used.

An exchange is begun by backwashing the resin column with 0.5M HCl (storage condition between exchanges) to remove any entrapped gases and to settle the resin. The column is pretreated with two column volumes of 9M HCl at a flow rate of 4 ml/min. The first fractional cut is made, and the effluent is collected as the pretreatment fraction.

An aliquot of the uranyl chloride feed solution, containing 5 to 7 g of uranium-234 and a maximum of approximately 50 mg plutonium-238 flows through the column at a rate of 2 ml/min. Both uranium(VI) and plutonium(IV) or (VI) are loaded or adsorbed on the resin. When the addition of feed has been completed, six to eight column volumes of 9M HCl / 0.05M NH_4I reagent are added to the column to reduce and elute the plutonium as plutonium(III). This plutonium eluent flows through at a rate of 4 ml/min, a flow rate which is maintained throughout the remainder of the separation. After the plutonium elution is completed, a wash of three column volumes of 9M HCl is added to the column. The second

fractional cut is made, and the effluent is collected as the plutonium raffinate-wash fraction.

Four molar HCl is added until a refractive phenomenon or color change to green is observed in the effluent under the frit. This requires about one column volume of 4M HCl . The third fractional cut is made, and the effluent is collected as the pre-neptunium fraction.

The addition of 4M HCl is resumed to elute neptunium(IV), which is identified by the green color of the effluent. The addition is continued until the green color disappears from the effluent. This requires about one-half column volume of 4M HCl . The fourth fractional cut is made, and the effluent is collected as the neptunium fraction.

Next, 0.5M HCl is added until a refractive phenomenon or color change to yellow is observed in the effluent under the frit. About one-column volume of 0.5M HCl is required. The fifth fractional cut is made, and the effluent is collected as the Np-U transition fraction.

Addition of 0.5M HCl is resumed to elute the uranium(VI), which is identified by the bright yellow color of the effluent. The elution is continued until the yellow color of the effluent has disappeared. Approximately two column volumes of 0.5M HCl are required to elute the uranium. The sixth fractional cut is made, and the effluent is collected as the uranium fraction.

Two column volumes of 0.5M HCl are added to the column as a wash. The final fractional cut is made and collected as a post-uranium fraction.

Final separations are continued until all the prepared feed has been processed. The uranium fractions, and sometimes the post-uranium fractions, are combined in one volume to ensure homogeneity and held for final uranium product preparation. All other fractions and hydroxide filtrates are wasted or recovered depending on uranium and plutonium content.

During the final separation step, both plutonium-238 and uranium-234 content in all exchange fractions and hydroxide filtrates are determined by total alpha count and alpha pulse height analysis of aliquot samples mounted on silver planchets.

Since uranium-234 and neptunium-237 have primary alpha energies very close together (4.773 and 4.787 MeV, respectively), it is difficult to distinguish the two isotopes by alpha pulse height analysis. Visual observations of recent operations do indicate effective separations; the neptunium fractions are characteristically green, and the uranium fractions are yellow. The Np-U transition fractions have been essentially colorless. In general, insignificant alpha peaks at the 4.7 - 4.8 MeV energy level have been seen in these transition fractions.

Preparation and Analysis of U_3O_8 Product

Uranium is precipitated as the hydroxide from aliquots of the uranium

product solution from the final separation, containing 3 to 5 g of uranium-234. Individually, each aliquot is transferred to a 400-600 ml beaker and warmed gently on a hot plate. While the solution is stirred with a glass rod, concentrated NH_4OH is added slowly from a wash bottle. When the precipitation is completed, the beaker is set aside to allow the precipitate to settle. After a few minutes, the precipitate is collected on a 12.5-cm Whatman 40, ashless filter paper by gravity filtration. The beaker and precipitate are washed with dilute NH_4OH .

The filter paper and precipitate are transferred to a 250-ml beaker and placed on a hot plate under a heat lamp for preliminary drying. When the filter paper begins to char, the contents of the beaker are transferred to a 150-ml platinum dish. The platinum dish is placed in a muffle furnace, where the temperature is raised to 500°C in 2 hr and held for 1 hr to burn off most of the filter paper. The furnace is allowed to cool overnight before the dish is removed.

Each aliquot of the product solution is precipitated, filtered, and dried in the manner described. Each filter paper is burned off separately in the furnace, while the precipitates are accumulated in the platinum dish. Following ignition of the final filter paper at 500°C, the furnace temperature is raised rapidly to 900°C and held for 1 hr to calcine the uranium precipitates to the oxide. When the furnace has cooled overnight, the platinum dish, with oxide content, is removed and weighed on a microbalance. Calcination and weighing are repeated to achieve a constant weight.

Approximately 10 mg of the U_3O_8 product from the dish is accurately weighed into

a tared, 5-ml volumetric flask as an analytical sample. The oxide product is transferred from the platinum dish to the appropriate number of tared, one-dram, screw-capped glass vials. Each loaded vial is weighed on the microbalance to determine the total oxide weight. The vials are removed from the glovebox line, decontaminated, wrapped in three layers of aluminum foil, and sealed in a screw-capped aluminum calorimeter vial. These are submitted for total heat determination by calorimetry. This containment is used also for eventual shipment of the product.

The analytical sample is dissolved in a few drops of hot, concentrated HNO_3 added to the 5-ml volumetric flask. The flask is filled to the 5-ml mark with 1M HNO_3 when dissolution is completed. A 50-lambda sample of this analytical solution is transferred to a one-dram, screw-capped glass vial and submitted for isotopic mass analysis.

Four 10-lambda aliquots of the analytical solution are mounted on 1-in. square stainless-steel planchets or slides. The samples are spread over a 1.5-cm diameter on the slide in a thin layer by a special technique. [7] This technique includes dissolution of the sample in dilute HNO_3 , precipitation with concentrated NH_4OH , and sublimation of the NH_4NO_3 . The slides are flamed and subjected to alpha pulse height analysis and to proportional alpha counting, with results being averaged for the four slides.

The remaining analytical solution is transferred to a two-dram, screw-capped

glass vial. The uranium is removed by three extractions with 2-ml portions of 0.1M tri-n-octylphosphine oxide (TOPO) in diethylbenzene. The solution in the vial is agitated vigorously by hand for 2 min for each extraction. When the phases have separated, the organic is removed with an eye dropper following each extraction. Next, the aqueous phase is agitated vigorously for 2 min with 2 ml of hexone to scrub out most of the organic. When the phases have separated, the hexone is removed with an eye dropper and stored with the organic for eventual disposal. The aqueous phase is evaporated to dryness, in the vial, on a hot plate under a heat lamp. A stream of argon is directed over the top of the vial to speed evaporation. The dry residue is dissolved in a few drops of concentrated HNO_3 and again evaporated to dryness to destroy any organic still present. Next, the residue is dissolved in a few drops of concentrated HCl and again evaporated to dryness to convert the residue to chloride form. The residue is submitted, in the two-dram vial, for a determination of impurities by emission spectroscopy.

The weight of uranium-234 in the oxide can be calculated by three methods using the analytical data obtained. In brief, these methods make use of (1) total alpha count, alpha pulse height data, total oxide weight, analytical sample dilution, and specific activity of uranium-234; (2) total heat value, corrected for other alpha emitters present using alpha pulse height data; and (3) isotopic mass analysis and total oxide weight corrected for impurity content.

Mass and alpha analyses of a uranium-234 product which was separated from waste

raffinates generated during recovery of a plutonium-238 heat source are presented in Table 1. In the processing of "cows", most uranium-238 contamination in the original plutonium is removed during the first uranium-234 separation. Subsequent separations should produce a uranium-234 product of 99.6 - 99.9% isotopic purity, depending upon the isotopic composition of the plutonium. Similarly, lesser quantities of neptunium-237 should be

observed during subsequent uranium-234 separations.

Since plutonium-236 decays approximately 30 times faster than the plutonium-238, the uranium-232 content of the uranium product will decrease with subsequent separations. Consequently, the presence of the thallium-208 daughter of uranium-232 will decrease also and lessen the gamma radiation levels with each subsequent separation cycle.

Table 1 - MASS AND ALPHA PULSE HEIGHT ANALYSES OF A URANIUM-234 PRODUCT

Mass Analysis		Alpha Pulse Height Analysis ^b	
Mass	wt %	Isotope	% Alpha
234	99.07	²³⁴ U	90.51
235	0.08	²³² U	7.52 ^c
236	0.06	²³⁸ Pu	0.81 ^d
238	0.79	²³² U Daughters	1.16
(some Mass 237 observed) ^a			
^a Probably neptunium-237			
^b Approximately 21 days after final separation			
^c 25 ppm			
^d 3 ppm			

Appendix

Concentration of Waste Solutions

Generated by Plutonium Recovery

In the anion exchange process formerly in use at Mound Laboratory for recovery of plutonium-238 from aged heat sources, part of the uranium-234 was washed through with the waste raffinate with variable quantities of plutonium contamination. Two methods were used to concentrate these large volumes for introduction into the "cow" processing procedure. One method consisted of extraction of the uranium and plutonium with 0.1M tri-n-octylphosphine oxide (TOPO) in Amsco solvent, followed by stripping of the uranium and plutonium from the organic with sodium carbonate and oxalic acid solutions. Final concentration was by hydroxide precipitation from the strip solutions and dissolution in a minimum volume of nitric acid. This method was used several times, and the plutonium levels were such that the concentrates could enter the intermediate separation step of the "cow" processing procedure.

Another method of concentrating the anion exchange raffinate consisted of absorbing uranium and plutonium from an aluminum nitrate solution of the raffinate in an anion exchange column and eluting the

uranium and plutonium together. This method was used once, and the plutonium level in the eluent was such that an oxalate precipitation of the plutonium was made and the uranium-rich oxalate filtrate concentrated by evaporation. These operations were performed in special large-scale equipment. The uranium concentrate entered the intermediate separation step of the "cow" processing procedure, and the plutonium oxalate was calcined and retained as "cow" material.

A third method used to recover and concentrate the uranium-234 from one large plutonium-238 heat source involved a special oxalate precipitation of the dissolved plutonium prior to the anion exchange in the plutonium recovery operation. The uranium-rich oxalate filtrate was concentrated by evaporation to a minimum volume. The plutonium level was such that this concentrate entered the initial separation step of the "cow" processing procedure for the homogeneous oxalate precipitation.

A method described by Russell [8] and reported in an earlier patent [9] was tried to selectively precipitate uranium as sodium uranyl acetate from a waste raffinate. Three successive precipitations were tried on a portion of the raffinate without success in separating the uranium from the plutonium, probably because of the high salt content of the raffinate.

References

1. P. E. Figgins and R. J. Belardinelli,
J. Inorg. Nucl. Chem., 28, 2193 (1966).
2. S. G. Abrahamson, J. Inorg. Nucl. Chem., 27, 842 (1967).
3. D. G. Boase and J. K. Foreman,
Talanta, 8, 187 (1961).
4. O. A. Vita, C. R. Walker, C. F. Trivisonno and R. W. Sparks,
Anal. Chem., 42, 465 (1970).
5. J. L. Ryan and E. J. Wheelwright,
Ind. Eng. Chem., 51, 60 (1959).
6. H. M. Ockenden and J. K. Foreman,
Analyst, 82, 592 (1957).
7. H. W. Kirby and J. J. Dauby,
Radiochimica Acta, 5, 133 (1966).
8. E. R. Russell, J. Inorg. Nucl. Chem.,
36, 1659 (1974).
9. J. W. Goffman, R. E. Connick and A. C. Wahl, U. S. Patent 2,871,251, U. S. Atomic Energy Commission (1959).

Distribution

EXTERNAL

TID-4500, UC-10 (142)

R. K. Flitcraft, MRC

J. A. Chacon, DoE/DAO

D. C. Klein, DoE/ALO

Monsanto Library, St. Louis

INTERNAL

W. T. Cave

P. E. Figgins (5)

C. W. Huntington

L. V. Jones

P. L. Keister (15)

J. R. McClain

R. A. Schwind

R. E. Vallee

R. M. Watrous (15)

Library (15)

Publications (10)