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AEC RESEARCH AND DEVELOPMENT REPORT

RECOVERY OF ^{147}Pm FROM SAVANNAH RIVER PLANT WASTE

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RECOVERY OF ^{147}Pm FROM SAVANNAH RIVER PLANT WASTE* (2)

Summarized by R. E. Greene

Supplementary Keywords: production, radioisotope; production, separation; reactor by-product recovery; solvent extraction; chromatography; plant-scale; plutonium; promethium-147; cerium-144; promethium-146; promethium-148m.

Abstract. Batch solvent extraction procedures were developed for recovering ^{147}Pm, as a mixture of fission product lanthanides, from the aqueous wastes obtained in processing irradiated nuclear fuels. Extraction of the lanthanides and plutonium with 50% tributyl phosphate (TBP) from concentrated $Al(NO_3)_3$ and/or $NaNO_3$ solution is followed by back extraction into dilute nitric acid. By-product plutonium isotopes are separated from the trivalent lanthanides by extraction, as Pu~~(VI)~~(IV), into TBP from strong nitric acid. Cerium-144 is separated from the mixture by equilibration of ^{144}Ce(III) with stable Ce(IV) and extracting ^{144}Ce(IV) formed with 50% TBP. Approximately 3 kg of ^{147}Pm was recovered in two plant tests.

(Introduction) (3)

A process for recovering the ^{147}Pm in a lanthanide mixture obtained from irradiated fuels of either natural uranium or alloys of aluminum and uranium enriched in ^{235}U was developed at the Savannah River Plant (SRP).

Promethium has several attractive properties as a possible isotopic power source---2.6-year half-life, which is long enough for many terrestrial and space applications[1]; decay by beta emission only to stable ^{147}Sm; and a maximum

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bremsstrahlung energy of only 0.224 MeV. Radioisotopic contaminants in reactor-produced ^{147}Pm are ^{146}Pm and ^{148m}Pm, both of which emit penetrating gamma radiation in high abundance. At reactor discharge, fission product promethium contains ~0.2 ppM ^{146}Pm (half-life 5.5 years) and 5% ^{148m}Pm (half-life ~~4.1~~ 41 days). The ^{148m}Pm decays to an insignificant level in about 2.5 years.

Although several processes have been recorded[2-4] for the recovery of ^{147}Pm, each of these involves steps not compatible with SRP operations. A process reported by Henry[5] for the recovery of americium and curium with tributyl phosphate (TBP) appeared to be readily adaptable to the SRP operations and was therefore evaluated. The adapted process is designed for simultaneous recovery of uranium, neptunium, by-product plutonium, and promethium in a lanthanide mixture (promethium is ~3% of the total mixture) from irradiated enriched uranium--aluminum alloy fuels and natural uranium fuels.

A brief description of the laboratory separation of promethium, plutonium, and ^{144}Ce and two plant tests is presented. The separation of neptunium and uranium was described previously.[6]

Process Description (3)

From the solution from which the bulk of uranium and neptunium has previously been separated, the lanthanides (including promethium), residual uranium, and plutonium are extracted into TBP and back extracted from the organic phase with dilute nitric acid containing a reductant for the plutonium. Plutonium is separated from the lanthanides by solvent extraction with TBP as Pu(IV) from strong nitric acid solution. The most successful method tested for the removal of ^{144}Ce impurity in large-scale separations was exchange of

$^{144}Ce(III)$ with stable Ce(IV), and extracting the tetravalent ^{144}Ce thus formed away from the less extractable trivalent lanthanides.

Extraction of Trivalent Lanthanides. (4)

In the acquiring of extraction data, ^{144}Ce was used in place of promethium since trivalent cerium is extracted only slightly less than promethium[7] and its determination is much less complicated than that of promethium; extraction data for ^{144}Ce were shown to be comparable to those of promethium. Distribution coefficient data using Ce(III) were determined using various concentrations of TBP in n-dodecane, various ratios of $Al(NO_3)_3$ and $NaNO_3$ at fixed nitrate concentrations, and various initial HNO_3 concentrations in the aqueous phase. The conditions for the extraction of lanthanides recommended from this part of the study were: (1) 50% TBP in the hydrocarbon diluent, (2) a nitrate concentration from $Al(NO_3)_3$ or $NaNO_3$ of 6.5 to 7.0 M (the distribution coefficient increases with an increasing aluminum fraction), and (3) an initial nitric acid concentration of 0.4 to 0.8 M. Although lanthanides are extracted more efficiently at lower acid concentrations, experience with test solutions showed that lowering the acidity to < 0.4 M is difficult without adding excess base, entailing the possibility of precipitating lanthanides in the feed solution. The lanthanides and plutonium are easily back extracted into dilute nitric acid.

Separation of Plutonium. (4)

Extraction of plutonium from nitrate solution into TBP increases[8] in the order Pu(IV) > Pu(VI) >> Pu(III). For the back extraction of plutonium with promethium and the lanthanides, the Pu(IV) must be reduced to Pu(III); ferrous sulfamate is the most satisfactory reducing agent. The Pu(III) in the back-extracted dilute nitric acid is oxidized to Pu(IV) with nitrous acid. This solution is then made 5 to 6 M in HNO_3 and the Pu(IV) is extracted into TBP. Under these conditions the promethium and other trivalent lanthanides have a very low distribution coefficient.

Extraction of Tetravalent Cerium. (4)

In the lanthanides produced by the fission of ^{235}U, the major source of radioactive decay heat is from ^{144}Ce; this heat complicates the subsequent separation of promethium from the other lanthanides. Because of the similarity of the chemical properties of the trivalent lanthanides, the most successful approach for rapid cerium--promethium separation is solvent extraction, which requires oxidation of Ce(III) to Ce(IV) before separation. Tetravalent cerium is almost completely extracted (98 to 99%) by TBP over a wide range of nitric acid concentrations[9] (under the same conditions only 5 to 10% of the trivalent lanthanides are extracted).

Very strong oxidizing agents are required to oxidize trivalent cerium in nitric acid because of its high oxidation potential.[10] Several oxidants were investigated but none was completely satisfactory. The most satisfactory results were obtained by equilibrating[11] stable Ce(IV) with the $^{144}Ce(III)$ in the reaction

$$^{144}Ce(III) + Ce(IV) \rightleftharpoons {}^{144}Ce(IV) + Ce(III)$$

and then extracting the $^{144}Ce(IV)$ into 50% TBP. Tetravalent stable cerium was added as a solution of ceric ammonium sulfate, $(NH_4)_2Ce(NO_3)_6$. Cerium(IV) ~~(IV)~~ must be extracted and removed from the organic phase rapidly because TBP is slowly oxidized by Ce(IV), a reaction that is more rapid with radioactive solutions.

Two process variations were evaluated to decrease the effects of reactions of Ce(IV) with the organic phase and with contaminants. The first was the addition of PbO_2 as a holding oxidant (the oxidation rate of PbO_2 is too slow for its use as a primary oxidant). In tests with high-activity waste solutions, ~85% of the ^{144}Ce was extracted with a Ce(IV)/Ce(III) ratio of 10, and the PbO_2 settled within a few minutes after agitation was stopped.

The second improvement was the use of a miniature centrifugal extractor[12] for rapid phase separation. In feed solutions reasonably free of Cr(III) (from the original raffinate), which reduces the Ce(IV), a centrifugal extractor could eliminate the need for a holding oxidant by reducing the separation time. In a feed solution containing 1260 Ci of ^{144}Ce per liter, 72% of the cerium was removed with a miniature extractor at a Ce(IV)/Ce(III) ratio of ~6.

Plant-Test Results (3)

Promethium-147 with associated lanthanides was recovered from waste solutions in two plant tests by batch extraction with 50% TBP, in amounts that agreed well with values predicted from the laboratory studies. In the first test, approximately 500 g of ^{147}Pm in a lanthanide mixture was recovered from accumulated waste solutions generated in the processing of irradiated natural-uranium fuel. In the second test, approximately 2.5 kg of ^{147}Pm---97% of that present in a lanthanide mixture---was recovered from highly active waste from the processing of enriched-uranium fuel. Simultaneously, 95% of the plutonium present was also recovered as a by-product.

Approximately 1 g of ^{147}Pm from the first plant test was used to demonstrate the separation of promethium from other lanthanides by displacement chromatography at high pressure.[13] As part of the feed preparation, ^{144}Ce was separated from the solution using stable Ce(IV) as described and a centrifugal extractor. Seventy percent of the ^{144}Ce was removed. A full-scale plant test for separation of promethium from the other lanthanides has not been conducted.

References (3)

1. "Use of Isotopic Power to Drive an Artificial Implanted Human Heart." Nucleonics Week 6, No. 23, 5 (1965).
2. T. A. Butler and E. E. Ketchen. "Solvent Extraction Separation of Cerium and Yttrium from Other Rare Earth Fission Products." Ind. Eng. Chem. 53, 651 (1961).
3. L. A. Bray and F. P. Roberts. Separation of Trivalent Rare Earths from Cerium. USAEC Report HW-78987 Rev, General Electric Co., Hanford Atomic Products Operation, Richland, Wash. (1963).
4. L. A. Bray and F. P. Roberts. Purification of Rare Earths from Hanford Wastes by Solvent Extraction. USAEC Report BNWL-C-92, Battelle-Northwest, Pacific Northwest Laboratory, Richland, Wash. (1965).
5. H. E. Henry. Isolating Americium and Curium from $Al(NO_3)_3$ - $NaNO_3$ - HNO_3 Solutions by Batch Extraction with Tributyl Phosphate. USAEC Report DP-972, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1965).
6. W. L. Poe, A. W. Joyce, and R. I. Martens. "^{237}Np and ^{238}Pu Separation at the Savannah River Plant." Ind. Eng. Chem., Proc. Design Develop 3, 314 (1964).
7. H. A. C. MacKay, K. Alcock, and D. Scaigell. The Extraction of Some Rare Earths by Tributyl Phosphate. USAEC report AERE-C/R-1514, Atomic Energy Research Establishment, Harwell, England (1954).
8. H. J. Groh and C. S. Schlea. "The Recovery of Neptunium-237 and Plutonium-238." Progress in Nuclear Energy, Series III, Process Chemistry, Volume 4, Pergamon Press, Ltd., Oxford (1970).

9. J. C. Warf. "Extraction of Cerium(IV) Nitrate by Butyl Phosphate." J. Am. Chem. Soc. 71, 3257 (1949).

10. J. Kleinberg, W. J. Argersinger, Jr., and E. Griswold, Inorganic Chemistry, p. 113, D. C. Heath and Company, Boston, Mass. (1960).

11. J. W. Gryder and R. W. Dodson. "Kinetics of the Exchange Reaction Between the Two Oxidation States of Cerium in Acid Solutions." J. Am. Chem. Soc. 73, 2890 (1951).

12. A. S. Jennings. A Miniature Centrifugal Contactor. USAEC Report DP-680 E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1962).

13. J. T. Lowe. Isolation of ^{147}Pm by Rapid Cation Exchange Chromatography. USAEC Report DP-1194, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1969).

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Isotope Separation
(TID-4500, U-22)

RECOVERY OF ^{147}Pm FROM SAVANNAH RIVER PLANT WASTE

by

John T. Lowe

Approved by

E. L. Albenesius, Research Manager
Separations Chemistry Division

October 1970

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ABSTRACT

Batch solvent extraction procedures were developed for recovering ^{147}Pm, as a mixture of fission product lanthanides, from aqueous wastes after processing irradiated nuclear fuels. Incidentally produced plutonium isotopes were also recovered. Extraction of the lanthanides with 50% tributylphosphate (TBP) from concentrated $Al(NO_3)_3$ or $NaNO_3$ solutions was followed by back extraction into dilute nitric acid. ^{144}Ce was separated from the mixture by oxidation to Ce(IV) and extraction with 50% TBP. Approximately 3 kg of ^{147}Pm were recovered in two plant tests.

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INTRODUCTION

Promethium-147 has several properties that make it attractive as a possible isotopic power source. Its 2.7 year half-life is long enough for many terrestial and space applications.[1] It decays to stable ^{147}Sm by beta emission only; the maximum bremsstrahlung energy is only 0.225 Mev. Radioisotopic contaminants in ^{147}Pm produced by reactor irradiations are ^{146}Pm (half-life = 4.4 years) and ^{148}Pm (half-life = 42 days), both of which emit penetrating gamma radiation in high abundance. At reactor discharge, the composition of fission product promethium is $\sim$0.2 ppm ^{146}Pm and $\sim$5% ^{148}Pm. The ^{148}Pm can be reduced to an insignificant radiation level by $\sim$2.5 years of decay.

The data presented in this report were used to develop a process for recovering a lanthanide mixture, containing ^{147}Pm, from either irradiated alloy of aluminum and ^{235}U-enriched uranium or natural uranium fuel. Incidentally produced plutonium isotopes are also recovered in the enriched uranium process. Approximately 3 kg of ^{147}Pm were recovered in two plant tests.

PROCESS DESCRIPTION

Several processes have been reported for recovering ^{147}Pm,[2-4] but each involves processing steps not compatible with Savannah River Plant processes. These processes require either precipitation steps or introduction of a new extractant such as di-2-ethylhexylphosphoric acid into Savannah River Plant separations processes, which are based on solvent extraction with tri-n-butylphosphate (TBP). A process for recovering americium and curium with TBP was reported by Henry[5]; because this process was readily adaptable to Savannah River Plant processing, it was also evaluated for ^{147}Pm recovery.

The process is designed for simultaneously separating ^{235}U, ^{237}Np, incidentally produced Pu, and ^{147}Pm in a lanthanide mixture from irradiated alloy of aluminum and ^{235}U-enriched uranium. Basically the same procedures could be used to recover ^{147}Pm from waste streams generated in processing irradiated natural uranium fuel. In this procedure:

- Uranium and neptunium are separated by the solvent extraction process that is operated in mixer-settler contactors in two sequential cycles.[6] The lanthanides, residual uranium, and plutonium are separated from the concentrated raffinate of the first cycle by batch extraction with 50% TBP. Batch extraction is desirable to minimize interference with uranium and neptunium recovery in mixer-settlers.

- The products are removed from the organic phase by back extraction with dilute nitric acid containing a reductant (such as ferrous sulfamate) for plutonium. The product solution is evaporated to reduce its volume before storage.

- Plutonium is removed from the product solution by batch extraction with TBP. If the $Al(NO_3)_3$ or $NaNO_3$ concentration in this concentrated solution is high because of cross-contamination from the original feed, the initial extraction and back extraction must be repeated to reduce cation impurities before ion exchange.

- For large-scale separations, it is also desirable to remove ^{144}Ce, the major source of fission product decay heat. The most successful method tested in this work was electron exchange with nonradioactive Ce(IV), and extracting Ce(IV) away from the less extractable trivalent lanthanides.

EXTRACTION OF TRIVALENT LANTHANIDES

Trivalent lanthanides are extracted by the reaction[7]

$$M^{3+}_A + 3(NO_3^-)_A + 3TBP_O \rightleftarrows M(NO_3)_3 \cdot 3TBP_O \qquad (1)$$

where the subscripts A and O refer to mutually equilibrated aqueous and organic phases, respectively. Adequate lanthanide extraction occurs only with relatively high nitrate ($\sim$6M) and TBP (>30%) concentrations.

To simplify the study, preliminary extraction data for cerium, instead of promethium, were obtained for a variety of possible plant applications. Trivalent cerium is extracted only slightly less than promethium,[8] and analysis for ^{144}Ce is considerably less complicated than ^{147}Pm analysis in highly salted solutions. In several extractions with ^{147}Pm tracer, the ^{144}Ce recovery data were shown to apply to promethium.

Figure 1 shows the effect of TBP concentration on distribution coefficient D_a^o (ratio of concentration in organic phase to concentration in aqueous phase) for trivalent cerium from 2M $Al(NO_3)_3$ solution at several acid concentrations. Distribution coefficients of >50 are required for more than 98% recovery in a single extraction, which in turn requires approximately 50% TBP.

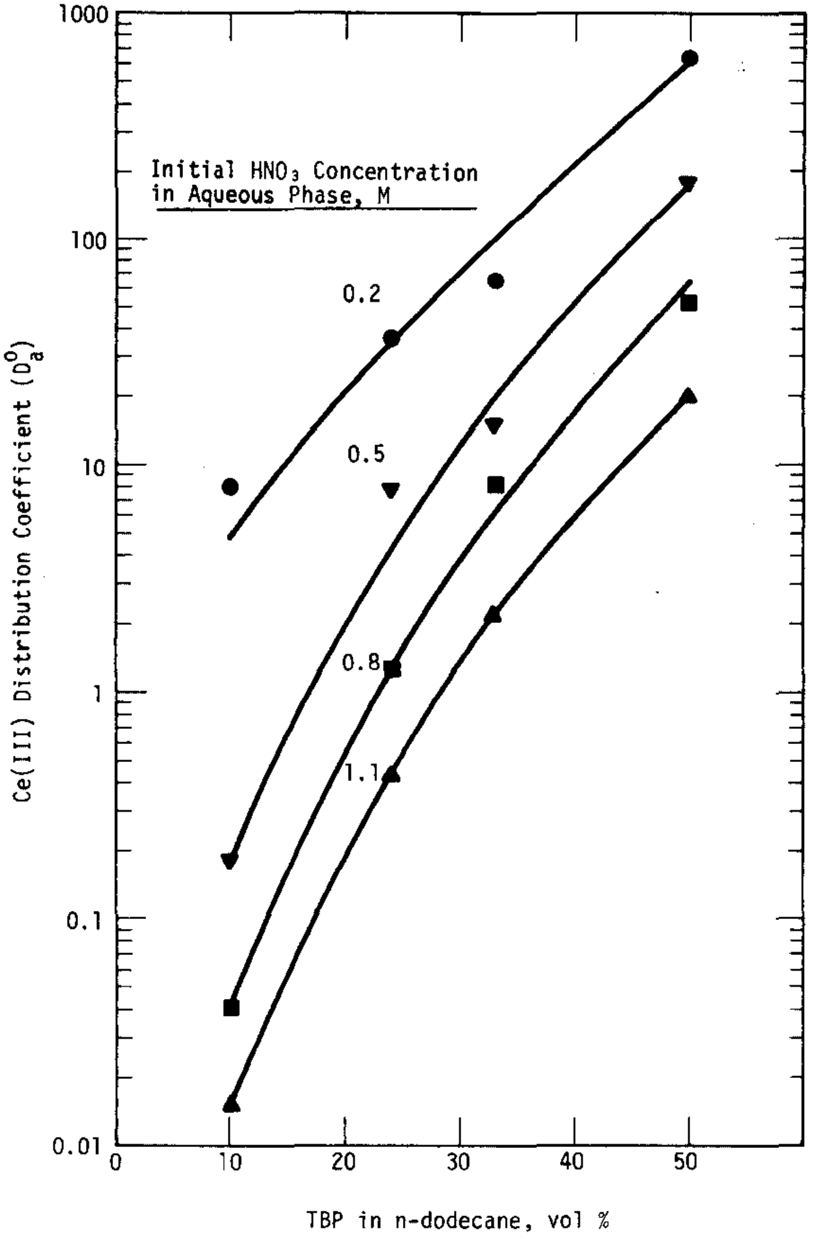

FIG. 1 CERIUM(III) DISTRIBUTION DATA FROM 2M $Al(NO_3)_3$

Reaction (1) indicates that the distribution coefficient for a trivalent lanthanide is independent of the cation in the nitrate salt; in practice, however, a dependence on the cation does exist. For a fixed nitrate concentration, distribution coefficients are higher with $Al(NO_3)_3$ than $NaNO_3$ because hydration of Al^{3+} decreases the amount of water present, hence increasing the nitrate concentration. Figure 2 shows the distribution of ^{144}Ce between 50% TBP and 6.5M NO_3^- solution, for a range of Na/Al ratios.

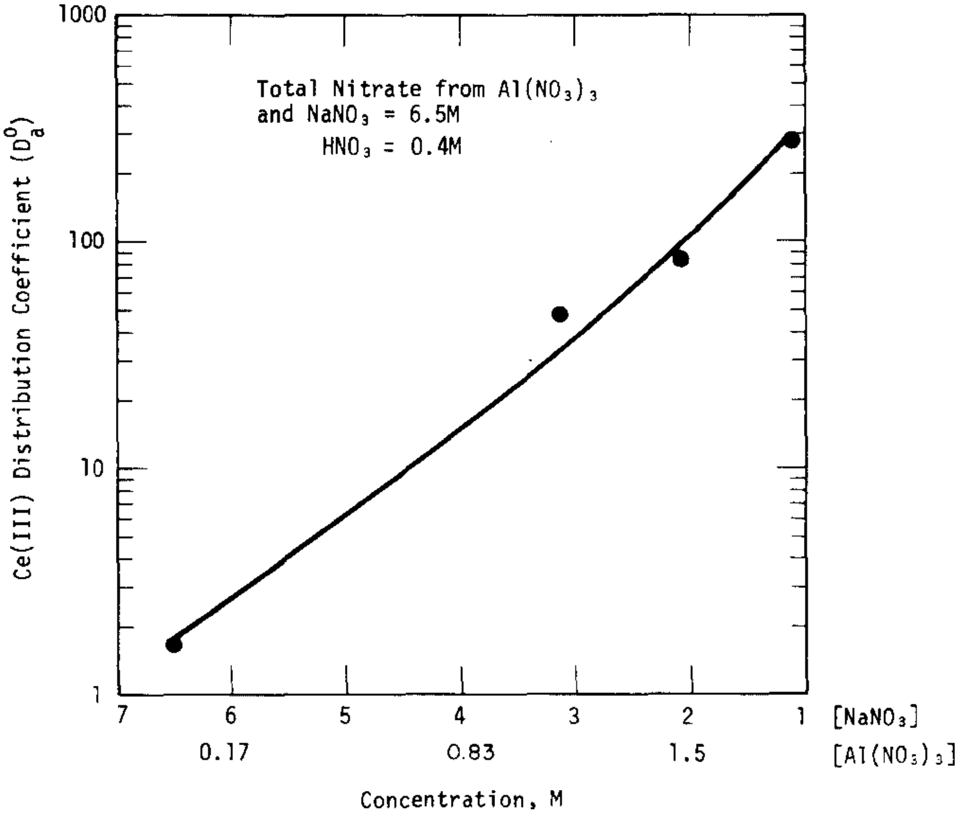

FIG. 2 EFFECT OF Na/Al RATIO, AT CONSTANT NITRATE CONCENTRATION, ON Ce(III) DISTRIBUTION

The effect of initial nitric acid concentration in the aqueous phase is shown in Figure 3, for several concentrations of $Al(NO_3)_3$ and $NaNO_3$, representing typical plant solutions. Nitric acid is preferentially extracted by 50% TBP from high salted solutions, thereby suppressing extraction of trivalent lanthanides and causing these curves to converge at higher acidities.

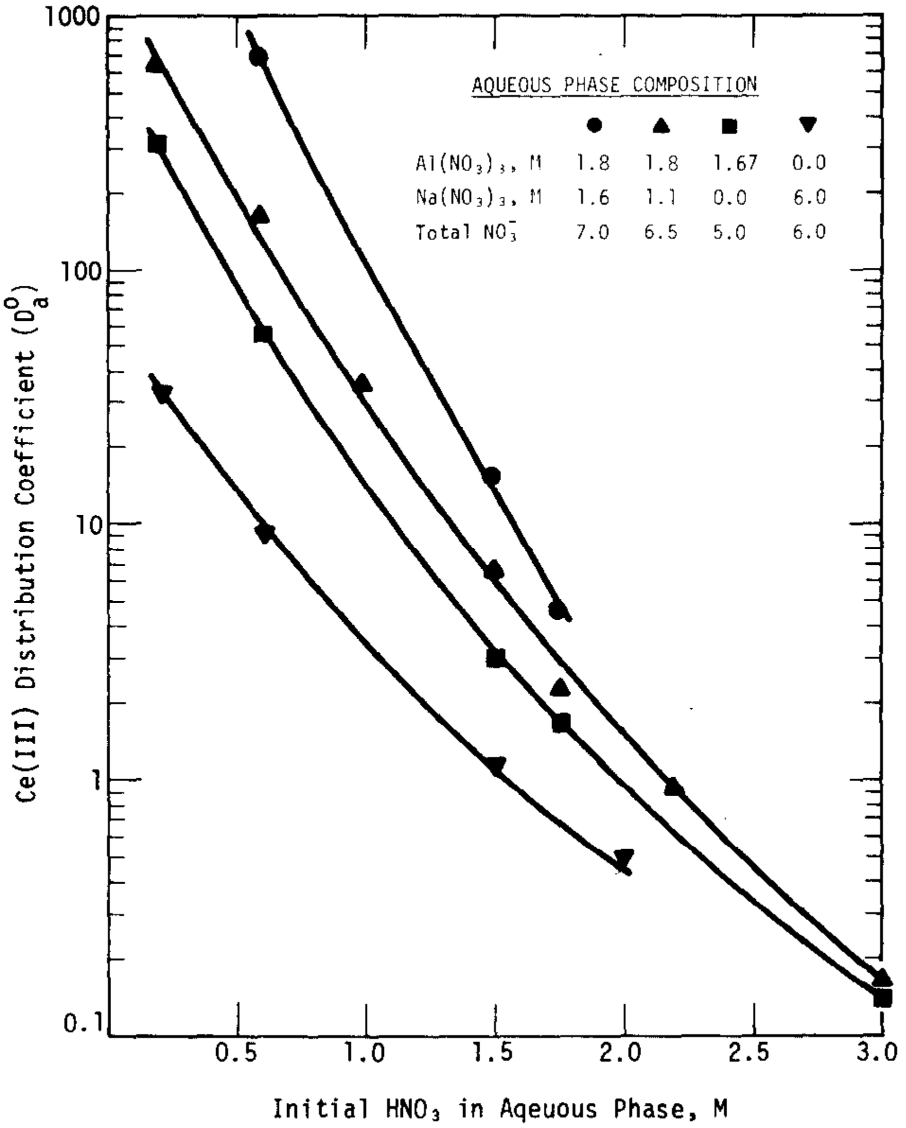

FIG. 3 Ce(III) DISTRIBUTION DATA FOR SEVERAL FEED COMPOSITIONS

The extraction conditions recommended for adequate extraction of lanthanides are: 6.5-7.0M nitrate as $Al(NO_3)_3$ or $NaNO_3$, 0.4-0.8M HNO_3, and extraction with 50% TBP in a hydrocarbon diluent. Although lanthanides are extracted more efficiently at lower acid concentrations, experience with test solutions showed that lowering acidities to <0.4M is difficult without adding excess base, and this entails the possibility of precipitating lanthanides in the feed solution. The lanthanides are readily back-extracted into dilute nitric acid; distribution coefficients increase from about 0.02 to 0.08 as the HNO_3 concentration increases from 0.1 to 1.0M.

EXTRACTION OF PLUTONIUM

Plutonium may exist as Pu(VI), Pu(IV), and Pu(III) in a nitric acid solution. The order of extraction into TBP from nitrate solutions is Pu(IV) > Pu(VI) >> Pu(III).[9] Strong oxidizing agents such as Ce(IV) or MnO_4 will stabilize Pu(VI). Fe(II) will reduce both Pu(VI) and Pu(IV) to Pu(III), and HNO_2-catalyzed HNO_3 will stabilize Pu(IV). No valence adjustment is required for plutonium which exists as Pu(IV) in the concentrated waste raffinate (feed for plutonium-lanthanide extraction). However, Pu(IV) must be reduced to Pu(III) for back extraction of plutonium with the promethium and other lanthanides; otherwise the highly extractable Pu(IV) will remain in the organic phase. Ferrous sulfamate is the most satisfactory reducing agent for Pu(IV),[9] although after several batches were recovered and evaporated, the sulfate concentration was high enough to suppress plutonium extraction in the plutonium-lanthanide separation. Distribution coefficients for Pu(III) in the back-extraction step are approximately the same as those for trivalent lanthanides.

Extraction data for Pu(IV) from simulated solutions of the plutonium-lanthanide concentrate are shown in Figure 4. The $Al(NO_3)_3$ is present in this solution from entrainment of ∿1% of the original feed in the organic phase at the time of the simultaneous plutonium-lanthanide back extraction into dilute nitric acid. Results obtained in a plant test are summarized in a later section.

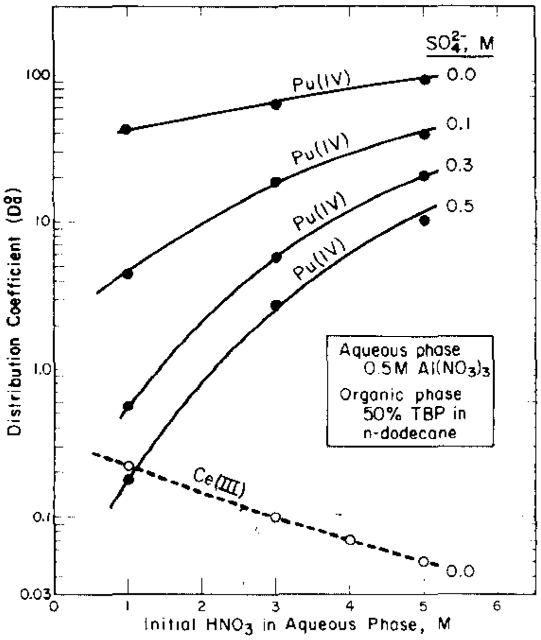

FIG. 4 EFFECT OF SULFATE AND NITRIC ACID CONCENTRATION ON Pu(IV) EXTRACTION

EXTRACTION OF TETRAVALENT CERIUM

^{144}Ce is the major source of heat generated by radioactive decay in the lanthanides resulting from fission of ^{235}U. Storage of large quantities of fission product lanthanides would be simplified if the radioactive cerium could be removed. Because of the very small variations in the chemical properties of the trivalent lanthanides, the most successful approach for a rapid Ce-Pm separation involved oxidation of Ce(III) to Ce(IV) before a separation. Tetravalent cerium is almost completely extracted (98-99%) by TBP over a wide range of HNO_3 concentrations,[10] conditions for which trivalent lanthanides are extracted only to the extent of 5-10%. Very strong oxidizing agents are required to oxidize trivalent cerium in nitric acid, however, because of the 1.61 volt standard oxidation potential.[11]

Several oxidants and solvents have been investigated for the oxidation and extraction of Ce(IV) from trivalent lanthanides. An oxidizing agent must have a sufficiently high potential to quantitatively oxidize cerium, must react very slowly with the organic solvent, and must have high radiation stability. Potassium permanganate,[2] hydrogen peroxide,[12] sodium bismuthate,[13] lead dioxide,[2] and ozone[14] have all been evaluated and rejected for reasons such as slow reactions, incomplete oxidation, or difficulty of phase separation if a solid oxidant is used. The most successful plant demonstration reported to date was obtained using silver-catalyzed persulfate as oxidant and di-2-ethylhexylphosphoric acid as extractant.[15]

Several oxidants were evaluated in this work; electron exchange with nonradioactive Ce(IV) followed by extraction with 50% TBP gave the most satisfactory results. Tetravalent cerium was added as a solution of ceric ammonium nitrate, $(NH_4)_2\,Ce(NO_3)_6$. At room temperature, the electron exchange reaction

$$^{144}\mathrm{Ce(III)} + \mathrm{Ce(IV)} \rightleftarrows {}^{144}\mathrm{Ce(IV)} + \mathrm{Ce(III)} \qquad (2)$$

reaches equilibrium in a few minutes.[16] Ce(IV) must be extracted and removed from the organic phase rapidly, however, because TBP is slowly oxidized by Ce(IV). With nonradioactive solutions, ∿5% of the Ce(IV) in the organic phase is reduced to Ce(III) in 35 hours.[10] With test solutions containing 0.1-0.5 Ci/ml of ^{144}Ce, reduction of Ce(IV) is much more rapid, probably because reducing agents are radiolytically produced and contaminants such as Cr(III) are present. In one test, 70% of the ^{144}Ce was in the organic phase after 10 minutes, but only 55% was in the organic phase after 40 minutes.

Two process variations were evaluated to decrease the effect of reactions of Ce(IV) with the organic phase and with contaminants in plant solutions. The first variation was the addition of a holding oxidant (PbO_2) with the Ce(IV). Figure 5 summarizes data obtained with PbO_2 alone and as a holding oxidant for Ce(IV). Tracer ^{144}Ce was used to determine the percent cerium present as Ce(IV). Although the rate of oxidation with PbO_2 is not sufficiently rapid for use as the primary oxidant, it is satisfactory as a holding oxidant. In a test with high activity waste solution, ∿85% of the ^{144}Ce was extracted with a Ce(IV)/Ce(III) ratio of 10. No stable emulsion was formed as a consequence of having solid PbO_2 present, and the PbO_2 present, and the PbO_2 settled within a few minutes after agitation was stopped. Batch extraction with several thousand liters of solution might present problems on a plant scale, if there were no method of centrifuging to remove the solids.

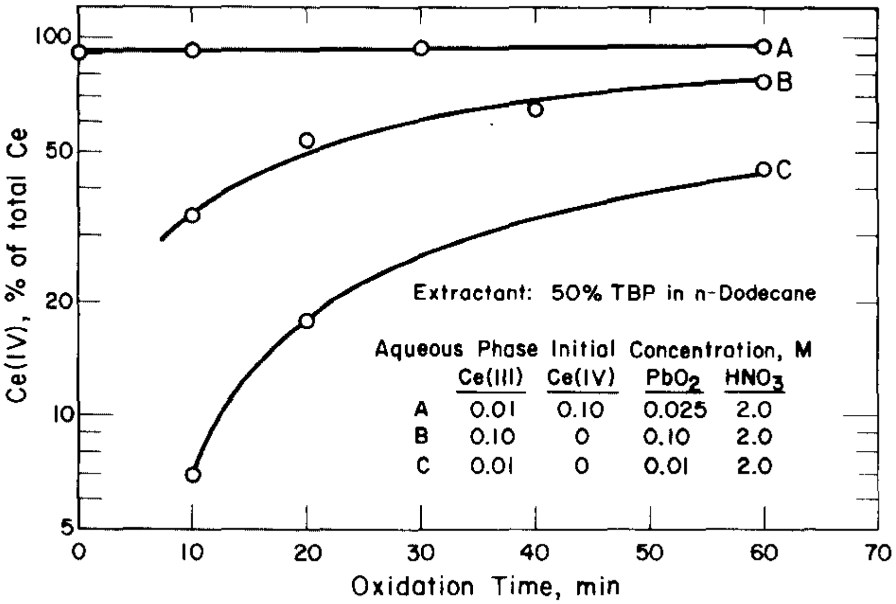

FIG. 5 OXIDATION OF Ce(III) WITH PbO_2 AS A HOLDING OXIDANT

A second improvement was to use a miniature centrifugal extractor[17] for rapid phase separations. If a feed solution were reasonably free of contaminants such as Cr(III) which reduce the Ce(IV), a centrifugal extractor could eliminate the need for a holding oxidant by reducing the time during which Ce(IV) is in the organic phase. With a feed solution containing 1260 Ci/ℓ of ^{144}Ce, 72% of the cerium was removed with a miniature centrifugal extractor at a Ce(IV)/Ce(III) ratio of ∿6 (83% theoretical rejection).

Several other oxidants were evaluated for cerium removal with TBP extraction, but they did not give satisfactory separations. Sodium dichromate gave excellent oxidation at tracer concentrations of cerium, but was not a sufficiently strong oxidizing agent if larger amount of cerium or small amounts of Cr(III) were present. Silver-catalyzed persulfate, which gave good separations with di-2-ethylhexylphosphoric acid,[14] gave poor separations with TBP because sulfate, formed by reduction of persulfate, complexes Ce(IV) and suppresses its extraction. Sodium paraperiodate, $Na_3H_2IO_6$, did not oxidize cerium in HNO_3 solution. Lead tetraacetate was hydrolyzed to insoluble PbO_2 before significant oxidation occurred.

PLANT TEST RESULTS

In two plant tests, ^{147}Pm was recovered from waste solutions. Approximately 500 g of ^{147}Pm in a lanthanide mixture were accumulated from waste solutions generated in processing irradiated natural uranium. Phase separation was hindered in the first extractions by ∿5 vol % of solid siliceous material in the feed. The solids were removed by settling and decanting before batch extraction with 50% TBP. The solutions were adjusted to 6.0 - 6.5M NO_3^- as aluminum or sodium salts and to 0.5 - 0.8M HNO_3 before extraction.

In the second test, approximately 2.5 kg of ^{147}Pm in a lanthanide mixture was recovered from high activity waste resulting from processing of enriched uranium fuel. Incidentally produced plutonium isotopes were also recovered in this test, although removing Pu(IV) from the organic phase vas very difficult unless 2 to 3 back extractions were made with ferrous sulfamate as the reductant. Promethium recovery was about 97%, and plutonium recovery was about 95%. Difficulty in plutonium reduction and removal from the organic phase was probably caused by dibutylphosphate produced in the radiolysis of TBP. Sulfate from the ferrous sulfamate caused precipitation of the lanthanides after several-fold evaporation, although the precipitate was subsequently dissolved by refluxing with ∿5M HNO_3. Plutonium was separated from the lanthanides by a further batch extraction with 50% TBP, as described on page 10.

The two plant tests demonstrated that ^{147}Pm can be recovered by batch extraction with 50% TBP and the recovery agrees with that predicted by extraction data shown in earlier sections of this report.

Approximately one g of ^{147}Pm from the first plant test was used to demonstrate separation of promethium from the other lanthanides[18] by displacement chromatography at high pressure. As a part of the feed preparation for the ion exchange test, the ^{144}Ce was separated by electron exchange with a miniature centrifugal extractor, with 70% ^{144}Ce removal. A full-scale plant test has not been conducted.

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REFERENCES

1. "Use of Isotopic Power to Drive an Artificial Implated Human Heart." *Nucleonics Week 6,* No. 23, 5 (1965).

2. T. A. Butler and E. E. Ketchen. "Solvent Extraction Separation of Cerium and Yttrium from Other Rare Earth Fission Products." *Ind. Eng. Chem. 53,* 651 (1961).

3. L. A. Bray and F. P. Roberts. *Separation of Trivalent Rare Earths from Cerium.* USAEC Report HW-78987 Rev, General Electric Co., Hanford Atomic Products Operation, Richland, Wash. (1963).

4. L. A. Bray and F. P. Roberts. *Purification of Rare Earths from Hanford Wastes by Solvent Extraction.* USAEC Report BNWL-C-92, Battelle-Northwest, Pacific Northwest Laboratory, Richland, Wash. (1965).

5. H. E. Henry. *Isolating Americium and Curium from* $Al(NO_3)_3$ - $NaNO_3$ - HNO_3 *Solutions by Batch Extraction with Tributyl Phosphate.* USAEC Report DP-972, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1965).

6. W. L. Poe, A. W. Joyce, and R. I. Martens. "^{237}Np and ^{238}Pu Separation at the Savannah River Plant." *Ind. Eng. Chem.,* *Proc. Design Develop. 3,* 314 (1964).

7. D. F. Peppard, J. P. Faris, P. R. Gray, and G. W. Mason. "Studies of the Solvent Extraction Behavior of the Transition Elements. I. Order and Degree of Fractionation of the Trivalent Rare Earths." *J. Phys. Chem. 57,* 294 (1953).

8. H. A. C. MacKay, K. Alcock, and D. Scaigell. *The Extraction of Some Rare Earths by Tributyl Phosphate.* USAEC report AERE-C/R-1514, Atomic Energy Research Establishment, Harwell, England (1954).

9. H. J. Groh and C. S. Schlea. "The Recovery of Neptunium-237 and Plutonium-238." *Progress in Nuclear Energy, Series III, Process Chemistry, Volume 4,* Pergamon Press, Ltd., Oxford (1970).

10. J. C. Warf. "Extraction of Cerium(IV) Nitrate by Butyl Phosphate." *J. Am. Chem. Soc. 71,* 3257 (1949).

11. J. Kleinberg, W. J. Argersinger, Jr., and E. Griswold, *Inorganic Chemistry*, p. 113, D. C. Heath and Company, Boston, Mass. (1960)

12. E. J. Wheelwright and N. C. Howard. *The Separation of Cerium from the Trivalent Rare Earths Using Hydrogen Peroxide and Sodium Acetate.* USAEC Report HW-62505, General Electric Co., Hanford Atomic Products Operation, Richland, Wash. (1960).

13. V. I. Levin, G. V. Korpusov, N. M. Man'ko, E. N. Patrusheva, N. P. Prokhorour, and G. F. Platnov. "Extraction of Tetravalent Cerium by Organic Solvents." *At. Energ. (USSR) 15*, 138 (1963).

14. R. E. Lerch. *Oxidation of Cerium by Ozone and by Electrolysis.* USAEC Report BNWL-805, Battelle-Northwest, Pacific Northwest Laboratory, Richland, Wash. (1965).

15. G. L. Richardson. *Continuous Separation of Cerium from the Trivalent Rare Earths by Persulfate Oxidation and D2EHPA Solvent Extraction: Pilot Plant Studies.* USAEC Report BNWL-173, Battelle-Northwest, Pacific Northwest Laboratory, Richland, Wash. (1965).

16. J. W. Gryder and R. W. Dodson. "Kinetics of the Exchange Reaction Between the Two Oxidation States of Cerium in Acid Solutions." *J. Am. Chem. Soc. 73*, 2890 (1951).

17. A. S. Jennings. *A Miniature Centrifual Contactor.* USAEC Report DP-680 E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1962).

18. J. T. Lowe. *Isolation of ^{147}Pm by Rapid Cation Exchange Chromatography.* USAEC Report DP-1194, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1969).

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