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CURIUM-244 ISOTOPIC POWER FUEL — CHEMICAL RECOVERY FROM COMMERCIAL POWER REACTOR FUELS*

John C. Posey
Isotopes Development Center
Oak Ridge National Laboratory
Post Office Box X
Oak Ridge, TN 37830

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ABSTRACT

The properties of $^{244}Cm_2O_3$ make it attractive as a radioisotopic power source material for any of several types of electrical power generators. Production quality $^{244}Cm_2O_3$ yields 27 W/cm^3 which is higher than the volume yield of most competing heat source materials. The half-life, 18.1 years, is adequately long for most applications. It emits some gamma and neutron radiation, but this does not prevent its use in many applications.

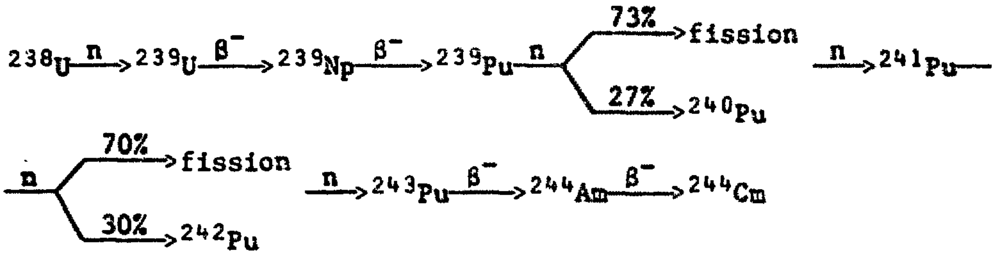
Curium is present in wastes resulting from the reprocessing of the irradiated fuel of nuclear power reactors. Consequently, a large potential supply will be available in future years. Estimates indicate that its cost will be substantially lower than that of ^{238}Pu.

A proposed process for curium recovery based on existing technology is outlined. A fraction containing the lanthanides and trivalent actinides is prepared using differential solvent extraction. Since this method of extraction is not widely known, it is described in some detail. The curium is separated from the lanthanides by a high pressure ion-exchange system.

INTRODUCTION

Curium-244 is one of the most attractive radioactive heat source materials. It scores high with respect to power density, availability, and physical and chemical properties. It is expected to be less costly than ^{238}Pu which is presently used in aerospace isotopic power generators. It emits comparatively little gamma radiation but does emit some high-energy neutrons because of the spontaneous fission of a very small fraction of the ^{244}Cm atoms. This paper reviews the properties of $^{244}Cm_2O_3$ and outlines a process for its recovery.

Curium-244 is formed in the operation of a nuclear reactor, primarily by the following sequence of neutron capture and beta decay reactions:



$$^{238}U \xrightarrow{n} {}^{239}U \xrightarrow{\beta^-} {}^{239}Np \xrightarrow{\beta^-} {}^{239}Pu \xrightarrow{n} \left\langle \begin{array}{l} \xrightarrow{73\%} \text{fission} \\ \xrightarrow{27\%} {}^{240}Pu \end{array} \right. \xrightarrow{n} {}^{241}Pu \xrightarrow{n} \left\langle \begin{array}{l} \xrightarrow{70\%} \text{fission} \\ \xrightarrow{30\%} {}^{242}Pu \end{array} \right. \xrightarrow{n} {}^{243}Pu \xrightarrow{\beta^-} {}^{244}Am \xrightarrow{\beta^-} {}^{244}Cm$$

Other reactions also occur and other actinide isotopes are formed. All of these substances accumulate in the uranium during reactor operation.

The trivalent actinides (primarily americium and curium) are separated along with the fission products in fuel recovery processing. The total amounts of curium which will be available in these wastes have been estimated[1] and are given in Table 1.

Table 1. Projected ^{244}Cm Available (Ref. 1) in Fission-Product Waste

Year	Annual Production of ^{244}Cm (kg)	Total Accumulated ^{244}Cm (kg)
1980	90	370
1990	220	1720
2000	280	3200

Most of the ^{244}Cm produced thus far has been made by the irradiation of mixed plutonium isotopes in the Savannah River plant reactors. The curium was separated by solvent extraction and high-pressure ion exchange in a comparatively small-scale operation. The term "production curium" refers to this material; curium made and separated by our process should be quite similar in properties.

The sesquioxide, Cm_2O_3, is the preferred compound of curium for heat source applications and has been investigated extensively. Other compounds such as the silicides, carbides, nitrides, sulfides, oxysulfides, phosphides, phosphosulfides, and borides have been studied to a limited degree.[2-5] In 1969 Rimshaw and Ketchen[6] summarized the then known properties of ^{244}Cm metal, $^{244}Cm_2O_3$, Cm_2O_2S, and CmF_3. More recently, McHenry[7] reviewed the current status of $^{244}Cm_2O_3$ technology.

Some of the properties of $^{244}Cm_2O_3$ are given in Table 2. The specific power (power production per unit weight) and power density (power production per unit volume) are higher than those of any competing radioisotope of reasonably long half-life. The high melting point and low vapor pressure show that Cm_2O_3 is a highly refractory material; it is compatible with high-temperature structural metals. Tests of up to 10,000-hr duration at 1650°C and 1850°C showed that Cm_2O_3 did not interact appreciably with tungsten, molybdenum, or tungsten-rhenium alloys. It did interact appreciably with tantalum and tantalum alloys.[13]

Table 2. Properties of $^{244}Cm_2O_3$ (Ref. 13)

Property	Value
Half-life	18.1 yr
Theoretical density at 25°C (Ref. 8)	11.7 g/cm^3
Specific power, pure $^{244}Cm_2O_3$ (Refs. 6-7)	2.58 W/g
Specific power, production $^{244}Cm_2O_3$ (Ref. 7)	2.45 W/g
Power density, production $^{244}Cm_2O_3$[a] (Ref. 6)	27 W/cm^3
Melting point (Refs. 9-10)	2220 to 2277°C
Vapor pressure at 1400°C	10^{-10} atm.[a]
Thermal conductivity (Ref. 12),	
25°C	0.023 W/cm·°C
1000°C	0.017 W/cm·°C

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[a] Material at 95% of theoretical density.

[b] Calculated from equation of Smith and Peterson[11] based on Knudsen cell data.

The radiation characteristics of $^{244}Cm_2O_3$, as reported by Stoddard,[14] are compared to those of $^{238}PuO_2$ in Table 3. The radiation from $^{244}Cm_2O_3$ does not seriously affect equipment or instruments unless sensitive radiation measurements are being made. Thus, Cm_2O_3 has potential for use in many space applications.

Like all alpha-emitting radioactive materials, ^{244}Cm produces helium as a result of radioactive decay. Helium is generated throughout the solid material and must diffuse to the surface to escape. These phenomena have been investigated by Angelini for both $^{244}Cm_2O_3$ (ref. 15) and PuO_2 (ref. 16). The rate of diffusion increases with temperature and with radiation damage. Experience indicates that at temperatures above approximately 1100°C the accumulation of helium does not greatly affect the properties of the solid. Long-range test data at lower temperatures are lacking.

The future cost of ^{244}Cm will depend largely on the cost of recovery from the wastes of the fuel reprocessing industry. No cost estimates are given in this paper for the process described. Earlier estimates of the comparative costs of electrical power produced by ^{244}Cm and by ^{238}Pu are compared in Table 4.

Table 3. Summary of Radiation Characteristics of $^{244}Cm_2O_3$ and $^{238}PuO_2$ (Ref. 14)

Energy Range (MeV)	$^{244}Cm_2O_3$	$^{238}PuO_2$
	X-Ray Photons/sec/W	
0.017	1.7×10^{11}	1.5×10^{11}
	Gamma Photons/sec/W	
0.0-0.5	3×10^{8}	5.2×10^{8}
0.5-1.0	2×10^{7}	$\sim 5 \times 10^{5}$
1.0-2.0	4.9×10^{6}	
2.0-3.0	1.6×10^{6}	
3.0-4.0 S.F.[a]	1.9×10^{5}	$\sim 1.1 \times 10^{4}$
4.0-5.0	6.4×10^{4}	
5.0-6.0	3.3×10^{4}	
6.0-7.0	5.6×10^{3}	
	Neutrons/sec/W	
S.F.[a] Spectrum	4.6×10^{6}	4.7×10^{3}

[a] Spontaneous fission.

Table 4. Comparison of Space Electric Power Costs (Ref. 7)

System	Power (W_e)[a]	Power Cost ($\$/W_e$)[a] Without Fuel Recovery	Power Cost ($\$/W_e$)[a] Fuel Recovered After 5 Years
Plutonium — MHW[b]	150	12,000	4,500
Curium — MHW[b]	150	3,850	2,500
Plutonium — Brayton[c]	1,000	2,900	650
Curium — Brayton[c]	1,000	900	400

[a] Watts of electric power generated.

[b] Multihundred watt radioisotope thermoelectric generator.

[c] Brayton-cycle turbine and electrical generator.

CRITERIA AND CONCEPT OF PROCESS

A preliminary design was made for a process to recover curium from fission-product waste. In addition to the normal requirements of technical feasibility, economy, and safety, the following requirements were imposed in the design of the process:

1. The volume of solid radioactive waste cannot be increased substantially.
2. The process equipment must be versatile.
3. The capital cost should be low.

The first of these requirements is related to the expensive safety requirements for the storage of radioactive waste. The other two reflect the uncertain demand for radioisotopic power fuels at the present time. Future developments may lead to the large-scale demand for other components of the fission-product mixture.

The process we have proposed is based on known technology and is technically feasible. However, available data are not sufficiently complete for the design of an optimum flow sheet. The process is designed so that it can be applied to the waste solution from the Purex process or to leached solid oxide waste. The calculated major components of a reference waste mixture[1] per metric ton of fuel charged to the reactor and their rates of heat production are given in Table 5.

Table 5. Principal Components of Waste Mixture (Ref. 1)

Diablo Canyon Reference LWR — Waste Decay Times (Processed 90 days)
Power = 30.00 MW/metric ton, Burnup — 33,000 MWd/metric ton,
Flux — 2.91×10^{13} n/cm^2•sec

Element	Mass[a] (g)	Heat Generated[a] (W)
Rb	334	
Sr	885	118
Y	465	480
Zr	3660	146
Nb	1.5	280
Mo	3460	0
Tc	835	0
Ru	2220	23
Rh	392	2640
Pd	1330	—
Te	566	—
I	273	—
Cs	2683	2000
Ba	1430	200
La	1270	—
Ce	2780	401
Pr	1200	3390
Nd	4000	—
Pm	91	44

Table 5. Continued

Element	Mass[a] (g)	Heat Generated[a] (W)
Sm	823	—
Eu	180	67
Gd	105	—
U	4780	—
Np	762	1
Pu	50	2.8
Am	144	6.3
Cm	31.9	315

[a] Per metric ton of original fuel after 1-year decay.

The separation process consists of the following major steps which also are illustrated in Fig. 1:

1. The zirconium, uranium, plutonium, and neptunium are removed from the fission-product mixture by differential solvent extraction using tributylphosphate (TBP).
2. A lanthanide-actinide fraction (containing the curium) is recovered from the mixture by differential solvent extraction using TBP.
3. Curium is separated from the lanthanides and other trivalent actinides by high-pressure cation exchange.

TBP was chosen tentatively as the extractant because of its availability and because of the large body of knowledge concerning its behavior. Differential extraction, described by McHenry, Posey, and Baker,[17] was chosen as the most suitable mode of carrying out the extraction processes. The high-pressure (1000 psi) ion-exchange process[25] applied by Savannah River Laboratory uses Dowex 50-X8 cation exchanger and DTPA complexing agent. It was chosen because of its proven effectiveness.

DIFFERENTIAL EXTRACTION

Differential extraction is not a widely known liquid-liquid extraction technique and consequently will be described in some detail here. It is analogous to a Rayleigh distillation. Typical differential extraction stages are shown in Fig. 2. The

FIGURE LIST

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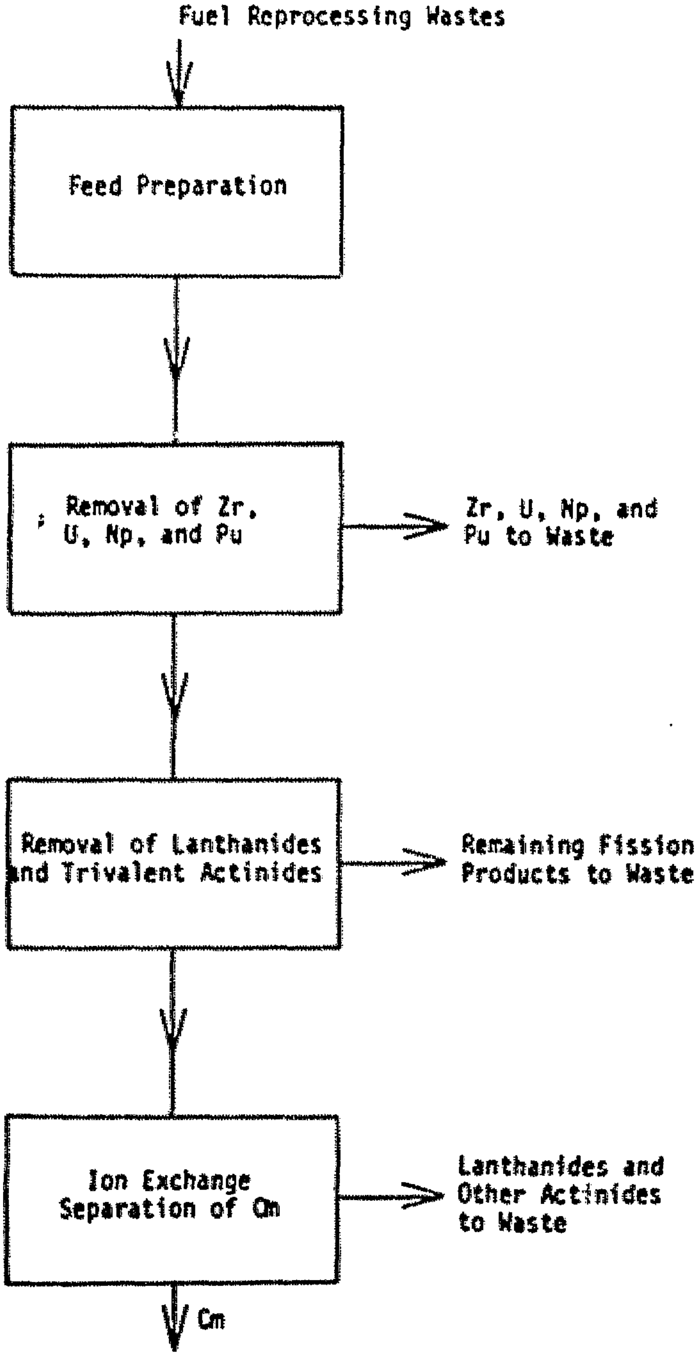
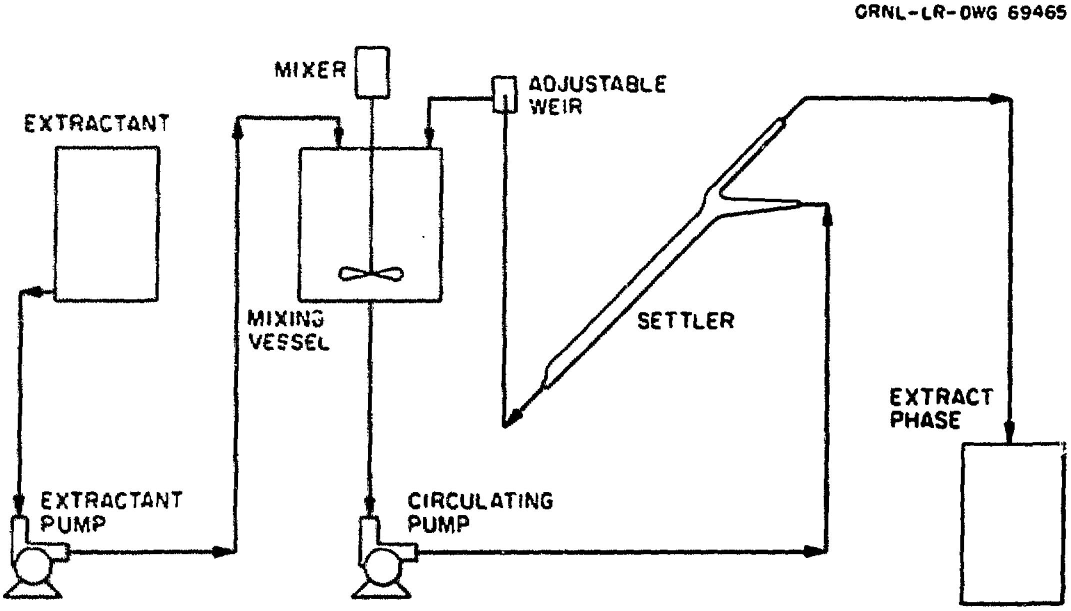
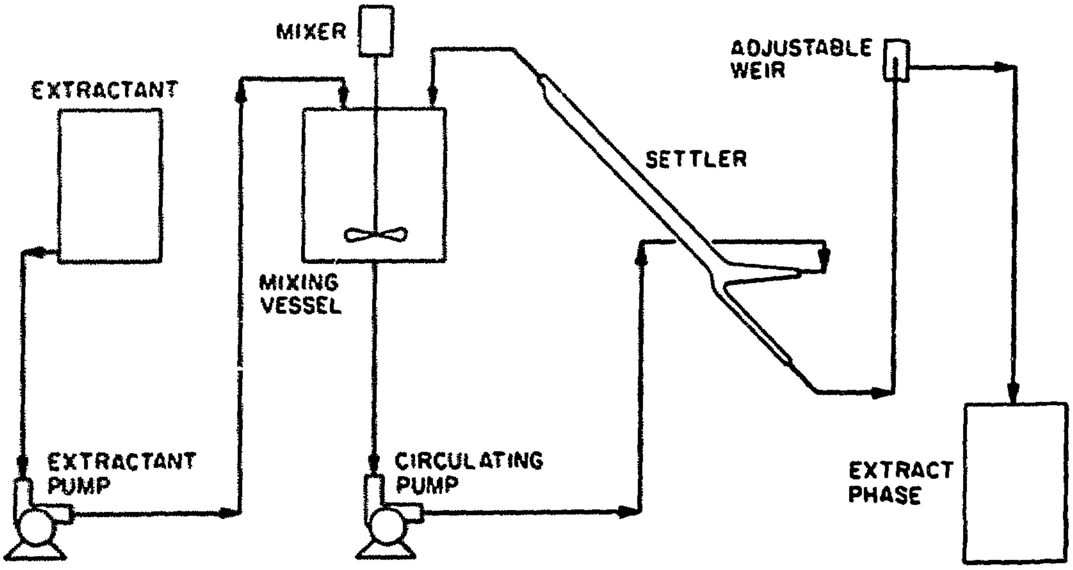




(a) APPARATUS WITH LIGHT PHASE AS EXTRACTANT (FIRST CYCLE)



(b) APPARATUS WITH HEAVY PHASE AS EXTRACTANT (SECOND CYCLE) mixing vessel holds a quantity of the original solution containing the solutes which are to be extracted. This solution remains in the stage and will be called the resident phase. A steady stream of the extractant enters the mixing vessel where it is thoroughly dispersed by vigorous agitation. A stream of the mixed phases is continuously circulated through the settler where the extractant is separated and leaves the stage. The resident phase returns to the mixing vessel.

An equation describing the extraction of a solute is derived with the following simplifying assumptions:

1. The distribution coefficient, D, of the substance being extracted is constant. D is defined as the ratio of concentration in extractant phase to concentration in the resident phase.
2. Because of a high circulation rate and small holdup in the settler the compositions of both phases at any time are essentially uniform.
3. The volumes of the phases do not change appreciably during extraction.
4. The mutual solubility of the two phases is negligible.

The derivation is based on a material balance on the stage. A differential volume of extractant dE enters the stage, and at the same time an equal volume dE leaves the stage. The resulting removal of extractable solute is given by Eq. (1):

$$YdE = -(SdX + HdY) \quad (1)$$

where

E = volume of extractant,

Y = concentration of solute in the extractant phase,

X = concentration of solute in resident phase,

S = volume of the resident phase, and

H = volume of extractant phase held up in dispersed form.

Equation (2) is obtained by substituting DX for Y, rearranging, and integrating:

$$E/S = (1/D + H/S) \ln (X_1/X_2) \quad (2)$$

The ratio, H/S, becomes very important when the process is used to separate one solute from a less extractable solute. The distribution coefficient, D, is the only quantity which is peculiar to a specific solute and H/S is additive to 1/D. It follows that a sharp separation between solutes will be favored by a small value of H/S as compared to 1/D. Furthermore, little will be gained by having a very large D unless H/S is very small.

The value of H/S can be reduced by increasing the rate at which the mixed phases are circulated through the settler. A small-volume, high-capacity settler or centrifuge is desirable. Another effective method of reducing H/S is based on the fact that point values of H/S sometimes vary greatly with location in the mixing vessel because of centrifugal and gravitational effects. If the recycle stream is removed at a point where the ratio is high, the effective capacity of the settler is increased and the average value of H/S is reduced. Reducing the rate at which the extractant passes through the stage also reduces H/S. However, this is undesirable since it increases the time required for the extraction. Values of H/S of 0.01 are obtainable with reasonably high extractant flow rates.

Any given unit of extractant remains in the stage only a short time as it passes through. Thus, the contact time for the extractant is short. It is equal to the extractant holdup divided by the extractant flow rate. The contact time of the resident phase is equal to the total time of the extraction. A short contact time is desirable when an organic extractant is used to extract material from a highly radioactive solution, since the radiation damage is proportional to the exposure time. However, if an extraction system exhibiting slow kinetics is used, a short contact time may not be feasible.

In most real extractions the distribution coefficients change during the extraction because of changes in solvent loading. The amount of extractant required for a given removal of a single solute can be estimated by a stepwise calculation using Eq. (3):

$$E = \Sigma\Delta E = \sum_{X_2}^{X_1} \frac{S\Delta X + H\Delta Y}{Y_{av}} \qquad (3)$$

A graph of Y as a function of X can be used to evaluate ΔX, ΔY, and Y_{av}.

Equation (4) can be used to estimate the extraction of a solute, B, of low distribution coefficient in the presence of a solute, A, of much higher distribution coefficient.

$$Y_B(av) = X/E \; \Sigma D_B \Delta E \qquad (4)$$

The solvent loading for the different ΔE intervals will be known if Eq. (3) has been used to calculate the extraction of solute A. The corresponding values of D_B can be measured or estimated.

Differential extraction has certain advantages over multiple stage countercurrent extraction:

1. The contact time of an organic extractant with a radioactive solution can be very low. The contact times for the two extractions in our process are only 1.5 and 1.1 min. Of course, if the radioactive material itself is extracted, it must be quickly stripped from the extractant to minimize radiation damage.
2. Several consecutive extractions of widely differing nature can be carried out easily without removing the resident phase from the mixing vessel. This can be

done by changing extractants or by altering the solution by the addition of an acid, salting agent, or a complexing agent.

3. Start-up and shutdown problems are minor.
4. The cost of equipment is lower.

Differential extraction gives much sharper separations than simple batch extractions. This is illustrated by the following example. Suppose that two solutes, A and B, are contained in 10 liters of aqueous solution. An extraction is carried out using 10 liters of extractant. The distribution coefficients for A and B are 10 and 0.1, respectively, and the H/S ratio for the differential extraction is 0.01. Calculation using Eq. (2) shows that only 0.011% of solute A will remain in solution after the differential extraction but 9.09% will remain after a simple batch extraction. The differential extraction will remove slightly more of solute B than the batch extraction, 9.5% vs 9.1%. The 94.5% residue of B has a high degree of purity with respect to A. Component A is recovered with great efficiency but it is not pure. If the A also is required in pure form, a second differential extraction can be made; now the organic solution is the resident phase and an aqueous solution is the extractant. In this case the amount of solute B in the A fraction can be reduced to 0.011% by 2.3 liters of extractant. This extractant will contain 2.28% of the original solute A.

Differential extraction has been used on a fairly large scale only once.[17] We recovered 15 kg of high ^{235}U assay uranium using two comparatively primitive differential extraction stages. More than 99% of the uranium was recovered. The overall decontamination factor was $>10^6$.

PROCESS FEED

The waste from one metric ton of recovered uranium was chosen as a unit batch for process design. This raw material will consist of essentially pure fission-product oxides. Estimates are based on the composition of one-year-old Diablo Canyon wastes[1] from reactor fuel with a burnup of 33,000 MWd/metric ton carried out at a 30-MW per metric ton power level. This waste contains 31.9 g of curium mixed with about 37,000 g of fission products and actinides per metric ton of original fuel. The wastes will produce about 10 kW of heat by radioactive decay. The composition of this waste was given in Table 5. The selection of one-year-old waste for preliminary estimates is based on the availability of data. Older waste would be preferable because of the reduced heat generation and radiation damage to solvents and resins and the elimination of ^{242}Cm by decay.

Because of heat dissipation problems, the minimum aqueous volume for the fission products from one metric ton of fuel is 600 liters when one-year-old waste is used. This volume was calculated by assuming an agitated, water-jacketed cylindrical vessel (H = D), an allowable temperature rise of 10°F, and an overall heat transfer coefficient of 80 Btu hr^{-1} $°C^{-1}$ ft^{-2}.

ZIRCONIUM, URANIUM, PLUTONIUM, AND NEPTUNIUM REMOVAL

A preliminary zirconium removal step is included in the process because this major fission product would extract with the curium and lanthanides. This step also separates the uranium, plutonium, and neptunium left by the fuel recovery process. Zirconium could be separated in the final ion-exchange process; however, this would require an increase in the size of this operation.

The batch of solid nuclear waste is first dissolved in nitric acid to produce 600 liters of solution, 10 *M* in nitric acid. If liquid Purex waste is used, the volume and acid concentration will be adjusted by distillation. The solution is placed in the mixing vessel of the differential extraction stage, and the extraction is carried out using 850 liters of 19% TBP in normal paraffin hydrocarbon (NPH) dilutent. The calculated results, by Eqs. (3) and (4), are given in Table 6. The effects of solvent loading were calculated using the knowledge that each extracted Zr, U, Pu, and Np ion is associated with two TBP molecules in the organic phase[18] and assuming that the distribution coefficients were proportional

Table 6. Removal of Zr, U, Np, and Pu by Differential Extraction

Element	Percent Removed
Zirconium	99.9
Uranium	>99.95
Plutonium	>99.95
Neptunium	94
Curium	0.4

to the square of the free TBP concentration. The distribution coefficients at zero loading are 11, 11, and 3 for U, Pu, and Np, respectively.[19] At zero loading, a distribution coefficient of 8.0 was used for zirconium.[20]

The value of the distribution coefficient of curium between 19% TBP and 10 *M* nitric acid was estimated from the distribution coefficient obtained using 100% TBP by Best, Hesford, and McKay[21] and the concentration dependencies observed with similar materials. The americium distribution coefficient is reported by Walsh[22] to vary as the 2.87 power of the TBP concentration. Scargill *et al.*[23] report that the distribution coefficients of yttrium and cerium vary as the 2.7 power of the TBP concentration. The corresponding values of the distribution coefficient at a 19% TBP concentration were calculated to be 0.0034 and 0.0045. The curium loss was calculated using the higher of these values in Eq. (4). The calculations assumed that equilibrium is reached in the extraction for all solutes.

The zirconium fraction could be scrubbed free of curium and rare earths by a second differential extraction using 10 *M* nitric acid as the extractant, but the recovery of 0.4% of the curium does not justify this step. The zirconium will be stripped from the TBP using water as an extractant. The water extracts the nitric acid dissolved in the TBP. As the nitric acid concentration in the solvent becomes low, the distribution coefficients of all the solutes greatly favor the aqueous phase and the solutes are rapidly removed. If equilibrium distribution coefficients are obtained, 99.9% of the zirconium will be removed by only 290 liters of strip solution, but 555 liters will be required for 99.9% removal of the uranium. Alternately, the TBP could be stripped of zirconium by a batch extraction. The addition of a suitable complexing agent to the aqueous phase would be advantageous in stripping the zirconium.

LANTHANIDE-ACTINIDE EXTRACTION

The zirconium-free solution will be adjusted to an acidity of 15.6 *M* prior to the lanthanide-actinide extraction. This will be done by a combination of distillation and the addition of concentrated HNO_3.

The lanthanide-actinide fraction will then be extracted in 2 hr, using 655 liters of 100% TBP. Results given in Table 7 were calculated using Eq. (3) and the data of Best, Hesford, and McKay[21] and of Scargill.[24]

The effects of solvent loading were estimated assuming that each lanthanide or actinide ion combined with three TBP molecules[18] and that the distribution coefficients were proportional to the cube of the concentrations of free TBP.

A simplifying assumption was made to avoid the complexity caused by the simultaneous loading effects of nine different

Table 7. Calculated Results on Differential Extraction of Lanthanides and Actinides

Element	% Extracted	Weight Extracted (g)
Curium	99.0	32
Americium	90	127
Europium	99.99	180
Samarium	99.8	823
Promethium	96.8	89
Neodymium	84.2	3370
Praseodymium	57	690
Cerium	35	980
Lanthanum	24	315

components. It was first assumed that all of the components had the same distribution coefficient as neodymium. (Neodymium is the most plentiful material and has an approximate average distribution coefficient.) A curve of neodymium concentration in the aqueous phase as a function of extractant volume was plotted using Eq. (3). It was then assumed that the value of $\ell n\ (x_1/x_2)$ for curium differed from $\ell n\ (x_1/x_2)$ for neodymium by the ratio $(1/D_{Nd} + H/S)/(1/D_{Cm} + H/S)$. Using this assumption $\ell n\ (x_1/x_2)$ for neodymium at 99% curium extraction was determined, and then using this value and the curve, the volume of extractant was determined. The degrees of extraction of the other solutes were determined using the same method of comparison to neodymium.

Fortunately, much of the cerium and lanthanium is left in the aqueous phase in this extraction. Cerium-144 and its short-lived daughter, ^{144}Pr, are the chief sources of radiation damage and of radioactive heat in this material. Also, a worthwhile reduction in the scale of the following ion-exchange step is achieved.

The curium is removed from the TBP by differential extraction using water as the extractant. Again, all of the distribution coefficients favor the aqueous phase when the nitric acid is stripped from the TBP. The use of 695 liters of water (E/S = 1.06) will remove 99% of the curium, and 879 liters (E/S = 1.34) will remove 99.9% of the curium. If the larger volume of water were used, the TBP would not require cleaning before reuse. All of the remaining lanthanides are stripped with the curium.

An alternate method of stripping the curium and lanthanides from the TBP would be used if the fission products were fresh enough so that radiation damage to the TBP were a serious problem. The TBP would pass directly into a batch extractor for quick removal of the radioactive material. The acid content of the strip solution will be reduced to ~1 *M* by distillation before it is used as feed for the following ion-exchange process.

ION-EXCHANGE PURIFICATION OF CURIUM

This process is based on a high-pressure chromatographic cation-exchange process which has been used at Savannah River for the recovery of curium from smaller batches of material.[25] In the Savannah River process the material is eluted at 70°C through four high-pressure ion-exchange columns in series. The process uses Dowex 50-X8 ion exchanger of 25-55 micron particle size. The eluant is a 0.05 *M* solution of DTPA (diethylenetriaminepentaacetic acid) adjusted to a pH of 6 with ammonium hydroxide. The separating power of the process results from the selective complexing action of the DTPA. The components are eluted from the column in the following order: Cf, Bk, Cm, Am, Eu, Sm, Pm, Nd, Pr, Ce, and La.

In our feed material considered here, due to its source, the ratio of curium to lanthanides is much less favorable than in the Savannah River operation. Consequently, a rough preliminary separation is indicated to produce a concentrated curium fraction.

This ion-exchange operation disposes of about 95 mole % of the impurities and about 80% of the heat-producing radioisotopes. The remaining batch of actinide-lanthanide elements is similar in total size to that used in the Savannah River operation. This preliminary cation-exchange step requires 42 columns (4 ft long and 3 in. diam) operating in parallel. The maximum column diameter is limited by heat dissipation considerations. The heat of radioactive decay is generated throughout the loaded resin and it must flow to surfaces to escape. The temperature difference between the center and the surface of the column is estimated to be about 30°C for a 3-in.-diam column. This temperature gradient causes a viscosity difference which results in a nonuniform flow of liquid within the ion-exchange bed and is deleterious to separation in a chromatographic process. Furthermore, excessively high temperatures cause rapid deterioration of the resin. Larger diameter and fewer columns could be used for processing waste older than one year because of reduced heat generation from radioactive decay.

The eluent is passed through at a rate of 30 liters/min total flow and collected in a holdup tank. When the europium band begins to emerge as detected by gamma rays from $^{152-154}$Eu, it is estimated that nearly all of the curium has been removed from the columns and the elution can be stopped.

After concentration the lanthanide-actinide prepared fraction is loaded on the first of four columns in series. The columns become progressively smaller (4, 3, 2, and 1 in.) in diameter. The curium is eluted through the columns — the flow being reduced as the curium band moves from larger to smaller columns. The curium fraction from the last column is collected. This solution is acidified and concentrated. The DTPA is destroyed by the alpha radiation from the curium.

The curium product will still contain an appreciable amount of americium, which can be separated by an additional small-scale ion-exchange process or by the precipitation process described by Burney.[26] In the latter process, $K_3AmO_2(CO_3)_3$ is precipitated from a K_2CO_3 solution. The curium remains in solution as a soluble carbonate complex recoverable by hydroxide precipitation. An ^{241}Am-^{243}Am mixture will be a by-product. This mixture could be reactor irradiated to produce ^{242}Cm and ^{244}Cm; ^{242}Cm decays to ^{238}Pu.

PROCESS VARIATIONS

If the proposed curium recovery process were applied to solid calcined oxide waste some substantial improvements could be made. The bulk of the actinides plus some other fission products could be dissolved, leaving most of the cerium as solid oxides. This would eliminate 37% of the total heat of radioactive decay of one-year-old wastes and 87% of the heat associated with the lanthanides and trivalent actinides. Heat dissipation problems and radiation damage would be reduced and the use of more concentrated solutions or larger batch sizes would be feasible.

If reactor fuel reprocessing waste substantially free of U, Np, and Pu were available, another simplification of the process would be possible. The zirconium removal step could be carried out using the same 15.7 *M* acid concentration used in the subsequent lanthanide extraction. The lanthanide extraction could be carried out immediately without removing the solution from the extractor. The evaporation and acid addition necessary to change the nitric acid concentration from 10 to 15.7 *M* would be eliminated. The present process assumes that the original uranium recovery was 99.5% efficient. This leaves a significant amount of uranium with the waste. The distribution coefficient of uranium is too low for efficient uranium removal when 15.7 *M* acid is used.

PRODUCTION OF ADDITIONAL PRODUCTS

The elements of the process could be modified easily to give a variety of separated waste products other than curium when desired for the purpose of waste management or utilization. Californium and berkelium emerge from the first stage of ion exchange before the curium and could be recovered if the need were sufficient. If elution is continued after the removal of the curium, the lanthanides will emerge in separate bands and could be recovered. Further purification, however, would be required for thorough decontamination from radioactive cross contaminants Ce, Pm, and Eu.

Strontium-90 could be recovered from the aqueous solution after a prior extraction of the lanthanides and curium. If this were done, the solution would be neutralized to a pH of approximately 2 and the strontium extracted with 1 *M* di(2-ethylhexyl)-phosphoric acid. Many processes for the removal of ^{137}Cs are also available.

SUMMARY

Curium-244 is an attractive material for use as a radioactive heat source. It will probably be used as $^{244}Cm_2O_3$. It is present in the waste materials from the recovery of irradiated uranium fuel and is expected to be cheaper than ^{238}Pu. A process for the recovery of ^{244}Cm from fission-product wastes is outlined.

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