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Process for the Recovery of Curium-244 from Nuclear Waste

J. C. Posey

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PROCESS FOR THE RECOVERY OF CURIUM-244 FROM NUCLEAR WASTE

J. C. Posey

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ABSTRACT

A process has been designed for the recovery of curium from purex waste. Curium and americium are separated from the lanthanides by a TALSPEAK extraction process using differential extraction. Equations were derived for the estimation of the economically optimum conditions for the extraction using laboratory batch extraction data. The preparation of feed for the extraction involves the removal of nitric acid from the Purex waste by vaporization under reduced pressure, the leaching of soluble nitrates from the resulting cake, and the oxalate precipitation of a pure lanthanide-actinide fraction. Final separation of the curium from americium is done by ion-exchange.

The steps of the process, except ion-exchange, were tested on a laboratory scale and workable conditions were determined.

I. INTRODUCTION

1.1 Background

Curium-244 is potentially useful as a heat source for radioisotope-powered thermoelectric generators. The power density of $^{244}Cm_2O_3$ is roughly 5 times greater than that of $^{238}PuO_2$ and 20 times greater than that of $^{90}SrTiO_3$, the two isotopic materials used in most radioactive heat sources to date. In addition, because curium is present in nuclear wastes, it is potentially much less expensive than plutonium-238.

The amount of curium available will depend on the growth of nuclear fuel reprocessing and on the fuel cycles used. In general, the curium content of spent fuel increases as the total burnup increases, and it is higher for fuels with a low uranium-235 content than for fuels with a high uranium-235 content, given the same level of total burnup. Data given by Blomeke, Kee, and Nichol[1] indicate that use of a plutonium recycle produces spent fuel with a curium content 50 times higher than that produced from fuel containing uranium alone. The cost of curium production also will be sensitive to the curium content of the spent fuel, since the cost per unit of curium is approximately inversely proportional to the curium concentration.

1.2 Assumptions

The development of an economical process for the removal of ^{244}Cm from nuclear waste was based on the following assumptions.

1. The process will have low capital and operating costs.
2. A large supply of low cost nuclear waste will be available. The fraction of curium recovered from the waste is only important as it affects the cost per unit of curium recovered.
3. Ion exchange will be used for the final separation of curium from americium. This step results in good contamination with respect to most impurities. Consequently, separation steps earlier in the process are chosen for ease and speed of operation rather than for maximum decontamination.
4. The process will minimize the volumes of liquid and gaseous effluents.

It was also assumed that the process will use nuclear waste from the Barnwell Nuclear Fuel Plant, Barnwell, South Carolina. The waste from one metric ton of nuclear fuel has the composition shown in Table 1 and is dissolved in 150 gal of 3 *M* nitric acid. This waste contains a large amount of gadolinium added as a nuclear poison.

1.3 Previous Proposals

A process designed to separate curium from irradiated plutonium targets has been proposed by Weaver and Kappelman,[2] the developers of the TALSPEAK extraction process. In this flow sheet, the lanthanides and actinides are separated from other fission products by extraction from an aluminum nitrate solution with tributyl phosphate (TBP), and the americium and curium are then separated from the lanthanides by the TALSPEAK process in a multiple stage countercurrent unit. The TALSPEAK process chemistry differs principally from that described in this report in its use of lactic acid rather than glycolic acid and of diisopropylbenzene (DIB) rather than diethylbenzene (DEB) as a diluent for the di(2-ethylhexyl) phosphoric acid (HDEHP) in the aqueous phase.

A flow sheet designed by Koch et al.[3] calls for the destruction of the nitric acid by reaction with formic acid. After acid destruction the pH is high enough to precipitate essentially all of the zirconium, niobium, molybdenum, noble metals, and iron. The lanthanides and actinides remaining in solution are extracted with 0.3 *M* HDEHP and 0.2 *M* TBP in an alkane diluent. The americium and curium are then selectively removed from the organic phase with a version of the TALSPEAK process. They are extracted with an aqueous phase containing diethylenetriaminepentaacetic acid (DTPA) and lactic acid; the remaining lanthanides are removed in a third extraction using an organic phase of the same composition as above. All extractions are carried out in 16-stage countercurrent mixer-settler units with center feed. The americium and curium are removed from the aqueous phase by an ion exchange process.

This flow sheet was tested at a tracer level and worked as predicted, except for the last extraction. In this step, europium removal was poor because of slow extraction kinetics.

Table 1. Composition of nuclear waste

Element	Grams/metric ton of fuel
Selenium	14.4
Bromine	13.7
Rubidium	347
Strontium	823
Yttrium	416
Zirconium	3,710
Molybdenum	3,560
Technetium	822
Ruthenium	2,330
Rhodium	505
Palladium	1,520
Silver	82
Cadmium	136
Indium	1.2
Tin	25.7
Antimony	10.8
Tellurium	535
Cesium	2,600
Barium	1,750
Lanthanum	1,320
Gerium	2,540
Praseodymium	1,280
Neodymium	4,180
Promethium	35.6
Samarium	1,010
Europium	174
Gadolinium	122
Terbium	1.8
Uranium	10,000
Neptunium	482
Plutonium	100
Americium	525
Curium	24
Sodium	100
Iron	2,000
Chromium	200
Nickel	80
Gadolinium (added as nuclear poison)	9,000
PO_4	2,000
Total	54,376

This process was considered for use with waste from the Barnwell plant but rejected because

1. the added TBP lowers the distribution coefficients of the higher lanthanides, which makes the removal of the gadolinium more difficult, and
2. difficulties have been encountered in achieving a sufficiently high pH with the formic acid denitration process.

A flow sheet proposed by Wheelwright et al.[4] calls for the separation of the curium from the other waste components by means of a single large chromatographic ion exchange process. The feed preparation involves clarification by centrifugation; removal of remaining neptunium, uranium, and plutonium by TBP extraction; denitration by reaction with sugar; and a second clarification. The uranium and plutonium removal step will be required in any process using wastes of the type currently available.

1.4 Description of Process

The process flow sheet is shown in Fig. 1. The steps of the process are described here in brief; details and experimental verification are given in Sects. 2-7.

1.4.1 Removal of nitric acid

The nitric acid and water are removed from the Purex waste by distillation at reduced pressure while the temperature is increased to 150-170°C at ∿30 torr. The nitric acid is quantitatively condensed. Thus, noncondensable gaseous effluents are released only during the initial evacuation at room temperature and during the removal of a small amount of nitrogen oxides released above 130°C.

1.4.2 Dissolving lanthanide and actinide nitrates

Water is added to the solids remaining after the removal of nitric acid, and the resulting solution is boiled and stirred for 1-2 min. The pH of the solution at the end of this step is 1.5-2.0.

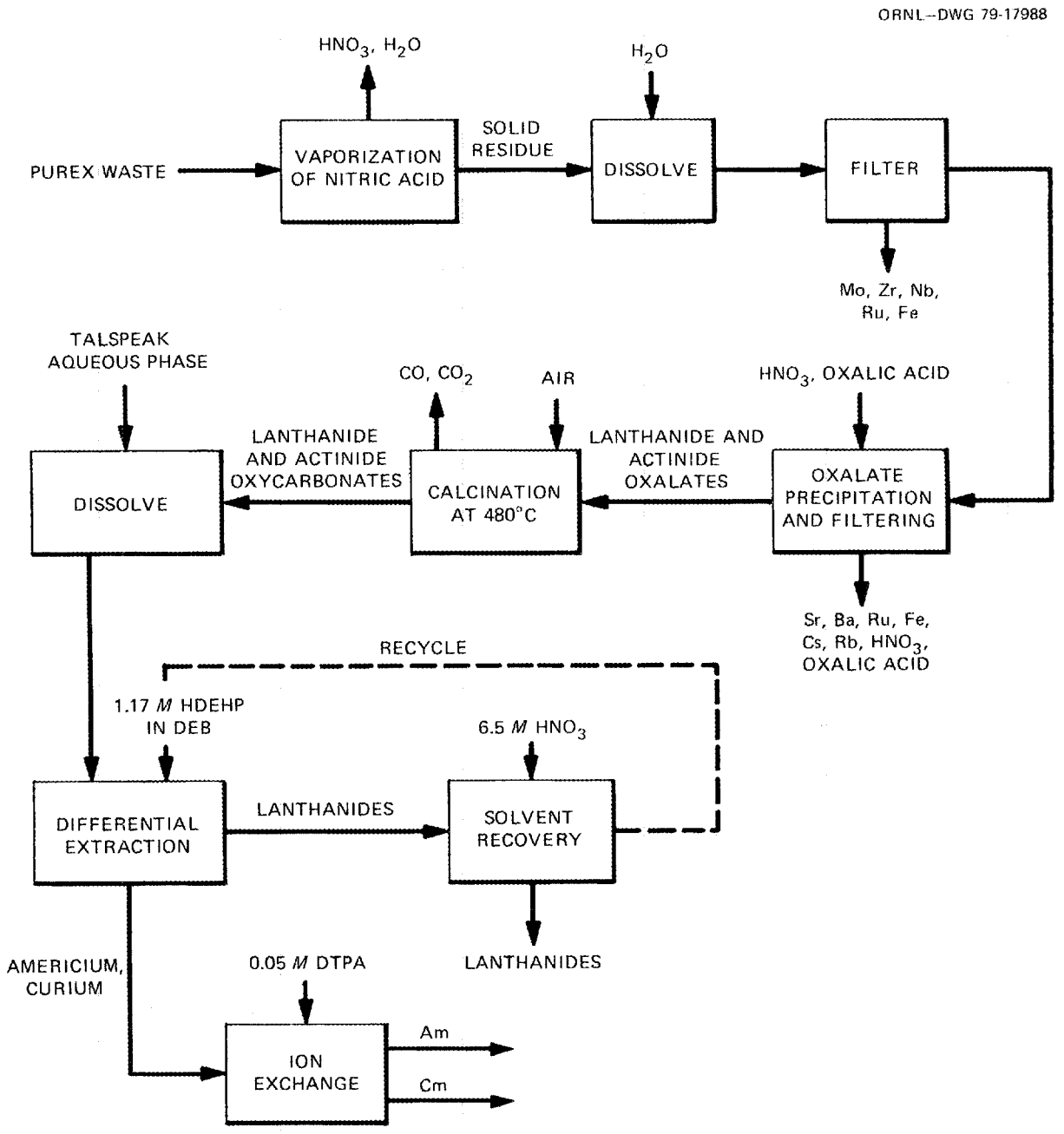


Fig. 1. Flow sheet for the process.

1.4.3 Filtering

Remaining solids are filtered from the solution. This step removes essentially all of the zirconium, niobium, and molybdenum and most of the ruthenium and iron. Less than 0.5% of the curium is removed with this insoluble residue.

1.4.4 Oxalate precipitation and filtering

Nitric acid is added to produce a 1 *M* hydrogen ion concentration, followed by 0.514 liters of 0.75 *M* oxalic acid per liter of solution over a 30-min period, during which the solution is agitated. After a 2-hr digestion period the precipitate, which contains the trivalent actinides and lanthanides, is filtered out. This step removes the remaining ruthenium and iron, the cesium and rubidium, and most of the strontium and barium. It is also a good general purification step that removes a large variety of minor fission and corrosion products.

1.4.5 Calcining

The oxalates precipitated in the last step are calcined for 90 min at 480°C in the absence of air. Air is then admitted for 60 min to oxidize a small amount of carbonaceous residue formed by this process. The lanthanides are now present in the form of oxycarbonates.

1.4.6 Dissolving of oxides

The TALSPEAK[2] aqueous solution is added to the oxides, which take 30 min to dissolve. The resulting solution is 0.106 *M* in the pentasodium salt of DTPA and 1 *M* in glycolic acid; the lanthanide concentration is 0.045 *M*.

1.4.7 Extraction

Differential extraction is used to separate the lanthanides from the actinides. For the organic phase, 40 vol % HDEHP in DEB is used at 46°C. Essentially all of the lanthanides and yttrium and approximately 20% of the americium and curium are extracted. The lanthanides, actinides, and

yttrium are then stripped from the HDEHP solution by differential extraction using 6.5 *M* nitric acid.

1.4.8 Ion exchange

After adjustment of the pH to 1.0 with nitric acid, the americium and curium are loaded directly from the TALSPEAK aqueous solution onto a Dowex 50 × 8 ion exchange resin and eluted by a solution of 0.05 *M* DTPA. This separates the curium from the americium and from any trace impurities.

1.5 Experimental Program

The original plan included pilot plant testing of the flow sheet and a demonstration of the separation of curium from nuclear waste. Due to curtailment of the program, these objectives were not accomplished. It was established that the feed preparation steps work, but they were not investigated in detail. The possible recovery and reuse of the TALSPEAK aqueous phase and the substitution of the ammonium salt of DTPA for the sodium salt are two other aspects that were not examined.

The separation of curium from the lanthanides was believed to be the most difficult part of the process and was investigated in greater detail than the other steps. Extraction rates in the TALSPEAK process received particular emphasis after early results indicated that the gadolinium extraction was too slow to be carried out efficiently in conventional equipment.

The separation of curium from americium by ion exchange was not tested. However, this process uses established technology.

2. REMOVAL OF NITRIC ACID

Purex waste usually contains about 3 *M* nitric acid, most of which must be removed before other process steps can be applied. Two methods of nitric acid removal were tested in this project: the destruction of the nitric acid with formic acid, as proposed in Ref. 3, and the removal of the nitric acid by vaporization. The formic acid method was originally favored; however, experimental results showed that the reaction was slower than expected and the precipitate was very fine and difficult to filter. The vaporization method was an obvious alternative and produced favorable results.

The experimental procedures and results for both methods are discussed and the methods are compared.

2.1 Reaction of Nitric Acid with Formic Acid

2.1.1 Previous work

The destruction of nitric acid in Purex waste by reaction with formic acid has been studied by Koch et al.,[3] Healy,[5] and Orebaugh.[6] The completeness of the removal of several major impurities (i.e., Fe, Zr, Ni, Mo, and the noble metals) is dependent upon the final pH of the solution. Different values were obtained in each study: Orebaugh[6] reported that a pH higher than 2 could not be obtained; Healy[5] obtained a pH of 3 after prolonged reaction with formaldehyde (which is converted to formic acid in the reaction); and Koch et al.[3] obtained pH's higher than 7.

The temperature, the concentrations of the two acids, and the rate of boiling all affect the relative concentrations of the reduction products formed by the reaction (NO_2, NO, N_2O, and N_2). Consequently, the stoichiometry of the reaction is hard to predict. Koch et al.[3] report, however, that if the waste is added to concentrated formic acid the stoichiometry is relatively consistent. The principal reaction is

$$2HNO_3 + 4HCOOH \longrightarrow 5H_2O + 4CO_2 + N_2O \ . \qquad (1)$$

The reaction is initially very rapid and then slows but can be controlled by the rate at which waste is added; the maximum feasible rate depends largely on the volume available for the separation of the liquid from the gas bubbles generated. According to Healy,[5] the reaction rate is described by the equation

$$\frac{d\,(\mathrm{HCOOH})}{dt} = k(\mathrm{HCOOH})^{n}\,(\mathrm{HNO_3})^{3}\ . \qquad (2)$$

The dependence of the rate on the cube of the acid concentration explains the slowness of the reaction at low acidities. Obviously, increasing the formic acid concentration will increase the reaction rate, but this causes two problems: first, an excess of formic acid can itself cause a low pH, and second, the formates of trivalent lanthanides and actinides have low solubilities and can be precipitated along with the impurities.

Koch et al.[3] controlled the pH by varying the amount of formic acid added and reported on two variations of the process. In the first, a pH of 2 is reached; essentially all of the zirconium, niobium, and molybdenum are precipitated, but only 80% of the noble metals and none of the iron are removed. Curium losses to the precipitate are very small. In the second, a pH of 7-8 is reached and the lanthanides and actinides are precipitated along with the impurities. Hydrogen peroxide is added to the precipitate to oxidize Fe(II) to Fe(III) (no mention is made of the reaction of hydrogen peroxide with cerium, americium, or formic acid), and then nitric acid is used to redissolve the lanthanides and actinides. If addition of acid stops when the pH reaches 3, decontamination factors of >1000 are obtained for Mo, Zr, Ru, Rh, and Fe, but ∿50% of the curium is lost to the precipitate. If the pH is held at 2, 80-90% of the curium goes into solution, but roughly 1% of the ruthenium and rhodium and 2% of the iron are dissolved as well (molybdenum and zirconium decontamination factors remain about 1000).

2.1.2 Experimental procedure

Tests were made on a synthetic waste solution with the following composition.

Linsay Code 350 mixed lanthanide nitrate hexahydrates	34.0 g/liter
Neodymium nitrate hexahydrate	110.1 g/liter
Zirconium hydroxide	13.6 g/liter
Strontium nitrate	4.1 g/liter
Ferric nitrate hexahydrate	30.5 g/liter
Ruthenium chloride hydrate	0.3 g/liter
Sodium sulfate decahydrate	7.8 g/liter
Sodium phosphate	14.0 g/liter
Molybdenum trioxide	9.3 g/liter
Nitric acid	3.0 moles/liter

The lanthanide mixture (composed of Linsay Code 350 mixed lanthanides and pure neodymium nitrate) contained a higher proportion of neodymium than the actual fission product mixture but the same proportion of cerium.

Test runs were carried out using 200- and 300-ml batches of solution in a 500-ml three-necked flask. One neck of the flask was closed except when samples were being withdrawn with a pipette for pH measurement. Gaseous reaction products left the flask through a reflux condenser, and the rate of gas evolution was determined by measuring the rate of water displacement in a burette.

In runs 8 and 9, radioactive tracers were added before acid destruction. Americium-241 tracer was used as a standin for ^{244}Cm because ^{241}Am can be rapidly and accurately measured by gamma counting, while ^{244}Cm requires a slow, expensive, and less accurate alpha counting procedure. The properties of ^{241}Am and ^{244}Cm are very similar, unless oxidation-reduction reactions are involved. The solids were later filtered out and assayed. Results are discussed in Sect. 2.1.3.

Additions of 30% hydrogen peroxide were made to some samples to test the peroxide destruction of formic acid and the precipitation of ceric peroxide. Results are discussed in Sects. 2.1.4 and 2.1.5.

2.1.3 Results and discussion

In the first four tests, small amounts of 88% formic acid were added to large samples of boiling waste solution. An induction period of several minutes after each acid addition, followed by a very vigorous reaction, made control difficult; in several cases, part of the waste boiled out through the reflux condenser.

In later tests, the waste was added to 88% formic acid. This shortened the induction period and also produced a predictable stoichiometry — 2 moles of formic acid consumed per mole of nitric acid destroyed [the principal reaction is that of Eq. (1)].

After the solution is completely mixed and the initial vigorous reaction is over, a long digestion period is required to reach the desired pH. The influence of the digestion period and of the amount of formic acid added is shown in Table 2. The table also shows that a pH higher than 2 can be reached if enough formic acid is present.

Table 2. Influence of the amount of formic acid added and of the digestion time on solution pH

Run	Formic acid added, ml/liter of waste	Digestion time, min	Rate of gas evolution, ml/min/liter of solution	pH
5	190	107	47	0.63
5	190	250	3	0.80
6	257	358	7	1.32
7	287	130	56	2.02
7	287	195	20	2.23
7	287	255	15	2.36

In run 7, titration of the final solution showed 0.50 *M* free acid. In view of the pH, this must be formic acid, not nitric acid (since 0.5 *M* nitric acid would have a pH of 0.3); this represents a 10% excess of formic acid if the stoichiometry of Eq. (1) was followed.

Run 8 was identical to run 7 except for the addition of ^{95}Zr, ^{103}Ru, and ^{144}Ce tracers before nitric acid destruction. Run 9 was identical to run 8 except that ^{241}Am tracer was used. The precipitates were filtered from samples taken at various intervals, rinsed with distilled water, dried overnight in flowing air, and weighed. The radioisotope contents of the samples were measured with a GeLi multichannel analyzer by the ORNL Analytical Chemistry Division; results are given in Table 3.

Table 3. Distribution of fission products as a function of solution pH

Digestion time, hr	pH[a]	Concentration in supernate, μCi/ml			Concentration in precipitate, μCi/g		
		^{95}Zr	^{103}Ru	^{144}Ce	^{95}Zr	^{103}Ru	^{144}Ce
0	*b*	0.35	0.049	0.46			
2	2.0	0.004	0.038	0.45	8.5	0.75	0.71
3	2.2	≤0.001	0.019	0.42	10.6	0.88	0.84
4	2.3	≤0.004	0.011	0.42	6.2	0.85	1.4

[a]Estimated from a parallel cold run.

[b]Initial nitric acid concentration was 3 *M*.

Most of the zirconium was removed at a pH of 2; however, an appreciable fraction of the ruthenium remained in solution even at a pH of 2.3. Better ruthenium decontamination could be achieved at a higher pH, but this would require a substantially longer reaction time. The high concentration of cerium in the precipitate was unexpected and implied that the precipitate also contained trivalent actinides, but because direct measurement of americium loss was planned it was not investigated further.

Table 4 shows the americium content of the precipitate, which is appreciable at a pH of 1.97 but does not increase significantly as the pH increases to 2.17. The large wet volume of the precipitate led to a hypothesis that much of the americium might be held in simple solution in the water associated with the precipitate.

The hypothesis was tested by washing the precipitate produced during the 4-hr digestion time (Table 4) with distilled water. As shown in

in Table 5, most of the americium remained with the precipitate; the concentration in the last of three washes was only 4.4% of that in the original solution, but the concentration in the precipitate was 84% of that measured after the first wash. It was concluded that much of the americium was present in an insoluble form.

Table 4. Americium found in precipitate formed

Sample	pH	Precipitate (g/ml of sample)	Americium in precipitate (% of total)
After 2 hr digestion	1.97	0.029	17
After 3 hr digestion	2.13	0.032	15
After 4 hr digestion	2.17	0.028	15

Table 5. Removal of americium from precipitate by washing with distilled water

Wash volume (ml/ml of original solution)	Americium in precipitate (% of total)	Concentration of americium in wash as % of concentration in original solution
0.35	12.9	50
0.35	11.2	12
0.30	10.8	4.4

2.1.4 Peroxide destruction of formic acid

Peroxide destruction of formic acid was tested by adding 5 ml of 30% hydrogen peroxide to 20 ml of the final solution obtained in run 7 (Table 4). A red-orange precipitate of ceric peroxide formed. When the solution was warmed, gas evolution started at about 35°C. When gas evolution stopped, the pH had reached 4.42, indicating that most of the formic acid had been destroyed. Most of the gas produced originated at the red-orange precipitate of ceric peroxide that appeared to catalyze

the reaction. Ceric peroxide also catalyzes the decomposition of hydrogen peroxide. In a separate test, pure formic acid began to react with hydrogen peroxide at 55°C, and the reaction required several hours — more time than was required for the reaction in the presence of ceric peroxide.

2.1.5 Coprecipitation of americium and ceric peroxide

Cerium isotopes are the principal source of radiation in nuclear waste that has decayed for only a short time. If such waste is to be used in this process, the removal of cerium early in the process is desirable in order to reduce radiation damage to the reagents used. The precipitation of ceric peroxide has been considered as a method for cerium removal; since cerium and americium both have a tetravalent form, coprecipitation appeared to be possible. Tests were performed on a pure cerium-americium system and on the synthetic fission product solution, with differing results.

A solution of pure cerium nitrate (0.103 g of cerium per milliliter) was spiked with ^{144}Ce and ^{241}Am tracers. Hydrogen peroxide (30%) was added at a rate of (0.4 ml)/ml, and the pH was raised in three stages by the addition of concentrated ammonia. Samples were taken at each stage and tracer concentrations in the precipitate were measured. Table 6 indicates that both elements were precipitated almost quantitatively.

This was not the case, however, for the solutions obtained from the synthetic fission product samples. Two tests were made on supernate remaining after nitric acid destruction by formic acid. Most of the remaining formic acid was removed from the first sample by reaction with hydrogen peroxide and from the second sample by evaporation at room temperature. To each sample, 6 ml of 30% hydrogen peroxide was added per 20 ml of sample volume. The ceric peroxide was filtered from the solutions, washed, and dried, and the precipitates were weighed and their americium contents determined.

The sample weights showed that 90-95% of the cerium was precipitated. Table 7 indicates that cerium removed from nuclear waste by this process will be heavily contaminated by americium, although the amount is not

great enough to make the reaction a useful method for separating americium from the lanthanides. Curium will probably be coprecipitated to a lesser degree than americium, because it is more difficult to oxidize to the tetravalent form.

Table 6. Coprecipitation of americium with cerium peroxide

	Remaining in solution (% of total)	
pH	Americium	Cerium
1.62	100	100
1.68	68	33
2.12	46	12
4.97	0.6	0.10

Table 7. Coprecipitation of americium with ceric peroxide from mixed fission products

Initial pH	Final pH	Am in precipitate (% of total)	Specific activity ratio (c/min/g)/(c/min/ml)
3.14	4.76	4.9	12.7
4.61	5.07	5.2	11.9

2.2 Removal of Nitric Acid by Vaporization

In removing nitric acid from nuclear waste by vaporization, both the acid and the water are vaporized, leaving a cake of nitrates. Water is then added and the soluble nitrates are dissolved. Determination of the proper temperature for vaporization — high enough to result in rapid removal of the residual acid in the cake but low enough to prevent partial decomposition of the lanthanide and actinide nitrates to insoluble oxides — was the focus of the experimental work.

2.2.1 Experimental procedure

Experiments were carried out using the synthetic waste solution described in Sect. 2.1.2. Radioactive tracers were added to each sample before vaporization, and aliquots were withdrawn for counting at appropriate points in the operation.

The acid and water were vaporized from a series of 20-ml samples in a 125-ml flask heated in a glycerol-water solution. The vapor passed into an air-cooled, 125-ml filter flask that acted as a condenser. The outlet of the filter flask was connected through a stopcock to a water aspirator.

Most of the runs were made at reduced pressure in a closed system using the aspirator. When the temperature reached about 80°C, the residual gas was removed and the stopcock closed while vaporization continued. After all visible liquid was removed, the stopcock was opened and pumping with the aspirator was continued. During this period the temperature rose rapidly.

Other runs were made at atmospheric pressure, with the stopcock open and the aspirator turned off. In some cases, the stopper of the boiling flask was removed to permit air circulation in the flask.

After vaporization was completed, the lanthanide and actinide nitrates were dissolved by adding 20-50 ml of distilled water and heating to boiling for about 1 min. The cake was slurried and the solids were filtered out and washed with distilled water. The pH of the filtrate was measured and the radioisotope contents of the filtrate and the precipitate were determined.

2.2.2 Experimental results

The nitric acid and water vaporized and condensed with very little production of noncondensable gas. Some $(NO_2)_2$ was visible when the sample was heated to 130-140°C, but this ceased after a few minutes. A small quantity of colorless gas evolution was observed at higher temperatures.

The insoluble residue was granular, small in volume, and easily removed from the solution by filtration.

In some runs, a deposit of yellow material that could only be removed by scraping was found on the walls of the flask. Very little of this material was observed when vaporization was carried out at reduced pressure; larger quantities were found for runs at atmospheric pressure. Apparently, the higher temperatures associated with the latter encouraged the deposit of this material from solution.

2.2.3 Experimental data

The pH of the solution containing the soluble part of the residue is determined by traces of acid remaining in the cake after vaporization. The pH's resulting from a variety of vaporization conditions are given in Table 8. They have been corrected to a standard volume of 30 ml of filtrate per 20 ml of original solution to eliminate dilution effects. The data show that the amount of residual acid decreased as the final drying temperature increased and as the final drying pressure decreased. Final drying in an oven was also effective in reducing residual acid.

Table 9 shows the amounts of impurities in the insoluble residue that remains after the nitrates are dissolved. Appreciable americium concentrations in the residue occurred when a residue was allowed to digest overnight before filtering. This residue was gelatinous and hard to filter and resembled precipitates formed when formic acid was used for nitric acid destruction.

Increased americium and cerium concentrations in the residue were also observed in those runs in which the drying temperature was $\geqslant$193°C. This was caused by the formation of CeO_2 and AmO_2. It is likely that curium losses would be lower than those for americium because curium's dioxide is much less refractory. The gadolinium content of the insoluble residue was very small, even when the drying temperature was 202°C. It should be noted that the hydroxides of trivalent actinides and lanthanides do not precipitate at pH's below 7. Thus, the cerium and americium in the residues were present as the dioxide.

Zirconium and niobium were completely removed from the filtrate in all cases except one. In this case, as a result of poor acid removal, the pH was only 0.89.

Table 8. pH of leach solutions of solid residues from acid vaporization as a function of drying conditions

Final drying temperature (°C)	pH	Other drying conditions
130	2.1	Final drying in 130°C oven for 1 hr after boiling dry at atmospheric pressure
131	1.4	Final pressure, 30 torr
135	1.2	Final pressure, 30 torr
139	1.0	Boiled dry at atmospheric pressure
145	1.7	Final pressure, 30 torr
150	1.4	Final pressure, 30 torr
150	1.6	Final pressure, 30 torr
155	2.1	Final pressure, 10 torr
160	1.7	Final pressure, 30 torr
170	1.8	Atmospheric pressure
180	2.4	Final pressure, 30 torr
183	2.1	Final pressure, 30 torr
193	2.5	Dried at 30 torr to 169°C, exposed to air to 193°C
197	2.5	Boiled dry at atmospheric pressure, no air admitted
202	2.0	Dried at 30 torr to 179°C, exposed to air to 202°C

The observed ruthenium removal was erratic; from 42 to 100% was found in the residue. However, good ruthenium decontamination is achieved with oxalate precipitation (see Sect. 3).

Strontium sulfate did not precipitate under the test conditions. However, it is removed by both oxalate precipitation (see Sect. 3) and the TALSPEAK extraction (see Sect. 5).

Iron decontamination was incomplete; even when a pH of 2.1 was reached, 2% of the total remained in solution. Good iron decontamination is desirable because iron's very high distribution coefficients in HDEHP extraction systems make it difficult to remove from the extractant. The oxalate precipitation step (Sect. 3) is useful for removing iron.

Table 9. Materials remaining in insoluble residue for various drying temperatures and solution pHs

Element	pH of solution	Maximum drying temperature (°C)	Amount in residue (% of total)
Am	1.9	130	0.5
Am	1.6	131	0.5
Am	1.4	135	0.5
Am	1.4	150	0.1
Am	1.9	165	1.9[a]
Am	1.8	197	12.5
Am	2.4	202	3.4
Ce	0.9	139	0.2
Ce	1.8	170	0
Ce	2.5	195	4.1
Gd	2.4	202	0.6
Zr-Nb	0.9	139	97
Zr-Nb	1.8	170	100
Zr-Nb	2.5	195	100
Ru	0.9	139	92
Ru	1.6	155	42
Ru	1.8	170	100
Ru	2.2	180	95
Ru	2.5	195	74
Sr	1.5	145	0.4
Sr	1.2	150	0.2
Sr	1.8	168	0.1
Fe	2.1	183	98

[a]Residue allowed to digest overnight before filtering.

2.3 Comparison of Methods

Either vaporization or the formic acid reaction could be successfully used to remove nitric acid from Purex waste. The direct vaporization of the nitric acid was chosen for the following reasons.

1. The solid residue produced by vaporization is coarse and easily washed and filtered. The precipitate produced by the formic acid reaction is very fine and difficult to filter and wash.
2. Curium losses to the residue produced by vaporization are less than 1% of the total (under the recommended operating conditions). In the formic acid reaction, about 10% of the curium is precipitated with the impurities and is difficult to recover.

3. In the vaporization process, nearly all of the nitric acid and water can be volatilized and condensed in a closed system, and any radioactive material carried in the vapor will be trapped in the condensed acid. (Some air, however, must be pumped from the system, and a small amount of nitrogen oxide gas is produced in the final drying stages.) In the formic acid reaction, a large amount of contaminated nitrogen oxides is produced. The trapping of these gases would require additional process equipment.

The balance might shift in favor of the formic acid reaction, however, if fresh Purex waste were used, because of the high radioactive cerium content of this material. In this case, the precipitation of the cerium as ceric peroxide (Sect. 2.1.5) would become attractive as a means of reducing radiation damage in the process.

3. OXALATE PRECIPITATION

3.1 General Characteristics

Oxalate precipitation is a traditional method of separating lanthanides from nonlanthanide impurities. The precipitation reactions of the trivalent lanthanides and actinides in acid solution follow

$$2M^{3+} + 3H_2C_2O_4 \longrightarrow M_2(C_2O_4)_3 + 6H^+ \ . \qquad (3)$$

As indicated, the solubility decreases as the oxalic acid concentration increases and increases as the hydrogen ion concentration increases. However, at high oxalate ion concentrations a second reaction occurs, and a small increase in solubility is caused by the formation of soluble lanthanide oxalate complexes.

According to Ephraim,[7] the precipitate is amorphous at first and contains extraneous anions; with digestion, it becomes crystalline. Only zirconium and thorium have oxalates less soluble than those of the lanthanides. Zirconium is precipitated with the lanthanides but forms a soluble oxalate complex and can be brought back into solution by digesting with ammonium oxalate.

When a mixture of trivalent actinides and lanthanides is precipitated, the elements are mixed in the crystal lattice as well as in solution. At equilibrium, the elements with the least soluble oxalates will be found in the crystal phase at higher concentrations relative to elements with more soluble oxalates than in the aqueous phase. Consequently, the concentration of any element (such as curium) depends not only on the oxalic acid and hydrogen ion concentrations, but also on the total lanthanide concentration, and will be less than that predicted from the solubility product of its pure oxalate.

Although initial precipitation of the lanthanide oxalates is very rapid, complete equilibrium requires a long digestion period. Grebenshchikova and Bryzgalova[8] reported that supersaturation was not completely removed even in 27 hr, and a comparison by Broadhead and Heady[9] of solubilities after 2- and 20-hr digestion times showed differences that were greatest at low temperatures and low initial lanthanide concentrations.

The decontamination accomplished by precipitation can be improved by the use of dilute solutions and high temperatures, but these conditions also increase curium losses. A slow increase in oxalate ion concentration and a long digestion time both enhance decontamination but increase the time required for the operation. Because a simple, relatively rapid precipitation was desired, the experimental work concentrated on demonstrating the effectiveness of comparatively rapid oxalic acid additions and short digestion times at room temperature.

3.2 Experimental Procedure

A series of precipitations was carried out on a lanthanide nitrate solution corresponding to the lanthanides in the synthetic fission product mixture. Radioactive tracers (^{241}Am, ^{153}Gd, ^{144}Ce, ^{95}Zr, ^{95}Nb, ^{106}Ru, ^{89}Sr, and ^{59}Fe) were used as appropriate.

The samples were acidified with concentrated nitric acid; then 0.75 *M* oxalic acid was added over a period of ∿30 min, during which the solution was stirred. After this, samples were allowed to digest for 45 min to 2 hr (some were allowed to digest overnight). The precipitate was filtered from the solution and washed with distilled water. Then the tracer contents of the precipitate and the filtrate were measured.

3.3 Results and Discussion

The results of seven precipitations are given in Table 10. In every case in which at least a stoichiometric amount of oxalic acid was present, the americium loss was <0.3%. Because curium oxalate is less soluble than americium oxalate,[10] curium losses will be even smaller. Losses could be reduced even further by using a greater excess of oxalic acid or a longer digestion time.

Results of precipitation of other materials can be summarized as follows.

Table 10. Results of oxalate precipitations

Tracer	Initial lanthanide concentration (*M*)	Oxalic acid concentration after precipitation (*M*)	H^+ concentration after precipitation (*M*)	% of total remaining in solution after precipitation
^{241}Am	0.15	0.067	1.0	0.34
^{152}Gd	0.15	0.067	1.0	1.50
^{241}Am	0.31	-0.028[a]	1.2	3.3[b]
^{153}Gd	0.31	-0.028[a]	1.2	6.6[b]
^{241}Am	0.31	0.037	1.1	0.29
^{153}Gd	0.31	0.037	1.1	1.3
^{144}Ce	0.31	0.037	1.1	1.9[b]
^{106}Ru	0.31	0.037	1.1	100[b]
^{95}Zr	0.31	0.037	1.1	8[b]
^{95}Nb	0.31	0.037	1.1	72[b]
^{144}Ce	0.31	0.096	1.0	1.2
^{106}Ru	0.31	0.096	1.0	100
^{95}Zr	0.31	0.096	1.0	7
^{95}Nb	0.31	0.096	1.0	73
^{144}Ce	0.25	0.041	1.5	2.8[c]
^{106}Ru	0.25	0.041	1.5	100[c]
^{95}Zr	0.25	0.041	1.5	0[c]
^{95}Nb	0.25	0.041	1.5	50[c]
^{144}Ce	0.25	0.14	1.4	N.F.[b,c]
^{106}Ru	0.25	0.14	1.4	100[b,c]
^{95}Zr	0.25	0.14	1.4	0[b,c]
^{95}Nb	0.25	0.14	1.4	54[b,c]
^{85}Sr	0.31	0.096	1.0	89
^{85}Sr	0.15	0.073	1.0	91
^{59}Fe	0.28	0.24	1.1	98

[a]Less than a stoichiometric amount of oxalic acid was added. The deficiency was equivalent to a 0.028 *M* concentration in the final solution.

[b]The precipitate was digested overnight in the supernate.

[c]The lanthanide solution was added to the oxalic acid rather than the reverse.

N.F. None found.

1. Gadolinium and cerium oxalates were shown to be more soluble than americium oxalate.
2. Most of the zirconium was precipitated with the lanthanides. Increasing the oxalic acid concentration and the digestion time did not improve the situation. Fortunately, good zirconium decontamination is achieved during nitric acid removal.
3. From 27 to 50% of the niobium accompanied the lanthanides — a comparatively poor decontamination. Good niobium decontamination is achieved during nitric acid removal.
4. No ruthenium was found in the precipitate.
5. About 90% of the strontium was removed by the precipitation. Strontium is also removed by the TALSPEAK extraction process.
6. About 2% of the iron remained with the precipitate. Partial iron decontamination is achieved during nitric acid removal.

3.4 Flow Sheet Recommendations

The conditions chosen for the oxalate precipitation step of the flow sheet are as follows.

1. The starting solution is 0.156 *M* with respect to total lanthanides and actinides. The hydrogen ion concentration is 1 *M*.
2. A total of 0.514 liters of 0.75 *M* oxalic acid per liter of solution is added over a 30-min period, during which the solution is agitated.
3. The mixture is allowed to digest for 2 hr with agitation.
4. The precipitate is filtered from the mixture.
5. The precipitate is washed with 0.5 liters of 0.05 *M* oxalic acid solution per liter of original solution.

4. CALCINATION AND DISSOLVING IN TALSPEAK SOLUTION

4.1 General Chemistry

The oxalates of the lanthanides and actinides decompose when heated. They are first converted to carbonates, then pass through a series of oxycarbonates, and are finally converted to sesquioxides. In the presence of air, the cerium, americium, and curium are further oxidized to higher oxides.

The calcination procedure must destroy all the oxalate ions and carbonaceous residue without completely converting the oxycarbonates to oxides, because the oxycarbonates dissolve more readily in the TALSPEAK aqueous solution than the oxides. Prolonged high temperatures with exposure to air should be avoided, because this can cause the growth of CeO_2-AMO_2 crystals that are difficult to dissolve.

4.2 Experimental Procedure

Two batches of lanthanide oxalate were prepared by precipitation from acid nitrate solutions. For the first batch, Linsay Code 350 mixed lanthanides, consisting of cerium nitrate ($\sim$50%) and a mixture of the other lower lanthanides, was used; for the second, pure neodymium nitrate. Other samples were prepared from the synthetic fission product solution, to which radioactive tracers were added before precipitation. Samples were weighed before and after calcination.

Samples were calcined in a quartz tube. Gas produced during calcination passed to a gas burette that was used to monitor the rate of gas evolution. When this rate became essentially zero, calcination was ended. In some cases the quartz tube was left open or was opened at the end of calcination.

In several cases the calcined material was dissolved in the TALSPEAK aqueous phase. The rate of solution and the presence of insoluble residue were observed, and the radioactive tracer contents of the solutions and residues were measured.

4.3 Results and Discussion

Table 11 shows the effects of time and temperature on the decomposition of the lanthanide oxalates (the average lanthanide present is represented by "M"). Product compositions were determined from the weight losses of the samples.

Products of calcination in the absence of air were black because of a carbonaceous residue, which was not soluble in the TALSPEAK solution. In runs 2 and 3, the residue was filtered out after solution of the lanthanides, washed, dried, and weighed. The residue weight was equal to 1.3% of the original sample weight in run 2 and 1.7% of that in run 3. A similar residue was present in run 4 but was not weighed.

When the dark material produced in run 5 was exposed to air at 480°C, its color changed to gray-green. The color change started at the surface and moved downward through the sample. Two sharply defined layers were visible, indicating that the rate was controlled by the rate of oxygen diffusion into the sample. Although the reaction appeared to be complete in 30 min, oxidation was continued for 1 hr. The oxidized material, which was a very fine powder, dissolved completely in the TALSPEAK solution.

A second type of insoluble residue, cerium dioxide, can be formed by calcining in the presence of air. The product from run 1, which was prepared from the Linsay Code 350 material, was oxidized overnight at 420°C and placed in the TALSPEAK solution. The sample did not dissolve entirely even after several days at 55°C. In a separate test reagent, cerium dioxide did not dissolve to an appreciable degree even after several days at 90-100°C.

Fortunately, further tests showed that cerium dioxide was much slower to form when the cerium fraction of the lanthanides was 12%, the value expected in nuclear waste (rather than the 50% of the Linsay Code 350 material). A sample with this fraction, oxidized for 4 hr at 470°C, showed no insoluble residue, and one oxidized for 1 hr at 500°C showed only a trace of residue. This residue contained 0.03% of the ^{241}Am tracer and no detectable amount of the ^{153}Gd tracer used in this experiment.

Table 11. Calcination of lanthanide oxalates

Run	Temperature (°C)	Time (min)	Products
1	370	98	$M_2(CO_3)_3$[a] + $M_2(C_2O_4)_3$
2	470	83	$M_2O(CO_3)_2$ + $M_2O_2CO_3$
3	420	166	$M_2(CO_3)_3$ + $M_2O(CO_3)_2$
4	415	100	$Nd_2(CO_3)_3$ + $Nd_2O(CO_3)_2$
5	480	87	$Nd_2O(CO_3)_2$ + NdO_2CO_3
5	480	+60 air	$Nd_2O_2CO_3$ + Nd_2O_3
6	465	1020	Nd_2O_3 + $Nd_2O_2CO_3$

[a]94% conversion to the carbonate.

Another sample of oxalate, containing ^{144}Ce and ^{241}Am tracers, was calcined in air for 19 hr at 600°C. The insoluble residue remaining after 30 min of boiling contained 0.1% of the cerium and 0.05% of the americium.

An oxalate sample containing ^{241}Am and ^{153}Gd tracers was calcined in air for 2 hr at 950°C. Solution required 3 hr at 100°C. The small amount of residue contained 0.2% of the americium and 0.1% of the gadolinium, as well as needle-like crystals resembling lanthanide oxalates. The presence of the crystals was explained by the formation of oxalic acid as a result of the oxidation by Ce(IV) and Am(IV) of the glycolic acid in the TALSPEAK solution.

The rate of solution of the calcined material in the TALSPEAK solution decreases as time and temperature of calcination increase. The material of run 4, calcined at 415°C, dissolved in 30 min at room temperature; the material of run 5, calcined at 480°C, dissolved in 35 min at 50°C; and material calcined at 950°C, as noted above, dissolved in 3 hr at 100°C.

The lanthanide concentration after solution in most tests was about 0.05 *M*. This is greater than the concentration required for the TALSPEAK extraction process. Higher concentrations are easily obtainable; a concentration of 0.17 *M* was obtained by contacting the TALSPEAK solution with an excess of the lanthanide oxycarbonates.

4.4 Flow Sheet Recommendations

The conditions chosen for the calcination and dissolving steps are as follows.

1. The lanthanide-actinide oxalates are calcined in the absence of air for 90 min at 480°C.
2. Air is then admitted to oxidize the carbonaceous material. Oxidizing time is estimated as 60 min.
3. The calcined powder is dissolved in the TALSPEAK aqueous solution at 50-60°C. Mild agitation is used. The final lanthanide concentration should be 0.045 *M*.

5. TALSPEAK PROCESSING

5.1 Differential Extraction

Differential extraction was chosen as the best method of using the TALSPEAK process. Because this is not a widely known extraction technique, it is described here in some detail.

Differential extraction is analogous to a Rayleigh distillation. Typical differential extraction stages are shown in Fig. 2. The mixing vessel holds the original solution containing the solutes to be extracted. This solution remains in this stage and is called the resident phase. A steady stream of the extractant enters the mixing vessel and is thoroughly dispersed by vigorous agitation, and a steady stream of the mixed phases is continuously circulated through the settler. Here the extractant is separated and leaves the stage, while the resident phase returns to the mixing vessel.

The following simplifying assumptions are used in deriving the equation describing the extraction of a solute.

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

The equation is based on a material balance in the stage: as a differential volume of extractant, dL, enters the stage, an equal volume leaves. The resulting removal of extractable solute is given by

$$y\ dL = -(S\ dx + H\ dy)\ , \tag{3}$$

where L is the volume of the extractant, y is the concentration of solute in the extractant phase, x is the concentration of solute in the resident

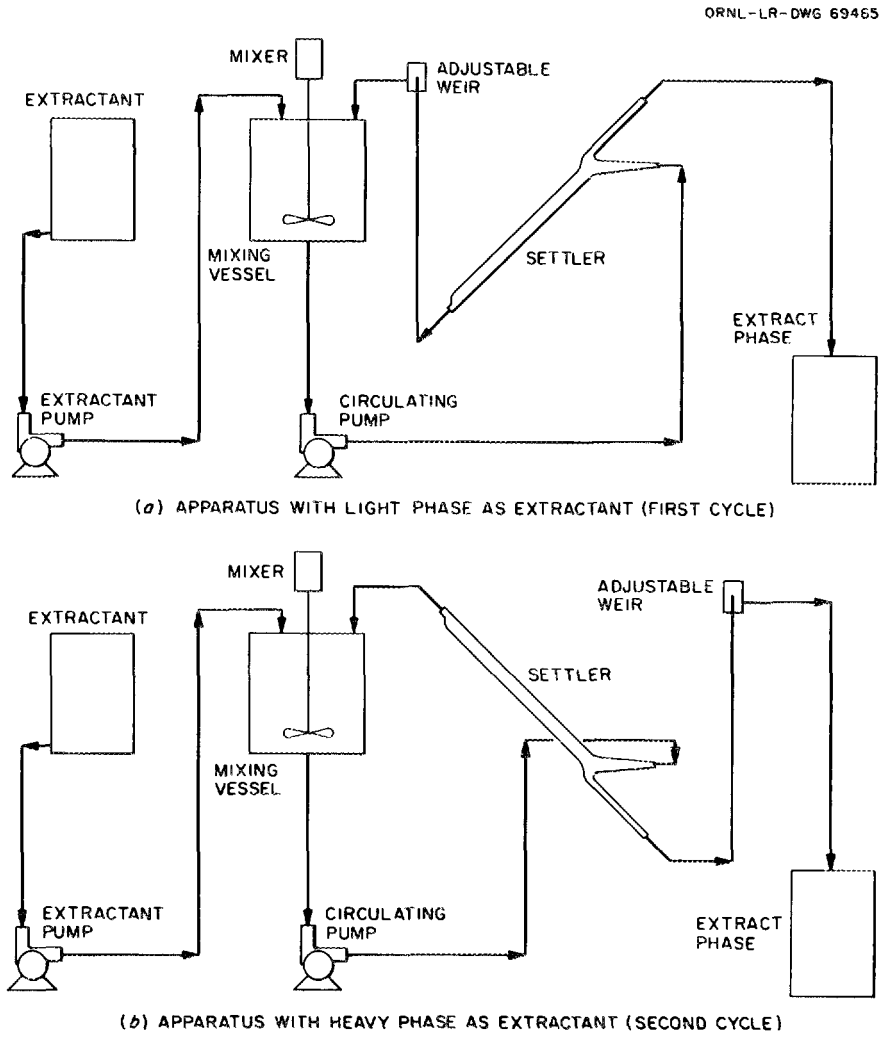


Fig. 2. Differential extraction stages.

phase, S is the volume of the resident phase, and H is the volume of the extractant phase held up in dispersed form.

By substituting Dx for y, rearranging, and integrating, the equation

$$L/S = (1/D + H/S)\ \ln\ (x_1/x_2) \tag{4}$$

is obtained. The ratio H/S becomes very important when the process is used to extract one solute from a less extractable solute. Because D is the only quantity in the equation that is peculiar to a specific solute and H/S is additive to $1/D$, a sharp separation between solutes

is favored by a value of H/S that is small compared to $1/D$, and having a very large value of D is of little advantage unless H/S is very small.

The value of H/S can be reduced in three ways. First, an increase in the rate at which the mixed phases are circulated through the settler will reduce the value of H/S; a settler or centrifuge with a high capacity and small volume is desirable. Second, point values of H/S may 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 value is high, the effective capacity of the settler is increased and the average value of H/S is reduced. Third, reducing the rate at which the extractant passes through the stage reduces H/S, although it increases the time required for the extraction. Values of $H/S = 0.01$ are obtainable with reasonably high extractant flow rates.

In most real extractions, the distribution coefficients change during the extraction process because of changes in solvent loading. The amount of extractant L required to remove a single solute can be estimated by a stepwise calculation using

$$L = \Sigma\Delta L = \sum_{x_2}^{x_1} \frac{S\Delta x + H\Delta y}{y_{av}} \quad . \tag{5}$$

A graph of y as a function of x can be used to evaluate Δx, Δy, and y_{av}.

The extraction of a solute with a low distribution coefficient, B, in the presence of a solute with a much higher distribution coefficient, A, can be estimated by

$$y_B(av) = (x/L)\ \Sigma D_B \Delta L \ . \tag{6}$$

If Eq. (5) is used to calculate the extraction of solute A, then the solvent loadings for the different ΔL intervals is known, and the corresponding values of D_B can be measured or estimated.

Because any given unit of extractant remains in the stage only a short time, the total contact time for the extractant, which is equal to the extractant holdup divided by the total flow rate, is short. The contact time for the resident phase is the total time required for extraction. When an organic extractant is used to remove material from a highly

radioactive solution, a short contact time will minimize radiation damage, which is proportional to the exposure time. However, if an extraction system exhibiting slow kinetics is used, a short contact time may not be feasible.

The choice of differential extraction was based on the following advantages.

1. The equipment is simpler and lower in cost than that needed for multiple-stage countercurrent extraction.
2. Startup and shutdown problems are minor, which means that intermittent operation causes few problems.
3. The extractant contact time with a radioactive solution can be very low. (Of course, if the radioactive material itself is extracted, it must be quickly stripped from the extractant to minimize radiation damage.)
4. The extraction process is easily altered to allow for changes in feed composition and batch size. For example, several consecutive extractions that are quite different in nature can be carried out without removing the resident phase from the mixing vessel by changing extractants or by altering the solution with an acid, a salting agent, or an oxidizing agent.
5. Differential extraction gives much sharper separations than simple batch extraction. An example calculation takes the case of two solutes, A and B, in 10 liters of aqueous solution. Extraction is carried out using 10 liters of extractant. The distribution coefficients are $D_A = 10$ and $D_B = 0.1$, and the value of H/S for the differential extraction is 0.01. Equation (4) shows that after differential extraction, only 0.011% of solute A will remain in solution, compared to 9.09% after batch extraction; 90.5% of solute B will remain after differential extraction, compared to 90.9% after batch extraction. The 90.5% residue of solute B has a high degree of purity with respect to solute A. Solute A is recovered with great efficiency but is not pure; however, a second differential extraction, in which the organic solution is the resident phase and an aqueous solution the extractant, can be used to provide

solute *A* in pure form. In this case, the amount of solute *B* in the solute *A* fraction can be reduced to 0.011% by 2.3 liters of extractant; this extractant will contain 2.28% of the original amount of solute *A*.

The differential extraction process removes the lanthanides to the same low level as multiple-stage countercurrent extraction, but curium losses are larger with differential extraction unless a curium recovery stage is added. As noted, however, the design of this process assumes that moderately large curium losses can be tolerated if minimum cost per unit of production is achieved.

Differential extraction has been carried out on a moderately large scale only once.[11] More than 99% (15 kg) of the high ^{235}U assay uranium was recovered with two comparatively primitive differential extraction stages. The overall decontamination factor was $>10^6$.

5.2 TALSPEAK Extraction Process

5.2.1 Chemistry of TALSPEAK extraction process

The TALSPEAK extraction process is a liquid-liquid extraction process, in which the organic phase is a solution of HDEHP in any of various organic diluents and the aqueous phase contains the sodium salt of DTPA and a buffering acid. The lanthanides and actinides exist in solution in three forms: (1) the majority as DTPA complexes of the form $MDTPA^{2-}$, (2) a small fraction as one or more complex compounds formed with the buffering acid, and (3) an even smaller fraction as free ions.

The instability constants, K_m, of the DTPA complexes of the lanthanides have been measured by Moeller and Thompson,[12] and those of americium and curium by Baybarz.[13] These data are shown in Table 12. The trivalent actinides are more strongly complexed by the DTPA than the lanthanides and consequently tend to remain in the aqueous phase.

The evidence indicates that more than one complex compound may exist in the organic phase. These compounds may contain both HDEHP and one or more ions of the buffering acid in combination with the

Table 12. Data and results for the calculation of TALSPEAK separation factors

Ion	$K_m \times 10^{23}$	E_A^O of HDEHP-ClO_4 ÷ E_A^O of lanthanum	$K_m E_A^O \times 10^{20}$	α, E_A^O of element/E_A^O of curium		
				HDEHP-ClO_4^-	TALSPEAK calculated	TALSPEAK measured
La^{3+}	3310	1	3.31	0.198	644	370
Ce^{3+}	316	2.98	0.913	0.590	177	126
Pr^{3+}	85.1	6.09	0.519	1.203	101	57
Nd^{3+}	25.2	8.42	0.212	1.670	41	39
Pm^{3+}		18.2	NA	3.60	NA	NA
Sm^{3+}	4.57	55.4	0.253	10.98	49	48
Eu^{3+}	4.07	105	0.427	20.80	83	107
Gd^{3+}	3.47	151	0.525	29.9	102	NA
Tb^{3+}	1.95	743	1.450	147.0	282	NA
Dy^{3+}	1.51	1,560	2.36	308.5	459	NA
Ho^{3+}	1.66	3,030	5.04	600	978	NA
Er^{3+}	1.82	6,840	12.42	1,352	2,420	NA
Tm^{3+}	1.91	17,000	32.50	3,462	6,700	7,040
Yb^{3+}	2.40	52,500	126	10,400	24,500	NA
Lu^{3+}	3.63	97,800	354	19,400	69,000	NA
Y^{3+}	8.91	50,000	44.6	990	8,660	670
Am^{3+}	1.20	3.63	0.00435	0.719	0.84	0.89
Cm^{3+}	1.02	5.05	0.00515	1.00	1.00	1.00

NA - Not available.

lanthanide ion or only HDEHP and the lanthanide. The chemistry of the latter type of compound is known from the study of extraction from simple mineral acids.

Peppard[14] concluded that the HDEHP exists as a dimer, $(HDEHP)_2$, in the organic phase and that the lanthanides are extracted according to

$$M^{3+} + 3(HY)_2 \longrightarrow M(HY_2)_3 + 3H^+ , \qquad (8)$$

where HY is an HDEHP formula unit. When the lanthanide molarity reached about one-tenth of the HDEHP molarity, a precipitate formed in the organic phase, limiting the useful capacity of the phase. However, Weaver and Kappelman[15] reported the extraction of lanthanum lactate complexes from TALSPEAK solutions containing lactic acid buffer, and Lunichkina and Renard[16] reported the extraction of lanthanum, neodymium, and americium lactate complexes. Both groups of investigators reported clear solutions at lanthanide concentrations greater than those of Peppard. Determination of the maximum phase loading was thus a major part of the experimental work.

The distribution coefficient, E_A^O, of a lanthanide is determined by competition for the lanthanide ion between the DTPA complex and the organic phase complex. The separation factors of the lanthanides vs curium were estimated by multiplying the instability constants (K_m) of the DTPA complexes by the distribution coefficients for the lanthanides in an HDEHP-ClO_4 system (obtained by Pierce and Peck[17] and reported in Table 12 as ratios to the distribution coefficient of lanthanum). These products were divided by the corresponding product for curium; the distribution coefficient for curium was calculated using formulas given by Baes[18] for americium and a ratio of 1.4 between the distribution coefficient of curium and that of americium as measured by Horwitz et al.[19]

The separation factors thus calculated are compared in Table 12 to the experimental values obtained by Weaver and Kappelman.[2] Even though the role of the buffering acid was ignored, the calculated and experimental values are in fairly good agreement, indicating that the values

of α for the higher lanthanides are approximately correct and that traces of these materials will be effectively extracted.

The absolute values of the distribution coefficients can be controlled by varying the HDEHP concentration, the DTPA concentration, and the pH of the aqueous phase. All of the trivalent actinides and lanthanides are affected proportionally. The ratios of their distribution coefficients remain approximately constant at pHs above $\sim$3.

5.2.2 Application of TALSPEAK extraction to the process

The determination of optimum conditions for using TALSPEAK extraction in this process required a great deal of experimental work. The areas of effort are discussed below.

Information available early in the project indicated that the speed of the extraction would be a problem. Koch et al.[3] found that the extraction of europium in their system was unsatisfactory and attributed the problem to slow extraction kinetics. Later studies by Kolarik et al.[20] found that extraction rates declined as the atomic number of the lanthanides involved increased. (These studies also showed that the extraction rate increased with lanthanide concentration, buffering acid concentration, and temperature.) The lanthanum and cerium extractions were too fast for precise evaluation; the praseodymium, neodymium, promethium, samarium, and europium extractions followed a first-order rate equation; and the yttrium extraction was faster than that of europium.

The variation of extraction rate with atomic number indicated that gadolinium would be extracted more slowly than any of the other lanthanides present in appreciable quantity, and this assumption was supported by preliminary tests in this project showing that gadolinium was slow in equilibrium. Because gadolinium is expected to be the chief lanthanide present in the nuclear waste used for this process, the determination of the optimum conditions for gadolinium extraction was the major task of this work and occupied more than half the total time. The extraction kinetics of americium, cerium, and curium were studied to a lesser degree.

The complex interactions among many of the process variables also complicated the determination of optimum conditions. For example, increasing the HDEHP concentration increases the maximum allowable lanthanide loading in the organic phase but also increases the distribution

coefficients, causing a decline in the lanthanide concentration in the aqueous phase in equilibrium with the fully loaded organic phase as the HDEHP concentration increases. Increasing the HDEHP concentration also increases the extraction rate constant, but the associated increase in distribution coefficient requires a decrease in H/S to maintain constant sharpness of separation and partially counteracts the effect of increasing the extraction rate constant.

Extraction rate equations were developed to determine optimum conditions in the presence of these interactions. These equations are at least one level more basic than those commonly used in this type of work and take into account the influence of phase ratio and distribution coefficient size on equilibrium time. Equations were also developed to allow the rate constants measured in batch extractions to be used for calculating extraction rates in differential extraction.

Finally, experiments were performed to obtain answers to the following questions.

1. What diluent should be used for the HDEHP?
   What buffering acid should be used for the DTPA?
   What concentrations of HDEHP and DTPA should be used?
2. How did the various operating parameters affect the extraction rate? What were the extraction rate constants?
3. What were the distribution coefficients of the elements involved under the various possible operating conditions?
4. What are the maximum lanthanide concentrations in each phase that are compatible with satisfactory process operation?

5.3 Experimental Work

The experimental work of this project was carried out in two stages, with an 18-month interruption between the first and second stages. After the interruption, experiments were resumed at a new location with new equipment.

Most of the experiments were carried out at room temperature. During the first experimental period, this was consistently 23-24°C.

During the second period, an energy saving program was in force and the thermostat was turned down at night; room temperature in the early morning was 17-18°C and increased during the day. Experiments at higher temperature were carried out by placing the extraction flask in a beaker of heated water.

All concentrations were measured by means of radioactive tracers; those used in the extraction rate measurements were ^{144}Ce, ^{153}Gd, ^{241}Am, and ^{244}Cm. The curium tracer was used in early experiments only, to establish directly the behavior of the element; americium was used in later experiments because the gamma counting used with ^{241}Am is less expensive and time-consuming than the alpha counting required with ^{244}Cm and because alpha counting in the presence of large amounts of solid impurities is of uncertain accuracy. In one case, a small quantity of mixed fission products was used in a mixed tracer run.

5.3.1 Testing of reagents

The HDEHP used during each experimental period was agitated with water for 16 hr to hydrolyze any pyrophosphates present and then titrated. For the first batch of HDEHP, the di(2-ethylhexyl) phosphoric acid concentration was 2.93 *M* and the mono(2-ethylhexyl) phosphoric acid concentration was 0.09 *M*. The second batch (from a different source) was initially free of monoester, but 0.03 *M* was found after several months of storage in contact with water. Diluents tested for use with HDEHP were DEB, (diethy benzene) DIB, (diisopropyl benzene) and Amsco.

The DTPA used in the experiments was a commercial sodium salt of DTPA, CHEL-DPTA by Geigy. The assay of this material presented difficulties, because the amount of sodium present was not stoichiometric and the neutralizations of the five replaceable hydrogens overlap so that only one clear break occurs in the acid-base titration curve. This break corresponds to the addition of the second hydrogen to Na_5DTPA, but because of the nonstoichiometry of the CHEL-DTPA, results obtained from direct use of the break are uncertain.

This problem was solved using the following chemistry. Moeller and Thompson[12] state that the DTPA lanthanide complex $H_2CeDTPA$ is a strong acid and gives a good titration curve. The Na_5DTPA sample was

titrated until the second hydrogen was added (to put the DTPA in a known form) and a small stoichiometric excess of $Ce(NO_3)_3$ was added. The sample was titrated to a pH of 7, and duplicate analyses were performed. Values obtained were 1.05 *M* and 1.07 *M;* the average value, 1.06 *M,* was used. Buffering acids tested for use with DTPA were lactic acid (as used in the original TALSPEAK process) and glycolic acid.

Differing concentrations of HDEHP and DTPA were tested to find the optimum conditions.

5.3.2 Measurement of extraction rates and rate constants

A number of batch extraction rate measurements were carried out in a 100-ml, three-necked, round-bottomed flask. A thermometer mounted in a rubber stopper entered through one of the side necks, and samples were withdrawn through the other. The agitation shaft entered through the center neck. The 0.25-in.-diam agitator was powered by a variable speed motor. During the first experimental period, agitator speed was designated by controller setting and not directly measured; during the second period, it was measured with a stroboscope. Two standard speeds, 2200 rpm and 5000 rpm, were used.

In a typical experiment, 50 ml of the aqueous phase was poured into the flask; then 20 ml of the organic phase was added slowly and carefully so that very little mixing took place. The agitator was turned on at time zero, and at carefully timed intervals eye droppers were used to take grab samples of the mixed phases. The samples were discharged into small test tubes where the phases separated; the two phases were sampled with micropipettes and their tracer contents assayed by a counting procedure.

For most of these measurements, a ratio of organic phase volume, *O,* to aqueous phase volume, *A,* was 0.4. A lower ratio would have more closely approached the low values used in differential extraction, but as O/A becomes lower, the organic layer in the separated samples becomes thinner. This increases the difficulty of sampling and speeds further equilibration by diffusion. Thus, $O/A = 0.4$ was judged the lowest value compatible with easy experimental procedure. When other values were used, the total volume $(O + A)$ was held at 70 ml.

The aqueous phase consisted of 10% CHEL-DPTA in 1 *M* glycolic acid unless otherwise noted. Stock solutions were prepared by dissolving weighed portions of lanthanide and yttrium oxides in the aqueous phase solution. Cerium was added separately as $Ce(NO_3)_3 \cdot 6H_2O$. One of the stock solutions contained 0.177 *M* gadolinium; the other two contained mixed lanthanides and yttrium in the proportions expected in the Barnwell waste and had total molarities of 0.149 and 0.104. Less concentrated solutions were prepared by mixing measured volumes of stock solutions and lanthanide-free aqueous solution.

5.3.3 Measurement of distribution coefficients

Many distribution coefficients were obtained during the extraction rate measurements. Others were obtained from experiments in which the two phases were agitated in a beaker with a magnetic stirrer. An equilibrium time of $\geqslant$30 min was allowed in these cases.

5.3.4 Measurement of phase loading

Early in the experimental work, it was found that solid material precipitated in the organic phase if the lanthanide concentrations were too high. The gadolinium concentrations at which this occurred were determined by equilibrating progressively stronger aqueous phase solutions with the standard organic phase. Tests were also performed with various alternate organic phases.

5.4 Results and Discussion

5.4.1 Selection of reagents

Selection of diluent for HDEHP. The results of exploration tests of several diluents for the HDEHP are summarized in Tables 13 and 14. The tables show that the solutions using DEB as a diluent gave the best separation factors, α (small differences are not necessarily significant because variations can be caused by impurities in reagents or by random error).

Table 13. Influence of diluent on distribution coefficient, *E*, and separation factor, α

Extractant	*E*			α^a	
	Am	Gd	Ce	Gd/Am	Ce/Am
40% HDEHP in DEB	0.25	36	100	141	400
40% HDEHP in DIB	0.29	32		110	
40% HDEHP in Amsco	1.21	130	235	107	194
0.3 *M* (10 vol %) HDEHP 0.2 *M* TBP in Amsco	0.046	3.14	6.74	68	147

[a]The separation factor, α, is defined as the ratio of distribution coefficients.

Table 14. Gadolinium and curium distribution coefficients and separation factors

Extractant	Temperature, °C	*E*		α
		Gd	Cm	
40% HDEHP in DEB	23	36.0	0.30	120
40% HDEHP in DEB	46	20.0		
40% HDEHP in DIB	65	12.5	0.21	59
40% HDEHP in DIB	25	32.0	0.35	92
100% HDEHP	99	106.0	1.63	66

The n-alkane (Amsco) with TBP used by Koch et al.[3] was rejected because the TBP depresses the distribution coefficients of the higher lanthanides. This makes it inappropriate for use with Barnwell waste, which will contain a large amount of gadolinium.

The distribution coefficients for DEB solutions were lower than for Amsco solutions. This means that larger *H/S* values can be used for differential extraction with DEB [see Eq. (5)]. The level of distribution coefficients could be lowered by decreasing the HDEHP concentration, but this would decrease the maximum allowable organic phase loading.

DEB and DIB are closely competitive, but the HDEHP solutions with DEB have lower viscosities, allowing quicker phase separation when the

organic phase is continuous. Measured viscosities for 1 *M* HDEHP in DEB were 2.28 centipoises (cP) at 25°C and 1.60 cP at 45°C, compared to 3.72 cP at 25°C and 2.42 cP at 45°C for 1 *M* HDEHP in DIB. The densities of the solutions are essentially identical (0.904 g/cm^3 at 22°C).

Selection of buffering acid. Preliminary tests confirmed Weaver's statement[21] that extraction rates were faster with glycolic acid than with lactic acid. Tests also showed that glycolic acid solutions have lower viscosities. Measured viscosities for a TALSPEAK aqueous phase containing 1 *M* glycolic acid and 0.1 *M* DTPA were 1.26 cP at 25°C and 0.88 cP at 45°C, compared to 1.42 cP at 25°C and 0.99 cP at 45°C for a similar solution containing 1 *M* lactic acid. Densities of the two solutions are essentially identical (1.047 g/cm^3 at 22°C). Consequently, the glycolic acid solution results in quicker phase separation and the glycolic acid is less expensive.

5.4.2 Extraction rates and rate constants

Correlation of data. The batch extraction rate data were correlated using equations that were derived under the assumption that the forward and reverse movements of the solute were first order with respect to the solute concentrations in the two phases. It was also assumed that the rate of transfer was proportional to the interfacial surface area and that this area was proportional to the quantity of dispersed phase, when other factors were constant.

The instantaneous total rate of transfer for extraction from the aqueous phase is given by

$$-A \frac{dx}{dt} = k_f Ox - k_b Oy \ , \tag{9}$$

where A is the volume of the aqueous phase and O the volume of the organic phase, x is the extractable solute concentration in the aqueous phase, y is the solute concentration in the organic phase, and k_f and k_b are the rate constants for forward and reverse movement, respectively, of the solute.

At equilibrium, $dx/dt = 0$ and Eq. (10) can be derived from Eq. (9).

$$k_f/k_b = y_{eq}/x_{eq} = E_A^O \ , \tag{10}$$

where y_{eq} and x_{eq} are the equilibrium concentrations of solute in the organic and aqueous phases, respectively, and E_A^O is the equilibrium distribution coefficient. At any given time, the following material balance will apply:

$$y = (A/O)(x_O - x) \ , \tag{11}$$

where x_O is the initial concentration of solute. Then by substituting for k_b and y, rearranging, and integrating, Eq. (9) becomes

$$\ln\ [(x - x_{eq})/(x_O - x_{eq})] = -k_f[(O/A) + (1/E_A^O)]\ t \ , \tag{12}$$

where t is the time from the beginning of the extraction.

In the correlation of the batch extraction data, it was necessary to add a correction factor, B, to t because the extraction rate was abnormally high during the first few seconds of extraction (resulting from the large amount of new droplet formation during initial dispersal of the organic phase) and because some extraction took place during both the addition of the organic phase and the separation of the phases by settling. The correction factor, B, is the time required for this extraction to have occurred during the period of steady agitation. Equation (12) now becomes

$$\ln\ [(x - x_{eq})/(x_O - x_{eq})] = -k_f[(O/A) + (1/E_A^O)(t + B) \ . \tag{13}$$

The simple first-order rate constant, k', is given by

$$k' = k_f(O/A + 1/E_A^O) \ . \tag{14}$$

It can be seen from Eq. (12) that the time required to reach a given fraction of equilibrium increases both as O/A becomes smaller and as E_A^O becomes larger. At very low values of E_A^O, equilibrium is reached very quickly. Unfortunately, the solute whose extraction is desired (which has a high E_A^O) will tend to reach equilibrium more slowly than the solute whose extraction is not desired (which has a low E_A^O). The equilibrium time is also inversely proportional to the k_f value of the individual solute.

When the solute is passing from the organic to the aqueous phase and the aqueous phase is continuous, the equation

$$\ln\ (1 - x/x_{eq}) = -k_b[1 + E_A^O(O/A)](t + B) \tag{15}$$

applies [the derivation of this equation is similar to that of Eq. (13)]. If the organic phase is continuous and the rate is diffusion controlled, the equation for organic to aqueous movement is

$$\ln\ (1 - x/x_{eq}) = -k_b(E_A^O + A/O)(t + B)\ . \tag{16}$$

[The rate constant k_b in Eq. (16) is not identical to that in Eq. (15).] The degree of completion of the extraction can also be expressed in terms of the concentration in the organic phase. For the aqueous to organic movement of solute,

$$(x - x_{eq})/(x_O - x_{eq}) = 1 - y/y_{eq} \tag{17}$$

applies; for the organic to aqueous movement of solute,

$$(1 - x/x_{eq}) = (y - y_{eq})/(y_O - y_{eq}) \tag{18}$$

applies. These functions can be substituted into Eq. (14), (15), or (16).

Analysis of first period data. The rate constants determined during the first experimental period are given in Table 15. The standard conditions were a temperature of 23°C, a motor controller setting of 40 (high enough to give the samples the appearance of a uniform emulsion), and an aqueous phase consisting of 1 *M* glycolic acid and 0.106 *M* Na_5DTPA. Variations from the standard conditions included a motor controller setting of 80 in runs 3 and 10; heavy lanthanide loading in runs 5, 11, 14, and 15; higher temperatures in runs 8, 9, 10, 12, and 13; and the use of DIB as a diluent in run 12 and of Amsco in runs 13-17.

The data from these experiments established the effects of several variables. Most significant was the increase in the extraction rate with increased agitation vigor, which indicated that there was diffusion control. This is not usually the case for extractions as slow as these, but it is reasonable considering that only a very small fraction of the gadolinium was in the form of extractable glycolate complex or free ions; consequently, the concentration gradient was necessarily low, which caused slow diffusion.

Extraction rates increased with lanthanide concentration, as noted by Kolarik et al.[20] In run 5, the aqueous phase initially contained 0.067 *M* gadolinium. In run 11, the aqueous phase was loaded to 0.11 *M* with a lanthanide mixture equivalent to that expected in Barnwell waste. This resulted in an organic phase loading slightly greater than would be allowable in a process, and some insoluble gadolinium-HDEHP compound precipitated in the organic phase. The rapid extraction of gadolinium in run 11 is surprising, considering the quantity of other lanthanides present. These were presumably more rapidly extracted than the gadolinium, which consequently displaced other lanthanides as it was extracted; in spite of this, the value of k_f for this run was the highest observed at room temperature. In runs 14 and 15, the organic phase was initially loaded to 0.093 *M* with the mixed lanthanides. In run 14, equilibration was complete when the first sample was taken (t = 1 min). This was expected, because $E_A^O + A/O = 55.7$ [see Eq. (16)], so k' was too large to measure and k_b could not be calculated (it was not necessarily large).

Table 15. TALSPEAK extraction rate constants

Run	Diluent	O/A	Direction	Element	E	k'	k_f	k_b	Special conditions
1	DEB	0.4	A → O	Gd	35.4	0.39	0.91	(0.026)	Standard
2	DEB	0.4	O → A	Gd	36.4	0.32	(0.69)	0.20	Standard
1	DEB	0.4	A → O	Cm	0.31	1.0	0.28	(0.90)	Standard
2	DEB	0.4	O → A	Cm	0.30	1.4	(0.36)	1.2	Standard
3	DEB	0.4	A → O	Gd	35.2	0.61	1.42	(0.040)	Increased agitation
5	DEB	0.4	A → O	Gd	7.5	0.57	1.07	(0.142)	Heavy loading
11	DEB	0.4	A → O	Gd	2.14	1.51	1.86	(0.87)	Heavy loading
6	DEB	0.4	A → O	Gd	25.6	0.28	0.64	(0.025)	Lactic acid used
8	DEB	0.4	A → O	Gd	20.3	0.56	1.25	(0.061)	46°C
9	DEB	0.4	O → A	Gd	20.6	0.43	(0.95)	0.046	46°C
10	DEB	0.4	A → O	Gd	22.5	0.92	2.1	(0.092)	46°C and increased agitation
12	DIB	0.4	A → O	Gd	12.5	0.98	2.04	(0.163)	65°C
13	None	0.4	A → O	Gd	106	2.2	5.3	(0.050)	99°C
16	Amsco	0.4	A → O	Gd	133	0.65	1.60	(0.012)	Standard
17	Amsco	0.4	A → O	Am	1.17	0.89	0.71	(0.83)	Standard
14	Amsco	2.5	O → A	Gd	55.3	Very high[a]	[a]	[a]	Heavy loading
15	Amsco	2.5	O → A	Am	0.46	1.6	(0.83)	1.8	Heavy loading
7	DEB	0.4	A → O	Ce	99.8	∿3[a]	∿7[a]	∿(0.07)[a]	Standard

[a]The extraction was too rapid for accurate determination of the constants.
( ) = calculated values [Eq. (9)].

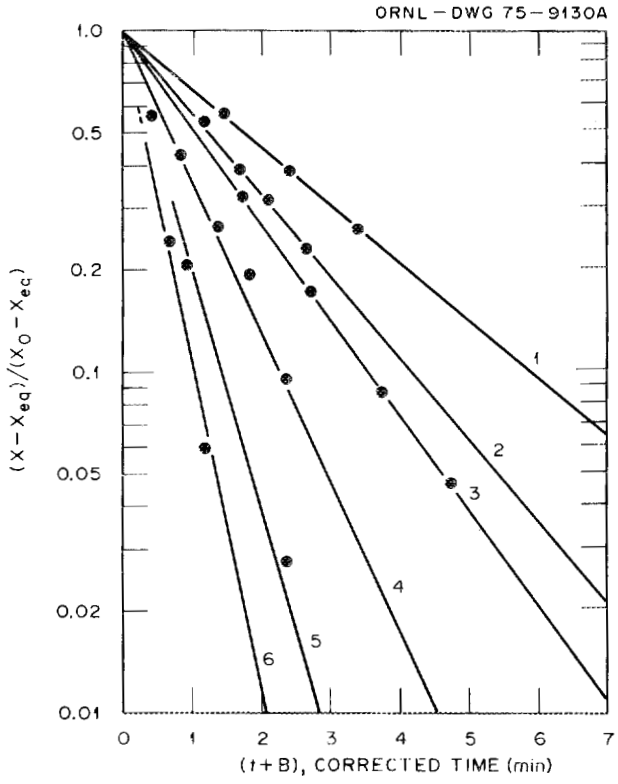
Extraction rates also increased with temperatures (as also noted by Kolarik et al.[20]). The 46°C temperature of the DEB in runs 8-10 and the 65°C temperature of the DIB in run 12 are approximately 10°C below the respective flash points of these compounds and were considered the highest safe temperatures. The 99°C temperature of run 13, in which pure HDEHP was used, is near the boiling point of the aqueous phase.

Faster extraction rates were observed when Amsco rather than DEB was used as the diluent. However, this diluent has disadvantages as noted in Sect. 5.4.1.

The values of k_f and k_b in Table 15 were calculated from Eq. (13), (15), or (16), as appropriate, or from the directly determined constant using Eq. (10). The values for gadolinium and americium are based on three or more points; those for curium, on a 1-min point and an equilibrium point (the value of b for curium was assumed to be the same as that in the similar gadolinium run).

All of the gadolinium extraction rate measurements followed a first-order rate equation; typical examples are shown in Fig. 3. The values of k_f and k_b calculated from $A \rightarrow O$ extraction data are consistently higher, by a ratio of 1.32 ± 0.01, than those calculated from $O \rightarrow A$ extractions carried out under nominally identical conditions (compare run 1 with run 2 and run 8 with run 9). This discrepancy results from the use of the organic phase from the previous $A \rightarrow O$ run in the $O \rightarrow A$ run; the extraction of a small amount of sodium in the first run causes the pH to be slightly higher in the second run. When this difference between $A \rightarrow O$ and $O \rightarrow A$ runs is taken into account, the agreement of the values of k_f and k_b calculated with Eq. (9) with the other values is good.

Analysis of second period data. During the second experimental period, the influence of the phase volume ratio, O/A, was verified. Rate constants for gadolinium were measured at 2200 rpm and 17°C with an organic phase of 40 vol % HDEHP in DEB and an aqueous phase of 10% CHEL-DTPA in 1 M glycolic acid for three different values of O/A. Results are given in Table 16. The values of k_f were calculated from those of k' with Eq. (14). The data show that as O/A increased, k' increased while k_f remained essentially constant. This verified the validity of Eq. (13).



1: 40% HDEHP IN DEB AT 23°C
2: 40% HDEHP IN DEB AT 46°C
3: 40% HDEHP IN AMSCO AT 25°C
4: 40% HDEHP IN DIB AT 65°C
5: 40% HDEHP IN DEB AT 25°C, AQUEOUS PHASE INITIALLY LOADED TO 0.05 *M* WITH MIXED LANTHANIDES AND YTTRIUM
6: 100% HDEHP AT 99°C
IN ALL CASES THE AQUEOUS PHASE CONTAINED 1.06 *M* Na_5DTPA, 1.0 *M* GLYCOLIC ACID, AND ^{153}Gd TRACER; O/A = 0.4.

Fig. 3. Extraction rates of gadolinium in the TALSPEAK system, including the effects of temperature, diluent, and loading.

Table 16. Influence of *O/A* on k' and k_f

O/A	k', min^{-1}	k_f
0.25	0.806	2.80
0.40	1.15	2.77
0.75	2.06	2.60

The extraction rate of gadolinium was found to be approximately proportional to the hydrogen ion concentration in a series of tests carried out at 2200 rpm and room temperature (which varied widely during this period). The pHs of the aqueous phases were adjusted by the addition of concentrated nitric acid or 10 *M* sodium hydroxide. The results of the tests are given in Table 17.

Table 17. Effect of pH on k_f

Element	pH	Temperature (°C)	k_f (min^{-1})
Gd	3.0	18	5.4
Gd	3.4	18	2.8
Gd	4.0	18	0.42
Am	3.0	28	1.69
Am	4.0	19	0.17
Ce	3.0	24	15.5[a]
Ce	4.0	28	8.3[a]

[a]These extractions did not follow a first-order extraction equation; values of k_f are average values.

The extraction rate was also found to increase with HDEHP concentration, as shown by the data in Table 18. These tests were carried out with the standard aqueous phase (10% CHEL-DTPA in 1 *M* glycolic acid) and phase volume ratio (O/A = 0.4).

The influence of temperature on extraction rates was evaluated by comparing runs that were identical except for differences in temperature. Three pairs of runs (runs 1 and 8 and runs 3 and 10 from Table 15 and runs 41 and 42 from Table 19) were compared; the first run of each pair was carried out at room temperature (24°C) and the second at 46°C. The average ratio of k_f at 46°C to k_f at 24°C was 1.43.

The influence of agitator speed was evaluated in a series of tests carried out at 5000 rpm (the highest speed the motor could deliver) with the standard organic phase and phase volume ratio. The aqueous phase was standard except for several cases in which the pH was adjusted to 3.0 with concentrated nitric acid. The thermometer passed close to

Table 18. Influence of HDEHP concentration on k_f

HDEHP concentration (vol %)[a]	Agitator speed (rpm)	Temperature (°C)	k_f (min^{-1})
20 ± 1.5	2200	25	1.6
26 ± 2	2200	25	2.3
42 ± 4	2200	25	3.4
23 ± 2	5000	25	4.8
41 ± 3	5000	25	6.8
55 ± 5	5000	45	15

[a]The concentrations of the stock solutions of extractants changed during this series of experiments, apparently because the diluent evaporated through the plastic walls of the storage bottles. Concentrations given here were calculated from the equilibrium distribution coefficients. The uncertainties are at the 95% level of confidence. They were calculated from the standard deviation of values of the distribution coefficient from the mean of a series of values obtained in another series of rate measurements.

Table 19. Influence of agitator speed, temperature, and pH on k_f

Run	Element	Agitator speed (rpm)	Temperature (°C)	pH	k_f (min^{-1})
33	Gd	2200	18	3.0	5.4
41	Gd	5000	24	3.0	10.0
42	Gd	5000	46	3.0	13.2
31	Gd	2200	17	3.4	2.8
19[a]	Gd	2200	24	3.4	3.3
20[a]	Gd	5000	24	3.4	6.7
28	Gd	5000	46	3.4	8.1
28	Gd	5000[b]	48	3.4	10.8
29	Gd	5000[b]	45	3.4	10.9
30	Gd	5000[b]	46	3.4	10.4
43	Gd	5000	46	3.4	7.1
38	Am	2200	28	3.0	1.7
47	Am	5000	46	3.0	2.0
44	Am	5000	46	3.4	1.4

[a]Estimated from data of Table 18.

[b]Clearance between agitator and baffle (thermometer) adjusted to minimum value.

the agitator and acted as a baffle; when it was deliberately placed very close (within 1/16 in.), the increased shear in the liquid caused an increase in the extraction rate. Results of the tests are given in Table 19, along with values obtained at 2200 rpm for comparison. Vigorous agitation at 46°C produced values of k_f of $\geqslant 10$; this degree of agitation should be obtainable in production equipment. The time required for phase separation was noticeably increased by the more vigorous agitation, but it was judged acceptable.

The extraction of cerium did not follow the first-order rate equation; instead, it was characterized by a very high initial rate followed by a slower movement toward equilibrium. At 24°C, 2200 rpm, and a pH of 3.0, the distribution coefficient was 40 after 10 sec, and only 44 after another 10 sec. It eventually reached 48. A similar pattern was exhibited at pHs of 3.4 and 4.0 and by the data points for cerium and lanthanum in Fig. 4 of Ref. 20. It is believed that this is caused by the very rapid extraction of one or more glycolate complexes that change slowly to a more stable form. The question was not investigated because no process problem exists; the extraction rate of cerium is much faster than that of gadolinium in all cases.

A single extraction rate constant of $k_f = 5\ \text{min}^{-1}$ was measured for yttrium, which is removed along with the lanthanides in the TALSPEAK extraction, at 2200 rpm, room temperature, and $O/A = 0.4$ with the standard solutions. This value is roughly twice that for gadolinium under similar circumstances. The extraction rate of yttrium does not create a process problem.

One extraction rate measurement was carried out with a mixed fission product tracer at 2200 rpm and room temperature. A rate constant of $k_f = 15\ \text{min}^{-1}$ for lanthanum was calculated with the first-order rate equation. Rate constants for the other elements could not be determined from the data, but zirconium, niobium, ruthenium, and barium apparently reached equilibrium within 30 sec.

Precision of data. A material balance was calculated using the data from each rate sample and the relationship

$$\text{total counts} = Ax + Oy \tag{19}$$

or

$$x + (O/A)y = x + 0.4y = \text{const.} \tag{20}$$

The values of $x + 0.4y$ were calculated and averaged for each run. The standard deviation of values varied from ∿1 to 5% for various runs, with ∿2% being the most common. This is indicative of the total error resulting from sampling and counting uncertainty.

For the slower extractions, standard deviations of the value of $\ln\,[(x - x_{eq})/(x_O - x_{eq})]$ from the line of Eq. (12) were typically around 0.02. For rapid extractions ($k_f \approx 10$), the standard deviations ranged from 0 to 0.17; a value of 0.10 was typical. During most of these runs, samples were withdrawn at 10-sec intervals. Time errors made a significant contribution.

The uncertainty in the values of k_f is greater and is influenced by the placement of the agitator, by uncertainties in the solution compositions, phase ratio, and temperature, and by impurities. The standard deviation of the five values of k_f determined at 5000 rpm, 46°C, and a pH of 3.4 (Table 19) was equivalent to 18% of the average value.

Because its E_A^O was small, resulting in a large $(1/E + O/A)$, americium reached equilibrium very quickly. In most cases, there were not enough data points below equilibrium to allow statistical analysis.

5.4.3 Distribution coefficients

A number of distribution coefficients were obtained as a part of the extraction rate measurements and are given in Tables 13-15. The influence of the diluent on the distribution coefficients was shown in

these measurements. The influence of the HDEHP concentration in DEB on the distribution coefficient of gadolinium at the tracer level was measured for concentrations ranging from 9 to 50 vol % HDEHP. The data were correlated by

$$E_A^O = 21.83\ M^{2.59} \tag{21}$$

or

$$E_A^O = 0.0023\ C^{2.59} \tag{22}$$

where M is the molarity of HDEHP and C is the volume percent of HDEHP. (It should be noted that the first batch of HDEHP (see Sect. 5.3.1) was used for these measurements and for determining the data of Tables 12-15. The distribution coefficients obtained are somewhat higher than those obtained using the second batch of HDEHP.)

The influence of temperature on the distribution coefficient of gadolinium at the tracer level was evaluated from data collected during the extraction rate measurements with the equation

$$\ln E_A^O = (2427/T) - 4.573, \tag{23}$$

where T is the temperature in kelvins, for gadolinium data at a pH of 3.0 and with the equation

$$\ln E_A^O = (2577/T) - 5.351 \tag{24}$$

for data taken at a pH of 3.4. Equation (23) is based on four points, with a standard deviation of 0.015, which is equal to ±1.5% of E_A^O. Equation (24) is based on 12 points taken over the range of 17 to 46°C, with a standard deviation of 0.075, which is equal to 8% of E_A^O.

Distribution coefficients for americium were also obtained during the extraction rate measurements and are given in Table 20. Data obtained at a pH of 3.0 were correlated by

$$\ln E_A^O = (1500/T) - 6.045 \tag{25}$$

and those obtained at a pH of 3.4 by

$$\ln E_A^O = (1422/T) - 6.115 \ . \tag{26}$$

Equations (23)-(26) were used to calculate the separation factors, $E_A^O(\mathrm{Gd})/E_A^O(\mathrm{Am})$, listed in Table 21.

Table 20. Americium and cerium distribution coefficients

Element	pH	Temperature (°C)	E_A^O
Americium	3.0	28	0.34
Americium	3.0	47	0.24
Americium	3.0	46	0.28
Americium	3.4	25	0.26
Americium	3.4	46	0.19
Americium	4.0	19	0.055
Americium	4.0	45	0.051
Cerium	3.0	24	47.5
Cerium	4.0	28	6.7

Table 21. Separation factors

Temperature (°C)	pH	E_A^O (Gd)/E_A^O (Am)
25	3.0	98
46	3.0	79
25	3.4	103
46	3.4	81
18	4.0	167

Distribution coefficients were also obtained for barium, zirconium, and ruthenium during the extraction rate measurements and for strontium and yttrium in separate tests; they are listed in Table 22. Yttrium will be present with the lanthanides, and the other elements may be present if previous process steps are not completely effective. This extraction will remove any strontium, barium, or yttrium from the curium but will not remove any zirconium or ruthenium.

Table 22. Miscellaneous distribution coefficients in TALSPEAK extraction[a]

Element	E_A^O
Yttrium	400
Strontium	6.7
Barium	5
Zirconium	0.05
Ruthenium	$\leq$0.05

[a]All tests used the standard aqueous phase at a pH of 3.4 and 40 vol % HDEHP in DEB at room temperature.

Before the HDEHP extractant can be reused, the lanthanides and yttrium must be removed by extraction into strong nitric acid. Because the distribution coefficient of yttrium is much higher than that of any of the lanthanides present, its value controls the conditions required for this process step. The results of a series of measurements are given in Table 23 and show that the distribution coefficient with 6.5 *M* nitric acid is low enough to allow the stripping of yttrium by differential extraction.

5.4.4 Phase loading

Gadolinium loading. During the extraction rate measurements, an attempt was made to measure the extraction rate of gadolinium at a high gadolinium concentration. The organic phase became a slushy mixture of liquid and solid; when the solid was separated and characterized, it was soluble in HDEHP, insoluble in the DEB diluent alone, and quickly

Table 23. Distribution coefficients of yttrium between HDEHP solutions and nitric acid

Diluent	HDEHP (vol. %)	Nitric acid concentration (M)	E_A^O
DEB	40	4.0	0.75
DEB	40	4.0	0.48[a]
DEB	40	6.5	0.31
DEB	40	9.0	0.46
DEB	20	4.0	0.085
DEB	20	6.5	0.069
DEB	29	4.0	0.255
Amsco	40	6.5	1.43
Amsco	20	6.5	0.70

[a]This test was carried out at 46°C; the others were carried out at room temperature.

converted to clear liquid when contacted with 4 M nitric acid. The weight percent gadolinium corresponded to a compound containing one gadolinium and six HDEHP units. It was concluded that this was the solid compound observed by Peppard.[14]

Since Weaver and Kappelman[15] and Lunichkina and Renard[16] had reported clear organic solutions at lanthanum molarities up to half of the HDEHP molarity when a lactic acid buffer was used, tests were performed to determine whether the use of glycolic acid rather than lactic acid or the use of gadolinium rather than lanthanum was responsible for the difference in results. No solids were formed when lanthanum was extracted from TALSPEAK aqueous solutions buffered with lactic or glycolic acid, but a solid was formed when gadolinium was extracted from a solution buffered with lactic acid. It was concluded that the presence of a large amount of gadolinium imposes a comparatively low limit on the organic phase capacity.

This limit was determined by equilibrating the standard organic phase with a series of aqueous phases containing increasing concentrations of gadolinium and determining the resulting concentration in each phase with ^{153}Gd tracer. Figure 4 shows that saturation occurs at about 0.135 M gadolinium in the organic phase; the value of E_A^O was 5.5 and the aqueous concentration was 0.0245 M. For a similar series of

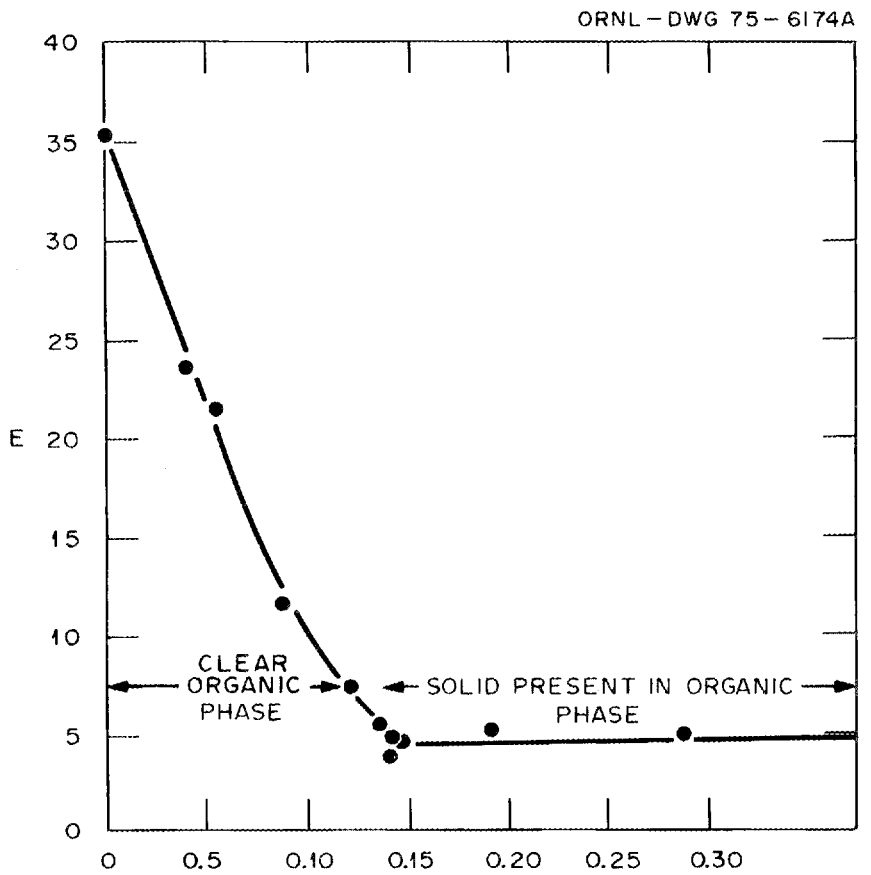


Fig. 4. Gadolinium distribution coefficient as a function of organic phase loading.

measurements on 0.30 *M* HDEHP in DEB, the maximum organic phase gadolinium concentration that could be obtained without the formation of solids was 0.028 *M*; the value of E_A^O was 0.36 and the aqueous concentration was 0.078 *M*.

Mixed lanthanide loading. The maximum phase loading that could be obtained with the lanthanide mixture expected in the Barnwell waste was determined in tests using the standard phase volume ratio and solutions [the first batch of HDEHP (see Sect. 5.3.1) was used]. The synthetic fission product lanthanide solutions contained the proper proportions of yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium, except that cerium was left out in some cases because its removal in an earlier process step was being

considered. Values of E_A^O for gadolinium, cerium, and americium were measured with radioactive tracers. Test results are given in Table 24.

The distribution coefficient for gadolinium at the concentration required for formation of solids was lower with the mixed lanthanides than with gadolinium alone. It was also lower when cerium was present in the mixture. This resulted from competition from the elements with higher distribution coefficients (yttrium, lanthanum, and cerium).

The maximum allowable aqueous phase loading is a function of the phase volume ratio because of the large variations in the distribution coefficients of the elements present. The maximum allowable lanthanide concentrations in the starting aqueous solution in differential extraction were estimated as follows: It was assumed that the ratios of distribution coefficients obtained for these elements at tracer levels (Table 12) could be applied under conditions of heavy loading. The distribution coefficients for gadolinium and cerium were taken from Table 24. A phase volume ratio of $O/A = 0.05$, a probable value for differential extraction, and a total organic phase lanthanide concentration of 0.135 M were assumed. Given these conditions, estimates of the maximum aqueous phase lanthanide concentration ranged from 0.042 to 0.049 M. Because of uncertainties in the calculation and in the data

Table 24. Distribution coefficients obtained from synthetic fission product lanthanide solutions

x_O, M Total lanthanide	E(Gd)	E(Ce)	E(Am)	Observed solids in organic phase
0.054[a]	10.5		0.094	None
0.068	5.8	7.4		None
0.075[a,b]	6.1	6.2		None
0.080	3.2	3.4		Possible trace of solids
0.097[a]	4.4			None
0.108[a]	4.0		0.036	Trace of solids in organic phase
0.137	3.1	3.7		Solids in organic phase

[a]Cerium not included in the mixture.

[b]Cerium tracer was present; dead cerium was not present.

used in making it, a conservative value of 0.03 M (corresponding to 40 vol % HDEHP in DEB at room temperature) was chosen for the flow sheet.

5.5 Conditions for Minimum Cost Operation

5.5.1 Application of rate constants to differential extraction

The rate of transfer of solute between phases is defined as $-A(dx/dt) = k_f Ox - k_b Oy$. The nonequilibrium distribution coefficient may be defined as

$$D = y/x \ . \tag{27}$$

If k_f/E_A^O is substituted for k_b [using the relationship of Eq. (10)], then the rate of transfer may be written as

$$dx/dt = - k_f x(O/A)(1 - D/E) \ . \tag{28}$$

Also, starting with Eq. (3) and using Eq. (27), it can be shown that

$$dx/dt = -[(x/S)/(1/D + H/S)] \ dL/dt \ . \tag{29}$$

If O is substituted for H, A for S, and F, the flow rate, for dL/dt,

$$dx/dt = (Fx/A)(1/D + O/A) \tag{30}$$

is obtained. Then by equating dx/dt in Eq. (28) with dx/dt in Eq. (30) and rearranging,

$$F/A = k_f(O/A)(1 - D/E_A^O)(1/D + O/A) \tag{31}$$

is obtained. Equation (31) can be used to calculate the extractant flow rate per unit volume of aqueous phase (F/A) needed to produce a given value of D, when k_f and E_A^O are known. Complete equilibrium ($D/E_A^O = 1$)

is achieved only at $F/A = 0$. For a specified value of D/E_A^O, the flow rate will increase as k_f, O/A, and $1/D$ increase. The significance of $1/D$ becomes great when D is very small.

The flow rates corresponding to a series of assumed values of D/E_A^O were calculated for gadolinium, americium, and curium for many possible sets of process conditions. The conditions and constants used in these calculations are given in Table 25. Measured values of E_A^O and k_f were used when available. Values of E_A^O for curium were estimated assuming that $E_A^O(\mathrm{Am})/E_A^O(\mathrm{Cm}) = 0.89$, the ratio from Table 12; values of k_f for curium were assumed to be 0.85 times those for americium, the ratio of the respective values of K_m for these elements in Table 12. Distribution coefficients at 20 vol % HDEHP were calculated from the values for 40 vol % HDEHP assuming that they were proportional to the 2.59 power of the concentration; values of k_f were assumed to be directly proportional to the concentration. The flow rates calculated in this way were then used to determine values of D/E at the same flow rates for these elements.

Equation (4) can be used to show that when curium and gadolinium are simultaneously extracted by differential extraction,

$$[(1/D + O/A)\ \ln\ (x_O/x)]_{\mathrm{Cm}} = [(1/D + O/A)\ \ln\ (x_O/x)]_{\mathrm{Gd}}\ . \tag{32}$$

If a constant M is defined as

$$M = (1/D + O/A)_{\mathrm{Cm}}/(1/D + O/A)_{\mathrm{Gd}}\ , \tag{33}$$

then

$$(x_O/x)_{\mathrm{Gd}} = (x_O/x)_{\mathrm{Cm}}^{M} = (x_O/x)_{\mathrm{Cm}}(x_O/x)_{\mathrm{Cm}}^{M-1} \tag{34}$$

and

$$\left(\frac{x_{O\mathrm{Gd}}}{x_{O\mathrm{Cm}}}\right)\left(\frac{x_{\mathrm{Cm}}}{x_{\mathrm{Gd}}}\right) = (x_O/x)_{\mathrm{Cm}}^{M-1}\ . \tag{35}$$

Table 25. Constants used in process calculations

Element	Temperature (°C)	pH	HDEHP concentration (vol %)	E_A^O	k_f
Gadolinium	24	3.0	40	36.6	10
Gadolinium	46	3.0	40	20.8	13.2
Gadolinium	24	3.4	40	27.8	6.8
Gadolinium	46	3.4	40	15.3	10.7
Gadolinium	24	3.4	20	(4.6)[a]	3.5
Americium	24	3.0	40	0.37	1.7
Americium	46	3.0	40	0.26	2.0
Americium	24	3.4	40	0.26	(1.0)
Americium	46	3.4	40	0.19	1.4
Americium	24	3.4	20	0.043	0.5
Curium	24	3.0	40	(0.42)	(1.4)
Curium	24	3.4	40	(0.29)	(0.85)
Curium	46	3.4	40	(0.21)	(1.2)
Curium	24	3.4	20	(0.043)	(0.42)

[a]Values given in parentheses are estimated.

The term $(x_{O\mathrm{Gd}}/x_{O\mathrm{Cm}})$ is determined by the composition of the raw material; for the Barnwell waste, it is 9122/24 or ∿380. The term $(x_{\mathrm{Cm}}/x_{\mathrm{Gd}})$ is determined by product specifications; a value of 100 was assumed in calculations. The resulting ratio is

$$(x_O/x)_{\mathrm{Cm}}^{M-1} = 38{,}000 \ . \tag{36}$$

In other calculations, the target was an americium to gadolinium ratio of 100; in this case,

$$(x_O/x)_{\mathrm{Am}}^{M-1} = 1737 \ . \tag{37}$$

This specification assumed that curium would be separated from the americium by ion exchange after extraction removed enough of the lanthanides so that they no longer constituted a significant volume of the material.

Using known values of (Cm/Cm_0) or (Am/Am_0) and Eq. (4), the ratios of extractant volume to aqueous phase volume (L/A) were calculated. Times required for extractions were then obtained by dividing the values of (L/A) by those of (F/A).

5.5.2 Calculation of optimum process conditions

The equations developed in Sect. 5.5.1 can be used to calculate numerous combinations of extractant flow rate, extractant volume, and extraction time that would produce a product of specified purity. In addition, economical operation of the process was a primary consideration. In order to determine the most favorable conditions for extraction, a function was derived that was approximately proportional to the total cost of the extraction process, and the different sets of conditions were evaluated using this function.

It was assumed that the rate of curium production was the same for all sets of conditions because the equipment for each case was sized to produce at this constant rate. This meant that the equipment size was proportional to the total time required for a run, which was equal to the extraction time, Θ, plus an arbitrary turnaround time of 60 min (this covers the time required to fill the extractor, adjust the pH, and load the americium and curium onto an ion exchange column). Because the volume of the primary extractor is proportional to A and that of the solvent recovery extractor is proportional to L, the total equipment volume was assumed to be proportional to $A + L$; it was also assumed to be inversely proportional to the curium yield. These criteria were used to define a function called the size factor,

$$SF = \frac{(A + L)(\Theta + 60)}{A_S(\text{yield})} = (A/A_S)\,\frac{(1 + L/A)(\Theta + 60)}{\text{yield}}\,, \tag{38}$$

where A_S is the standard aqueous phase volume, defined as the aqueous phase volume when extraction is carried out at 46°C and a pH of 3.4 with 40 vol % HDEHP in DEB.

It was assumed that the total cost of the extraction process, including solvent recovery is proportional a cost factor CF_1

$$CF_1 = (SF)^{0.8} . \tag{39}$$

However, this does not include the cost of the feed to the extraction process. To take this into account, a second cost factor,

$$CF_2 = CF_1/\text{yield} , \tag{40}$$

must be used. This cost factor is proportional to the cost of the process if the costs of feed preparation and solvent extraction are equal. This is an arbitrary assumption but CF_2 indicates the influence of feed cost.

The values of SF, CF_1, and CF_2 for different sets of conditions were calculated as follows. All of the calculations assumed a total of 20,078 g of lanthanides, the standard aqueous phase (0.106 *M* DTPA and 1.0 *M* glycolic acid) and DEB as the organic phase diluent. Table 26 lists the conditions used in the calculations. The initial aqueous phase lanthanide concentration, x_0, is the highest that can be used without the danger of formation of solids in the first increment of extractant.

Table 26. Conditions used for first set of minimum cost factor calculations

Temperature (°C)	pH	HDEHP concentration (vol %)	x_0 (total lanthanides)	A (liters)	A/A_S
24	3.0	40	0.023	5992	2.38
46	3.0	40	0.0399	3406	1.36
24	3.4	40	0.030	4552	1.81
46	3.4	40	0.054	2505	1.0
24	3.4	20	0.090	1517	0.601

The value of 0.03 *M* at 24°C, 40 vol % HDEHP, and a pH of 3.4 is taken from Sect. 5.4.4; other values were calculated assuming that the organic phase capacity was proportional to the HDEHP concentration but otherwise

unaffected by the extraction conditions. The average distribution coefficient was assumed to be proportional to that of gadolinium. Thus, the value of x_O was inversely proportional to that of E_A^O under the extraction conditions. The values of A were obtained by dividing the total moles of lanthanides and yttrium per metric ton of fuel (136.55) by x_O.

The temperature, pH, and HDEHP concentration of each set of conditions determined the values of E_A^O and k_f for both components, as well as the values of A and A/A_S. Values of O/A and of D/E_A^O for gadolinium were then chosen and used to calculate F/A [Eq. (31)]. The value of D/E for curium at this flow rate was calculated and used to calculate $1/D$ and $(1/D + O/A)$ for this component. From these values, the constant M was calculated [Eq. (33)] and used in Eq. (36) or (37) to calculate the curium yield. Equation (4) was used to calculate L/A from this yield, and θ was obtained by dividing L/A by F/A. Finally, Eqs. (38)-(40) were used to calculate SF, CF_1, and CF_2. This sequence of calculations was carried out on a programmable Hewlett-Packard HP-25 calculator.

The sequence was repeated using a fixed O/A and a series of values of D/E until minimum values of CF_1 and CF_2 were obtained. Table 27 shows the values obtained for conditions of 40 vol % HDEHP at 46°C with a pH of 3.4 with O/A fixed at 0.05 and the desired product being curium containing 1% gadolinium. Minimum values of both CF_1 and CF_2 occurred at D/E = 0.6.

Table 27. Extraction parameters as a function of D/E_A^O

D/E_A^O for gadolinium	F/A (min^{-1})	Curium yield	L/A	θ (min)	SF	CF_1	CF_2
0.9	0.0066	0.764	1.33	202	799	210	275
0.8	0.0141	0.754	1.43	101	519	149	197
0.7	0.0230	0.742	1.55	68	438	130	175
0.6	0.0340	0.725	1.73	51	417	125	172
0.5	0.0483	0.704	1.97	41	424	126	180

Similar tables were calculated for a series of values of *O/A*. The minimum cost factors for each value were determined and are listed in Table 28. In all cases, the minimum cost occurred at *D/E* = 0.6; however, the flow rates required to produce this value varied widely. The minimum value of CF_1 occurred at *O/A* = 0.075, but the minimum CF_2 occurred at *O/A* = 0.05 because of the greater weight given to the curium yield. The arbitrary 60-min turnaround time has a strong influence on these values. A shorter time would cause the minimum cost factors to occur at a smaller value of *D/E* and a larger value of *O/A*.

Table 28. Influence of *O/A* on conditions for minimum cost operation

O/A	*D/E*	*F/A* (min^{-1})	Curium yield	*L/A*	θ (min)	SF	CF_1	CF_2
0.025	0.6	0.0143	0.756	1.45	101	522	149	198
0.050	0.6	0.034	0.725	1.73	51	417	125	172
0.075	0.6	0.059	0.693	2.01	34	408	123	182
0.100	0.6	0.089	0.664	2.29	26	424	126	190

These calculations were repeated for several other sets of process conditions. These conditions, the calculated conditions for minimum cost operation, and the cost factors are listed in Table 29. The product specified for these calculations was curium containing 1% gadolinium.

The data indicate that the most economical conditions occur at 46°C with an aqueous phase pH of 3.4. Since this pH occurs naturally when the aqueous phase ingredients are mixed, no pH adjustment is required. During an actual differential extraction, there will be a downward drift in pH because of the extraction of part of the sodium. (The extraction of the lanthanides causes very little change in pH, because the $MDTPA^{2-}$ ion is converted to the H_3DTPA^{2-} ion, thus taking up the three H^+ ions received from the HDEHP in exchange for the M^{3+} ion.) This downward drift in pH causes an upward drift in the distribution coefficients (in addition to the increase that occurs because of the decrease in solvent loading). However, the increase in pH is not appreciable until late in the run, when most of the lanthanides have been extracted and there is no danger of overloading the organic phase.

Table 29. Conditions for minimum cost operation and cost factors for curium containing 1% gadolinium

Temperature (°C)	pH	HDEHP concentration, (vol %)	A/A_S	O/A	D/E	F/A (min^{-1})	Curium yield	L/A	θ (min)	SF	CF_1	CF_2
24	3.0	40	2.38	0.05	0.6	0.0191	0.675	1.04	55	829	216	320
46	3.0	40	1.36	0.05	0.6	0.0344	0.696	1.42	41	477	139	200
24	3.4	40	1.82	0.05	0.5	0.0207	0.718	1.32	64	729	195	272
24	3.4	40	1.82	0.075	0.5	0.0375	0.677	1.61	43	722	193	286
46	3.4	40	1.00	0.05	0.6	0.0340	0.725	1.73	51	417	125	172
46	3.4	40	1.00	0.075	0.6	0.059	0.693	2.01	34	408	123	177
24	3.4	20	0.60	0.175	0.6	0.131	0.796	5.77	44	534	152	191

Other calculations were made assuming a pH of 3.4, 40 vol % HDEHP, temperatures of 24 and 46°C, and a product specification of americium containing 1% gadolinium. This specification, which is that recommended for the flow sheet, requires the removal of enough of the lanthanides so that they do not constitute a significant volume of the material to be processed by ion exchange. Table 30 lists the calculated results that yielded the minimum values of CF_1 and CF_2.

Table 30. Conditions for minimum cost operation and cost factors for americium containing 1% gadolinium

O/A	*D/E*	*F/A* (min^{-1})	Curium yield	*L/A*	θ (min)	SF	CF_1	CF_2
				24°C				
0.05	0.5	0.021	0.792	0.93	45	465	136	171
0.075	0.5	0.038	0.761	1.13	30	459	135	177
				46°C				
0.05	0.6	0.034	0.797	1.21	36	266	87	109
0.075	0.6	0.059	0.773	1.42	24	263	86	112

The extractant volumes (*L/A*), extraction times (θ), and cost factors are lower for the americium product than for the curium product because the nuclear waste contains 525 g of americium and only 24 g of curium per megaton of spent fuel. Thus, the separation factor for americium is only 1658, instead of the 38,000 required for curium. Some estimates indicate that waste from plutonium recycle would contain as much as 50 times more curium than the Barnwell waste. Calculations show that if the specifications of Table 29 were applied to this waste, CF_1 and CF_2 would be reduced to 1.6 and 2, respectively.

The neodymium content of the product containing 1% gadolinium in americium, obtained with 46°C, a pH of 3.4, $O/A = 0.05$ and $F/A = 0.034\ min^{-1}$ was calculated to be 1.8%. The values of $E_A^O = 7.3$ and $k_f = 45$ used in these calculations were estimated from the data of Table 12 and the rate constants of Kolarik et al.[20]

The influence of phase loading was ignored in all of these calculations. The initial high lanthanide concentrations in the real process would substantially reduce all distribution coefficients but would also

increase values of k_f. No method is available for calculating these effects for the multicomponent system involved, but they were estimated as follows.

Calculations were made using Eq. (5) and assuming that all of the lanthanides had the properties of gadolinium, and that equilibrium was reached. Under conditions of 46°C, a pH of 3.4, 40 vol % HDEHP, and O/A = 0.05, the increase in L/A was 0.2. In a real nonequilibrium run, the increase will be partially counteracted by the increase in k_f noted above, and the downward drift in pH caused by sodium extraction will increase the distribution coefficients and consequently lower L/A. Thus, the overall error is comparatively small.

In any case, because phase loading would affect all extractions in a similar manner, it has little influence on the selection of optimum conditions.

5.5.3 Recovery of extracted curium

Calculations were made to determine whether the recovery of the curium in the organic extractant was economical or not by backextraction, using the TALSPEAK aqueous phase for the recovery of the curium in the extractant of the best case in Table 30.

The curium recovery in the forward extraction was 79.7%; it was assumed that the overall curium recovery for both extractions should be 99%. The extractant volume after the forward extraction was 1.21 times the original aqueous phase volume. For the differential backextraction, values of A/O = 0.05 and E/D = 0.7 were assumed; the aqueous extractant volume equaled 0.75 times that of the organic phase or 0.91 times that of the aqueous phase in the original forward extraction.

Calculations showed that 14% of the neodymium and lesser amounts of the other lanthanides (e.g., 7% of the gadolinium) would be backextracted along with the curium. The aqueous extract can be combined with the next batch of aqueous feed to the forward extraction or processed separately; in either case, the aqueous phase volume would be nearly doubled, but curium production would be increased only 19%. It was concluded that the recovery of this material is not economical, unless a high cost is attached to the feed to the extraction process.

If essentially quantitative removal of the americium and curium were required for waste management purposes, it could be accomplished with differential back extraction, but the process cost would be increased substantially. A decontamination factor of 1,000,000 would require an aqueous extractant volume 3.2 times greater than the organic volume.

5.5.4 Solvent recovery

Calculations were carried out to establish a solvent recovery process using 6.5 *M* nitric acid in a differential extraction to strip the lanthanides and yttrium from the HDEHP.

The capacity of this extraction is determined by the volume of extractant used in the TALSPEAK extraction. A TALSPEAK aqueous phase of 2500 liters and an HDEHP extractant volume of 3025 liters were assumed. It was also assumed that $D/E_A^O = 0.6$ was achieved in the TALSPEAK extraction and that the curium product contained 1% yttrium (if DTPA eluent is used in the ion exchange separation of curium from americium, a much larger yttrium content can be tolerated). Because of the very large yttrium distribution coefficient in the TALSPEAK extraction, a moderate concentration can be tolerated in the organic phase after stripping and the solution decontamination factor required for yttrium is only 7.55.

With these assumptions and room temperature data, the volume of nitric acid required was calculated at 0.73 liters per liter of HDEHP solution or 0.88 liters per liter of original TALSPEAK aqueous phase; the acid volume corresponding to the waste from 1 metric ton of recovered uranium is 2200 liters. When values of E_A^O estimated at 46°C were used, a slightly lower acid volume was calculated. The nitric acid can be recovered by distillation and reused.

5.6 Radiation Effects

The influence of alpha and gamma radiation on the TALSPEAK extraction solutions was tested by Weaver and Kappelman.[2] They concluded that the DTPA was the most sensitive material present and that its destruction

caused a gradual change in distribution coefficients. One of their tests involved an aqueous phase similar to that of this flow sheet, an organic phase consisting of 0.3 *M* HDEHP in DIB, and curium in solution as the radiation source. The distribution coefficient of curium fell slightly at first and then increased slowly; after 200 Wh/liter of exposure it had reached its original value and after 450 Wh/liter it had approximately doubled. The distribution coefficient of lanthanum did not change.

If 1-year-old waste is used in this process, the aqueous phase will be exposed to 1.7 W/liter of ionizing radiation for <2 hr per run, or less than 2% of the 200-Wh/liter exposure that produced no net increase in the distribution coefficient in the test cited above. If 10-year-old waste is used, the exposure would be only 0.05 Wh/liter. It was concluded that no problem exists.

5.7 Flow Sheet Recommendations

The conditions chosen for the TALSPEAK extraction are as follows.

1. The extraction is carried out at 46°C and a pH of 3.4, with an organic phase containing 40 vol % HDEHP in DEB and an aqueous phase containing 1 *M* glycolic acid and 0.106 *M* Na_5DTPA.
2. The differential extractor operates with a phase volume ratio of $O/A = 0.05$.
3. The estimated extractant flow rate is 0.034 liters/min per liter of aqueous phase. (This flow assumes agitation exactly equivalent to that in the experiments; agitation in the production process should be as vigorous as feasible.)
4. The estimated amount of extractant is 1.21 liters per liter of aqueous phase. (There is some uncertainty in this figure because of the lack of pilot plant data, and impurities in commercial HDEHP will cause some variation in distribution coefficients. Appreciable variation in the americium and curium contents of the feed stock is also possible. Consequently, equipment design should allow for appreciable variation in the ratio of extractant volume to aqueous phase volume.)

5. The lanthanides and most of the yttrium are removed from the HDEHP solution by differential extraction with 6.5 *M* nitric acid at 46°C and $A/O = 0.05$. An acid volume of 0.73 liters per liter of HDEHP solution (0.88 liters per liter of TALSPEAK aqueous phase) is required.

6. REMOVAL OF CURIUM AND AMERICIUM FROM TALSPEAK SOLUTION

6.1 Experimental Work and Previous Investigations

The flow sheet calls for the curium and americium to be loaded onto a Dowex 50 ion exchange resin directly from the TALSPEAK aqueous phase. In a limited investigation of this step, ^{153}Gd was used as a standin for curium on Dowex 50 × 4. At a pH of 2.0, the distribution coefficient was 1900; at a pH of 2.35, it fell to 3.5.

In more extensive investigations by Koch et al.,[3] Dowex 50 × 4, Dowex 50 × 8, Dowex 50 × 12, Lewatit SP 106, Lewatit SP 112, and Lewatit SP 120 ion exchange resins were tested at 21 and 60°C. The results showed that the higher cross-linked resins had a higher capacity but were slower to reach equilibrium; 8% cross linkage was selected as the best compromise. Increasing the temperature from 21 to 60°C increased the usable capacity of the resin as well as the sorption rate. For Dowex 50 × 8, the usable capacity was 0.76 meq/ml (this was lower than the theoretical capacity because of competition from the sodium ion). Some sorption of H_5DTPA was noted. It was concluded that loading is best carried out at a pH of 0.9 to 1.0.

Weaver and Kappelman[2] adjusted the pH of the TALSPEAK aqueous phase to 1.5 and extracted the curium and americium using 1 *M* HDEHP in n-dodecane diluent. The distribution coefficient exceeded 100. The curium and americium were then stripped from the extractant with nitric acid. This appears to be a feasible alternative procedure.

6.2 Flow Sheet Recommendations

The conditions chosen for the removal of americium and curium from the TALSPEAK solution are as follows.

1. The TALSPEAK aqueous phase pH is adjusted to 1 by the addition of nitric acid.
2. The solution is pumped under pressure into a column containing Dowex 50 × 8 ion exchange resin of 25- to 55-μm particle size (about 400 mesh) at 70°C.

3. The loaded resin is washed with two column volumes of 0.1 *M* nitric acid. (The americium and curium from 1 metric ton of irradiated uranium will occupy 3 liters of column volume.[3])

7. SEPARATION OF CURIUM FROM AMERICIUM

7.1 Previous Work

No experimental work was done in this program, but a number of separations have been reported in the literature. Some of these are briefly discussed here.

Burney[22] separated americium from curium by precipitating the americium as $K_3AmO_2(CO_3)_3$ from a potassium carbonate solution. The curium remained in the solution as a soluble carbonate complex.

Ion exchange processes have been used by most other investigators; Wheelwright and Roberts[23] used 50 to 100 mesh Dowex 50 × 8 and tested ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetriacetic acid (HEDTA), nitrilotriacetic acid (NTA), α hydroxisobutric acid, and DTPA as eluting agents. DTPA was chosen for separating americium and curium from the lanthanides and NTA for separating americium from curium. When DTPA was used, the elution sequence was curium, americium, gadolinium, europium, samarium, and yttrium; when NTA was used, it was yttrium, curium, gadolinium (americium-europium), and samarium. A zinc barrier ion was used. The elutions were troubled by the formation of radiolytic gas bubbles, but the separations were successful.

The problem of radiolytic gas bubbles can be largely eliminated by using the high pressure ion exchange technique described by Cambell and Buxton[24] and Cambell.[25] The ion exchange resin used in this method has a very small particle size (∿40 μm in diameter), which speeds equilibration, produces sharper separations, and allows higher eluent flow rates. The high pressure required to force the eluent through the column at a reasonable rate increases the solubilities of the radiolytic gases, causing them to stay in solution.

A high pressure ion exchange process was used by Lowe et al.[26] to separate curium from fission product lanthanides and from americium. The process used Dowex 50 × 8 resin of 25- to 50-μm size and an eluent consisting of 0.05 *M* DTPA adjusted to a pH of 6.0 with ammonium hydroxide. Four 4-ft-long columns in series, respectively 4, 3, 2, and 1 in. in diameter, were used. The operating temperature was 70°C, and a zinc

barrier ion was used. A total of 3 kg of curium was separated by the process. (The material was produced by irradiation of plutonium and contained a much higher ratio of curium to lanthanides and to americium than expected in the Barnwell waste.)

7.2 Choice of Eluting Agent for Flow Sheet

The choice of the eluting agent for this step depends on the age of the waste being processed — more particularly, on the amount of radioactive yttrium present in the waste. When old waste is used, no radioactive yttrium is present. New waste, however, contains an appreciable amount of ^{91}Y.

If old waste is being processed, NTA is the best choice of eluting agent. The small amount of gadolinium present falls between the americium and curium and aids separation. The fact that yttrium falls immediately before curium in elution sequence with NTA, causing relatively poor yttrium decontamination in the ion exchange process and a fraction of a percent of yttrium in the curium, can be ignored when no radioactive yttrium is present.

If new waste is being processed, the presence of ^{91}Y will impose the requirement of a higher decontamination factor. This can be achieved by (1) ensuring a higher decontamination factor in the solvent extraction step or (2) using a different eluting agent. Yttrium decontamination factors of >100,000,000 have been calculated for TALSPEAK extraction with yttrium-free extractant, but because of the cost of removing the yttrium from the extractant only partial removal is planned; the decontamination factor is 2200 (this could be increased by using a greater volume of acid in the extractant recovery step). The use of DTPA as the eluting agent will allow a high yttrium decontamination factor to be achieved in the ion exchange process. While the americium-curium separation is not as sharp, it is adequate if high pressure ion exchange is used.

7.3 Flow Sheet Recommendations

Details of the ion exchange process are left to experts in the field. The size of the operation has been estimated using data from similar processes.

The volume of the resin bed required was assumed to be proportional to the total number of moles of lanthanides plus curium and americium handled in one batch. Volumes taken from the detailed flow sheet calculations of Ref. 4 lead to an estimate of 7.5 liters eluting solution from 1 metric ton of uranium; data from Ref. 26 lead to an estimate of 15 liters. Similar scaling calculations from Ref. 4 indicate that 91 liters of high level waste (HLW) and 46 liters of intermediate level liquid waste (ILLW) will be produced per metric ton of uranium. These are total volumes and include column regeneration and washing.

These calculations were made assuming that the waste has the americium content given in Table 1, which is the content that would be present in the first waste produced by the Barnwell plant. It will be produced from fuel that has decayed for several years. Because ^{241}Am, the principal isotope, is produced by the decay of ^{241}Pu in the fuel rod, the americium content of the waste depends on the decay time before fuel recovery processing. If only 90 days (rather than several years) were allowed before reprocessing, the americium content would be lower by a factor of nearly 4. Because americium is the principal material in the ion exchange process, the resin and solution volumes are approximately proportional to the amount of americium present.

8. TIME REQUIRED FOR OPERATION OF PROCESS

The estimated times required for the steps in the flow sheet are listed in Table 31. Allowances were made for transport of material, filling and draining equipment, etc. Ideally, all units of equipment would be operated continuously, without storage of inventory between steps. This can be achieved if the steps are of the same duration.

The boiler used for acid vaporization cannot be reused until resolution and filtering are complete; thus, the times for these steps were summed. The times in Table 31 are then approximately the same except for those estimated for solution and extraction. The solution equipment will be comparatively inexpensive and will consist of a tank and agitator. Consequently, the capital cost will not be greatly increased if this unit is larger than would be necessary if it were operated continuously. The time required for solvent extraction is roughly half that required for the other steps; to make continuous operation possible, two small batches will be processed in this step for each batch passing through the earlier stages.

Table 31. Times required for process steps

Process step	Time required (hr)
Vaporization of acid	2.5
Resolution of lanthanides and actinides	0.1
Filtering	0.5
Total time per batch for boiler	3.1
Oxalate precipitation	3
Calcining	2.5
Solution	0.7
Extraction	1.6
Loading resin	*a*
Ion exchange	*a*

[a]Not determined.

9. WASTE MANAGEMENT

9.1 Process Wastes

9.1.1 Nitric acid wastes

Appreciable volumes of nitric acid solutions are produced at three points in the flow sheet:

1. during distillation of acid from the original Purex waste,
2. during oxalate precipitation, and
3. during the solvent recovery process.

In all three cases, recovery by distillation is possible.

The acid removed from the original Purex waste will be contaminated by ^{106}Ru, which volatilizes to some degree as RuO_4, and by entrained droplets of the fission product solution. The latter can be controlled in the design of the distillation process. It is estimated that the waste from 1 metric ton of uranium will produce 480 liters of 3.5 *M* HNO_3, which will contain 1680 moles or 106 kg of nitric acid.

The oxalate precipitation will produce 1792 liters of 0.75 *M* HNO_3. This solution will be 0.075 *M* in oxalic acid and will contain most of the ^{137}Cs and ^{90}Sr from the original waste, as well as small amounts of ^{106}Ru and iron. During distillation, up to 20% of the nitric acid will be destroyed by reaction with the oxalic acid. The remaining nitric acid content will be 1073 g-moles or 68 kg.

The solvent recovery process will produce 2500 liters of 6.3 *M* HNO_3, which will contain essentially all of the lanthanides and yttrium, about 20% of the americium and curium, and small amounts of ^{90}Sr and sodium. The nitric acid content will be 15,840 g-moles or 992 kg.

The nitric acid recovered from the acid removal and oxalate precipitation steps can be used as makeup acid in the solvent recovery process, because the ruthenium contaminating the acid has a low distribution coefficient in the HDEHP-nitric acid extraction system and good ruthenium decontamination is achieved in the ion exchange process. The acid removal step alone will provide sufficient makeup acid for the other two steps if the average acid recovery for all three steps is at least 95% efficient.

9.1.2 Residue from acid removal

The residue remaining after acid removal will consist of oxides, hydroxides, and phosphates and will contain essentially all of the zirconium, niobium, and molybdenum and most of the corrosion products and noble metals. The waste from 1 metric ton of recovered material will produce from 20 to 30 kg of material, depending on the degree of hydration and the completeness of removal of the corrosion products and noble metals.

9.1.3 TALSPEAK extraction wastes

The largest single waste stream from the flow sheet is that resulting from loading the resin. It contains both the used TALSPEAK aqueous phase and the resin wash liquid. The waste from 1 metric ton of uranium will produce 2530 liters, containing 191 kg of glycolic acid, 137 kg of Na_5DTPA, and 79 kg of nitric acid. (Recovery of the DTPA and the glycolic acid is theoretically possible, but no technology is currently available.) Complete evaporation and incineration would reduce this residue to 30 kg of sodium ion plus the associated anion, assuming that all of the sodium remained in this waste solution.*

The organic phase can be reused many times, but the HDEHP will eventually deteriorate in three ways.

1. A slow hydrolysis to mono(2-ethylhexyl)phosphoric acid will take place. This monoester is somewhat soluble in the TALSPEAK aqueous phase and will be removed in the extraction process.
2. Some HDEHP will be lost because of direct solubility in the aqueous phases.
3. The capacity of the HDEHP will be reduced by the accumulation of substances with very high distribution coefficients — principally iron, which will enter the system as stainless steel equipment corrodes and traces of the iron in the purex waste may pass the feed preparation steps in trace amounts.

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*A small amount of sodium will be removed in the TALSPEAK extraction and will accompany the lanthanide waste, and a small amount will be sorbed by the ion exchange resin and will be found in the waste from that process.

In addition, decomposition will be caused by ionizing radiation. The damage rate will depend on the age of the waste processed; the intensity will be ∿1.4 W/liter with 1-year-old waste and 0.06 W/liter with 10-year-old waste. These effects can be counteracted by the addition of pure HDEHP, but impurities will accumulate, and eventually the HDEHP must be purified or replaced.

In an attractive method of purification described by Partridge and Jensen,[27] the compound $Cu(DEHP)_2$ is formed by contacting a 1 *M* HDEHP solution with cupric hydroxide slurry. The $Cu(DEHP)_2$ is precipitated by adding acetone, and contact with a strong mineral acid releases pure HDEHP. Results from tests conducted with an HDEHP solution containing monoester, neutral organic impurities, and iron indicated a chemically pure product. It may also be possible to use the gadolinium-HDEHP compound observed in this work (Sect. 5.4.4) for HDEHP purification. The cost of any solvent recovery process must be weighed against the cost of simply replacing the solvent.

In any case, some contaminated liquid organic waste will be produced. This will require incineration either on- or off-site.

9.1.4 Ion exchange process wastes

The estimated amounts of liquid wastes from ion exchange are 91 liters of HLW and 46 liters of ILLW for the waste from 1 metric ton of uranium, assuming that curium alone is recovered. These wastes will contain 80% of the americium, small amounts of lanthanides, sodium, and zinc, and the complexing agent. The volume can be reduced by evaporation and the complexing agent destroyed by oxidation.

The principal nondestructible substance present is americium; if the Barnwell waste (Table 1) is used, 420 g of americium will be present. However, as noted in Sect. 7.3, the amount of americium is dependent on the age of the waste. Thus, the amount of americium present may vary greatly. If a decision were made to recover americium as a by-product, the volume of liquid would be increased.

The ion exchange resin can be reused a number of times but must eventually be replaced (no data are available for estimating the resin's useful life). The contaminated resin will be incinerated.

9.1.5 Gaseous effluents

Small amounts of nitrogen oxides will be produced during acid vaporization. The calcining of the lanthanide-actinide oxalates and their dissolution in the TALSPEAK aqueous phase will produce 9320 liters of mixed CO and CO_2, which will be filtered to remove radioactive dust particles before the CO is burned to CO_2. Comparatively small amounts of contaminated air will also be produced and must be filtered.

9.2 Ultimate Solid Wastes

After all solutions are evaporated, all organic wastes burned, and all nitrates calcined, the additional solid waste will be 30.4 kg of sodium ion for the waste from 1 metric ton of recovered fuel. Small quantities of sulfate and phosphate ion will be added when the ion exchange resin and the HDEHP extractant are incinerated. The 54 kg of fission and corrosion products present in the original waste will also be present.

9.3 Waste Management Opportunities

The greater part of the ^{137}Cs and ^{90}Sr will be found in the supernate from oxalate precipitation; these two isotopes and their short-lived daughters account for >90% of the heat generated by fission products in 10-year-old waste and the ^{137}Cs and its daughter account for most of the hard gamma radiation. The solubility of most cesium compounds also creates problems in forming leach-resistant material for waste storage. Storing the ^{137}Cs and ^{90}Sr separately would simplify the fixing and storage of the other fission products.

The waste from the solvent recovery process contains a relatively pure lanthanide fraction. This should allow synthesis of specific compounds of low solubility for lanthanide waste storage.

10. SUMMARY

A flow sheet has been designed for the recovery of curium from nuclear waste, and the principal process steps have been investigated on a laboratory scale to determine conditions for successful operation. It was assumed that the nuclear waste used in this process will come from the fuel recovery plant planned for Barnwell, South Carolina. Thus, the process was designed to handle waste containing a significant amount of gadolinium (added as a nuclear poison) and an abnormally large amount of americium (produced by several years' decay of ^{241}Pu).

The nitric acid is distilled from the nuclear waste at reduced pressure. The lanthanide and actinide nitrates are leached from the resulting solid cake (molybdenum, zirconium, niobium, and most of the noble metals and corrosion products remain in the insoluble waste). The solution is acidified to 1.0 *M* with nitric acid and the lanthanides and trivalent actinides are precipitated as oxalates, which are then calcined to oxycarbonates.

The oxycarbonates are dissolved in the aqueous phase of the TALSPEAK extraction process, and differential extraction is used to extract the lanthanides from the actinides. The aqueous phase consists of 0.106 *M* Na_5DTPA in 1.0 *M* glycolic acid; the organic phase, of 40 vol % HDEHP in DEB. The lanthanides and yttrium are stripped from the extractant with 6.5 *M* nitric acid, and the actinides, which remain in the aqueous phase, are loaded directly onto Dowex 50 × 8 resin after the solution pH is adjusted to 1.

The curium is separated from the americium and from remaining traces of lanthanides by a high pressure ion exchange process. The expected losses of curium for each step of the flow sheet are given in Table 32.

Table 32. Expected curium losses

Process step	Expected loss (%)
Acid vaporization	0
Leaching of cake	0.5
Oxalate precipitation	0.5
TALSPEAK extraction	21
Ion exchange	0-5[a]
Total	22-27

[a]The separation of curium from americium was not tested.

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