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RECOVERY OF ACTINIDES PRODUCED BY A NUCLEAR DETONATION IN SALT FORMATIONS

D.G. Karraker
W. C. Perkins

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Savannah River Laboratory

Aiken, South Carolina

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RECOVERY OF ACTINIDES PRODUCED BY A NUCLEAR DETONATION IN SALT FORMATIONS

by

David G. Karraker

and

William C. Perkins

Approved by

L. H. Meyer, Research Manager
Separations Chemistry Division

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E. I. DU PONT DE NEMOURS & COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA

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ABSTRACT

A chemical process was developed for the recovery of actinide elements produced by the explosion of a nuclear device in impure salt. The process includes separation of salt by dissolution in water, metathesis of sulfate minerals to carbonates with ammonium carbonate solution, dissolution of the metathesized solids in 6M nitric acid, precipitation of silica from the solution by gelatin, and two alternating solvent extraction and evaporation steps to produce a concentrated product solution. Developmental tests of the process with samples of debris from the Gnome test indicated that gram quantities of actinides could be recovered in greater than 85% yield from 3 x 10^4 tons of debris. The two solvent extraction cycles demonstrated a separation of actinides from major cationic impurities—Ca^{2+}, Mg^{2+}, and Fe^{3+}—by a factor of $>10^5$ and, combined with evaporation, gave a product solution equivalent to 100 gallons per 10^4 tons of original salt debris.

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RECOVERY OF ACTINIDES PRODUCED BY A NUCLEAR DETONATION IN SALT FORMATIONS

INTRODUCTION

One objective of the Plowshare Program(1) is to produce gram quantities of transplutonium actinides by irradiation of a uranium target with neutrons from the explosion of a thermonuclear device. One approach in the program is to explode the device(2) in an underground salt formation near Carlsbad, New Mexico, and to recover the actinides by mining and processing the salt debris. The major problems in recovery of the actinides arise from the amount and composition of the shot debris.(3) About 500 tons of salt are melted per kiloton of energy.(4) A 10-kiloton shot will thus melt about 5000 tons of salt, and the total debris will be increased to 20,000 to 30,000 tons by spalling of salt from the roof of the surrounding cavity. The recovery of gram amounts of product from this quantity of material requires a concentration factor of about 10^9.

The salt beds of the Carlsbad area, in common with other salt beds of the southwestern United States, are layers of impure salt separated at 5- to 10-foot intervals by thin layers of silt, sand, or clay. The gross composition of the salt is about 95% sodium chloride, with the remaining 5% comprised of about thirty elements, all of which are present in larger amounts than the actinides produced in the detonation.

Despite the problems associated with chemical recovery from these salt beds, this medium is one of the best available for chemical recovery of the actinides.(5) The solubility of salt in water offers a convenient beginning for an aqueous process, and the trace elements serve as carriers for the actinides in the debris by collecting the actinides in a separate solid phase during post-shot condensation. The absence of rare earth elements as impurities renders the separation of actinides from impurities a relatively routine chemical processing task, similar to the processing involved in the recovery of actinides from reactor-irradiated uranium.

This report describes the development of a chemical process for recovery of actinides from the debris of nuclear detonations in salt. After consideration of the alternatives, solvent extraction was selected as the most economical unit process. Debris samples from the Gnome Shot (December 1961) were used in the development program. Gnome was detonated in the salt strata near Carlsbad, in the immediate vicinity of the site considered for future isotope production experiments; the composition of the Gnome debris was essentially the same, except for actinide products, as the debris expected from isotope production in this area. Moreover, the plutonium in the Gnome debris proved to be an excellent tracer in developmental studies.

SUMMARY

A chemical process was developed for recovery of transplutonium actinides produced by a thermonuclear explosion in salt strata. The process involves (1) removal of salt from the debris by leaching with water, (2) ammonium carbonate metathesis of the water-insoluble fraction of the debris to remove sulfate, (3) dissolution of the metathesized debris in boiling 6M nitric acid, (4) adjustment of the solution to 6M total nitrate—0.1M nitric acid, and (5) recovery and concentration of the actinides by solvent extraction with 30% tri-n-butyl phosphate (TBP). This solvent extraction product is evaporated, and then adjusted for a second stage of solvent extraction for additional purification and concentration. Evaporation of the product solution from the second solvent extraction cycle produces a solution that contains in a small volume about 85% of the actinides and rare earths present in the original debris (ca. 100 gal/10^4 tons of debris). This concentrate is suitable for the operations necessary to separate and purify the separate actinide elements. A detailed flowsheet of the process is shown in Figure 1.

Developmental studies and a process demonstration were made with samples of debris produced in the Gnome shot. In process demonstration tests, 99.4% of the salt was removed from the debris by water dissolution, with a loss of only 0.1-0.2% of the actinides. A one-hour agitation of the water-insoluble fraction of the residue with a 300% stoichiometric excess of ammonium carbonate solution replaced 95% of the sulfate with carbonate with an actinide loss of <1%; residual salt was also reduced in this step. The excess ammonium carbonate can be recovered for reuse by distillation of the waste carbonate solution.

The actinides were dissolved from the water-insoluble residue, after carbonate metathesis, with boiling 6M HNO_3. From samples of high silicate content, 97% of the actinides and 54% of the total solids were dissolved in two consecutive 6-hour treatments. The dissolver acid and wash solutions were separated from the undissolved solids by decantation, and then evaporated to reduce their volume and to coagulate colloidal silica. Silica remaining in the solution was precipitated by adding gelatin to 100 ppm, and was removed by filtration. Neutralization of the acid with sodium hydroxide to a final concentration of 6M total nitrate—0.1M HNO_3 produced a satisfactory feed solution for subsequent solvent extraction processing.

Actinides and rare earths were separated from inert impurities and concentrated to a small volume by two cycles of solvent extraction and evaporation of each product stream. Demonstration tests of the first cycle of solvent extraction indicated a product loss of only 1% (based on curium recovery) and a product contamination of less than 0.01% of the total iron, calcium, magnesium, sodium, and copper in the original

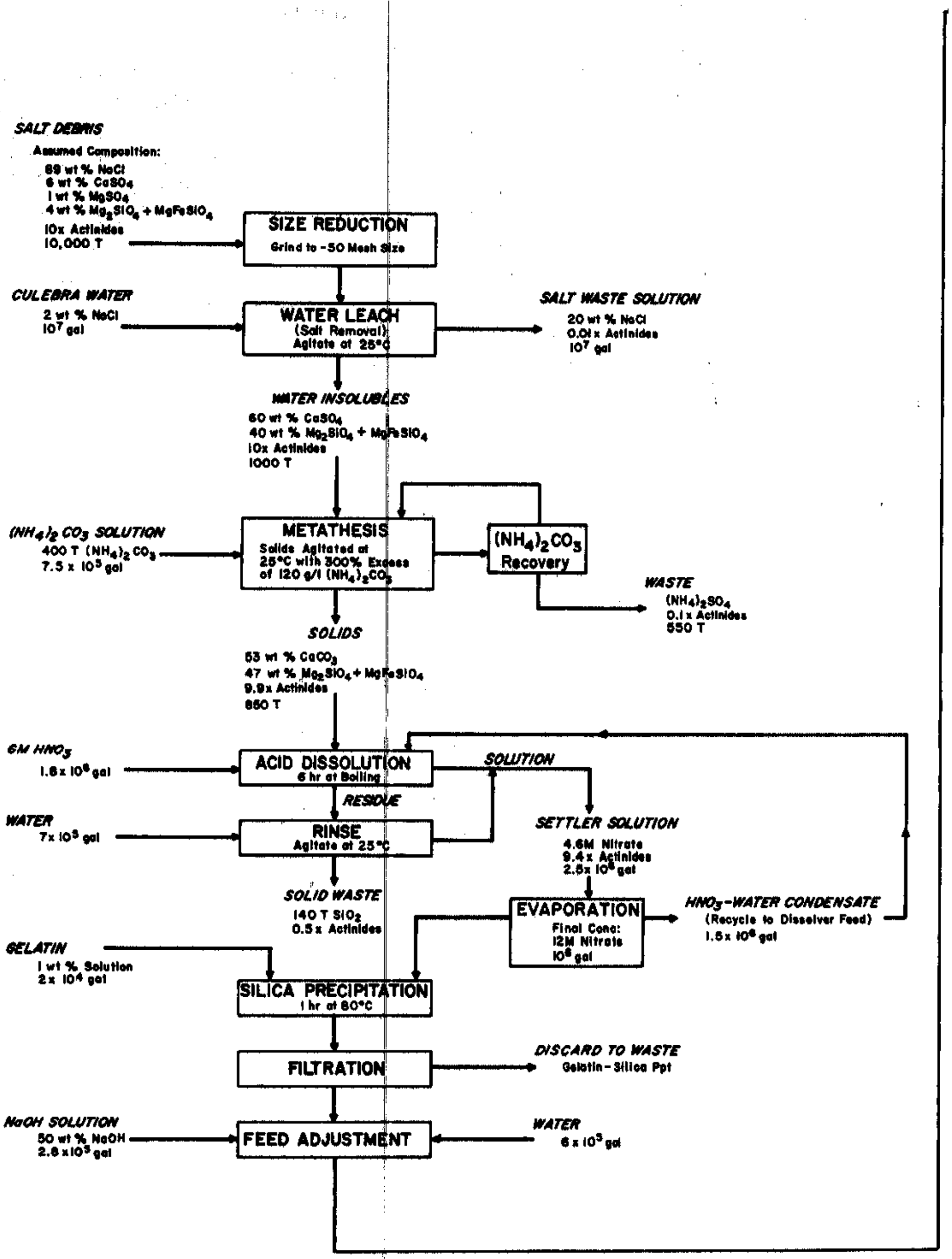
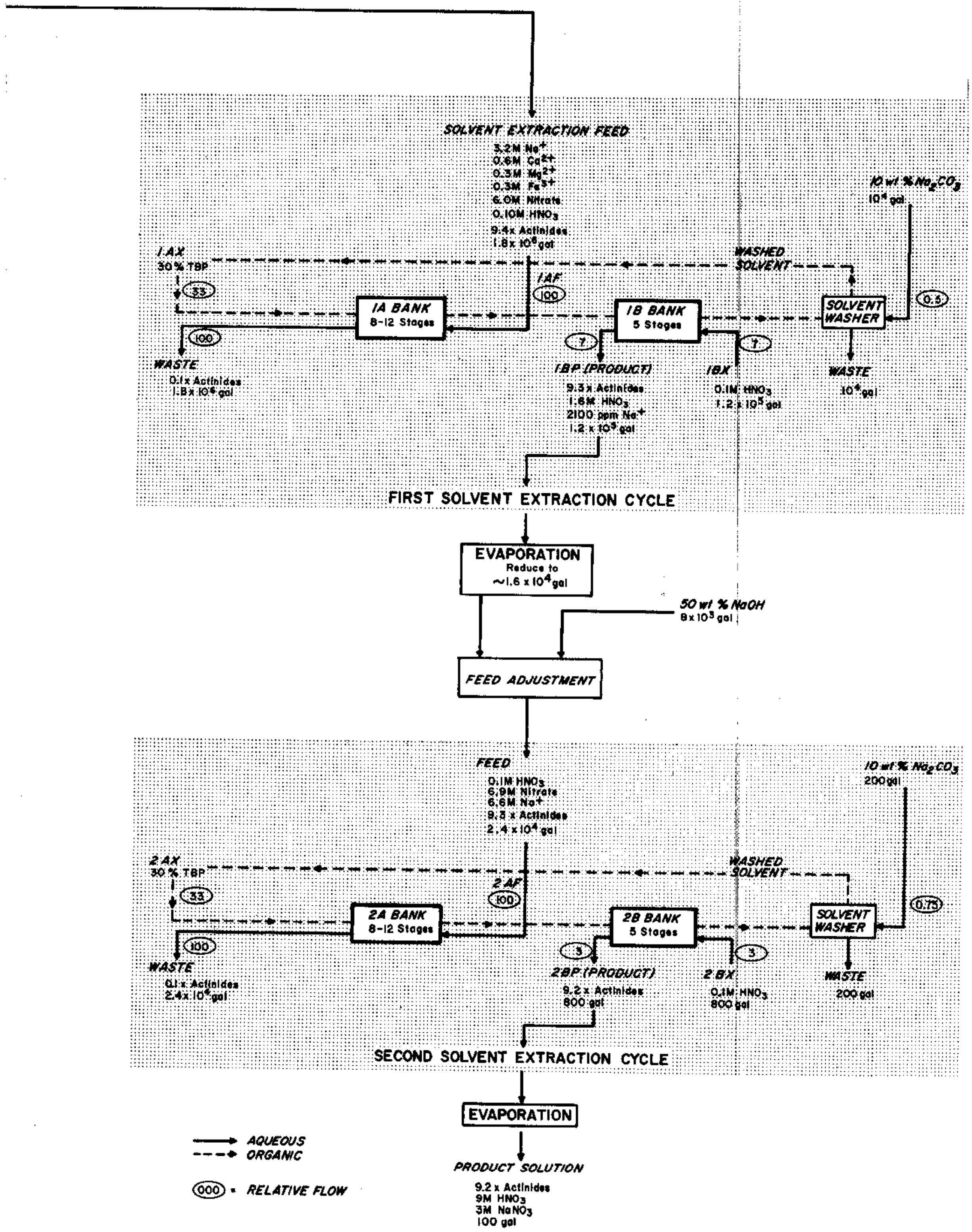


FIG. 1 RECOVERY PROCESS


SOLVENT EXTRACTION FEED
3.2M Na+
0.6M Ca2+
0.3M Mg2+
0.3M Fe3+
6.0M Nitrate
0.10M HNO3
9.4x Actinides
1.8x 10^6 gal
10 wt % Na2CO3
10^4 gal
1AX
30 % TBP
33
WASHED SOLVENT
1AF
100
1A BANK
8-12 Stages
1B BANK
5 Stages
SOLVENT WASHER
0.5
100
7
7
WASTE
0.1x Actinides
1.8x 10^6 gal
1BP (PRODUCT)
9.3x Actinides
1.6M HNO3
2100 ppm Na+
1.2 x 10^5 gal
1BX
0.1M HNO3
1.2 x 10^5 gal
WASTE
10^4 gal
FIRST SOLVENT EXTRACTION CYCLE
EVAPORATION
Reduce to
~1.6 x 10^4 gal
50 wt % NaOH
8x 10^3 gal
FEED ADJUSTMENT
FEED
0.1M HNO3
6.9M Nitrate
6.6M Na+
9.3 x Actinides
2.4 x 10^4 gal
10 wt % Na2CO3
200 gal
2AX
30 % TBP
33
WASHED SOLVENT
2AF
100
2A BANK
8-12 Stages
2B BANK
5 Stages
SOLVENT WASHER
0.75
100
3
3
WASTE
0.1 x Actinides
2.4x 10^4 gal
2BP (PRODUCT)
9.2 x Actinides
800 gal
2BX
0.1M HNO3
800 gal
WASTE
200 gal
SECOND SOLVENT EXTRACTION CYCLE
EVAPORATION
AQUEOUS
ORGANIC
000 = RELATIVE FLOW
PRODUCT SOLUTION
9.2 x Actinides
9M HNO3
3M NaNO3
100 gal

debris. A concentration factor of 16 was demonstrated for the first solvent extraction cycle, and a concentration factor of 10 for evaporation of the product stream. Adjustment of this solution to 6M $NaNO_3$—0.1M HNO_3 provided a satisfactory feed to the second cycle of solvent extraction. Tests with synthetic solutions indicated that concentration factors of 16 and 10 would be attained in the second solvent extraction cycle and evaporation of the product stream, as in the equivalent first cycle operations. Based on the tests with synthetic feed solutions, the final product solution would contain less than 10^{-4}% of the total cationic impurities in the original debris. Concentration factors demonstrated in laboratory tests are considered quite conservative, and the concentration in plant-scale operation would actually be limited by equipment performance.

DISCUSSION

PRELIMINARY INVESTIGATIONS

Selection of Dissolvent

Initial studies on the processing of salt debris demonstrated that the salt could be separated from the bulk of the debris by leaching with water, and that essentially all the actinides would remain with the water-insoluble residue. Both leaching and dissolution of this residue were explored as methods to produce an aqueous solution for further processing. Leaching would be successful if the actinides were held on the water-insoluble debris by adsorption on the surface of the particles; if the actinides were distributed through the bulk of the particles, dissolution of the water-insoluble debris would be necessary to produce a solution for processing. Preliminary tests showed that leaching was unsuccessful; plutonium was dissolved approximately in proportion to the mass of the water-insoluble residue dissolved (Table I). These tests demonstrated that nitric acid was a satisfactory dissolvent.

TABLE I

Dissolution of Water-Insoluble Residue

Sample[(a)]	Dissolving Solution	Residue Dissolved, wt %	Pu Dissolved, %
B	1.7M K_2CO_3	9.4	6.5
E	1.7M K_2CO_3	6.8	11
F	1.7M K_2CO_3	6.7	13
B	10M NaOH	-	2
B	H_2O (following Na_2CO_3 fusion)	-	1
B	8M HNO_3	67	92
E	8M HNO_3	72	89
F	8M HNO_3	71	96

(a) Samples were obtained from corings of Gnome debris and are lettered to correspond to the drill hole.

Investigation of Recovery Processes

Three possible processes were considered for separation and recovery of the actinides from the nitrate solution: ion exchange, solvent extraction, and precipitation. A preliminary evaluation of the cost for construction and operation of a processing facility indicated that the most economic unit process would be ion exchange, and the least economic, precipitation. After this evaluation, scouting experiments on tracer curium solutions were initiated to discover an ion exchange process that was practical in a system that was not chemically corrosive to stainless steel. Several excellent ion exchange processes[6] have been developed for actinide separations, but all require strong chloride solutions. Chloride solutions are extremely corrosive to stainless steel, the normal construction metal for chemical processing plants. "Monel"* or nickel equipment for use with chloride solutions was judged to be excessively expensive; plastic-lined equipment was considered to have an uncertain process life.

Scouting experiments showed excellent adsorption of tracer curium on "Dowex" 21K** anion exchange resin from dilute carbonate solution. Distribution coefficients (K_d***) were 400-1600 from 0.1M CO_3^{2-}—HCO_3^- solutions at pH values of 8.5-11. Above pH 11, curium adsorption decreased, and strong (>0.5M) carbonate solutions displaced curium from the resin. The probable species adsorbed is $Cm(CO_3)_2^-$; the adsorption decreases rapidly as the K_2CO_3 concentration exceeds 0.1M, probably because the carbonate ion is more strongly adsorbed than $Cm(CO_3)_2^-$.

Attempts to use carbonate ion exchange for processing Gnome debris, however, were unsuccessful. A process based on ion exchange requires that the nitrate solution of actinides be adjusted to a solution containing about 0.1M CO_3^{2-}—HCO_3^-. Calcium and magnesium carbonates precipitated during this adjustment and scavenged 94-99% of the curium from the solution. Anion exchange from strong nitrate solutions was unsuccessful. Scouting experiments showed K_d values for "Dowex" 21K of only 2-5 from nitrate concentrations of 4M to 9.5M, and acidities from 1M to pH 7.3.

The failure of these tests to provide the practical basis for a process led to investigation of solvent extraction.[6,7] Preliminary tests on the extraction of curium, americium, and cerium tracers from calcium nitrate—magnesium nitrate—nitric acid solutions into TBP showed adequate extraction for a recovery process (Table II).

The extraction was increased at higher TBP concentrations and at greater aqueous salt concentrations. Decreased extraction under even stronger salting and/or greater TBP concentrations was attributed to back-salting of curium, americium, and cerium by nitric acid and to

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* Registered trademark of International Nickel Co.

** "Dowex" is a trademark of Dow Chemical Co.

***K_d = (curium concentration in resin)/(curium concentration in the aqueous phase) ferric nitrate extracted into the organic phase. The extraction coefficients were adequate for either a batch or continuous solvent extraction process.

TABLE II

Extraction Coefficients of Cm, Am, and Ce Between Nitrate Solutions and TBP

	$E_{o/a}$ of Cm	$E_{o/a}$ of Am	$E_{o/a}$ of Ce
4.8M Nitrate[(a)]			
30% TBP[(b)]	14	15	8
50% TBP	25	21	9
70% TBP	10	25	9
7.6M Nitrate[(c)]			
30% TBP[(b)]	7	13	4
50% TBP	60	75	17
70% TBP	13	44	6

(a) 2.1M $Mg(NO_3)_2$, 0.2M $Ca(NO_3)_2$, 0.07M $Fe(NO_3)_3$, 0.16M HNO_3.

(b) TBP diluted with "Adakane 12" (Trademark of Archer Daniels Midland Co.).

(c) 3.5M $Mg(NO_3)_2$, 0.2M $Ca(NO_3)_2$, 0.07M $Fe(NO_3)_3$, 0.16M HNO_3.

An investigation of the effect of chloride on the extraction of curium by 30% TBP showed an insignificant decrease in the extraction coefficients for chloride concentrations up to 3500 ppm (0.1M). At 4.8M NO_3^-—0.1M HNO_3, the extraction coefficient for iron was sufficiently low to permit rejection of iron in solvent extraction. These tests were made by extraction of ^{242}Cm tracer from an aqueous phase composed of 2.1M $Mg(NO_3)_2$, 0.3M $Ca(NO_3)_2$, and 0.1M HNO_3 with varying amounts of NaCl and $Fe(NO_3)_3$. The extractant was 30% TBP, washed consecutively with 0.2M NaOH and 0.01M HNO_3 just prior to use. The distribution coefficients determined are tabulated in Table III.

These results indicate that the solvent extraction process can tolerate rather high levels of chloride without any serious effect on efficiency, and that no appreciable increase in iron extraction results from the chloride impurity. Limitations on chloride are considered more likely to arise from corrosion of equipment than from its effect on the solvent extraction chemistry.

TABLE III

Effect of Chloride on Extraction of Curium with 30% TBP

Chloride Concentration[(a)]		$HNO_3 \cdot TBP$,	Fe^{3+}, M		$E_{o/a}$ for
M	ppm	M	Aqueous	Organic	^{242}Cm
0.003	100	0.103	0.054	0.0011	21.0
0.012	440	0.102	0.054	0.0011	20.9
0.022	780	0.103	0.054	0.0012	20.2
0.031	1100	0.102	0.054	0.0014	18.4
0.003	100	0.122	0.10	nd[(b)]	18.3
0.012	420	0.119	0.10	nd	18.6
0.021	740	0.121	0.10	nd	17.0
0.029	1000	0.115	0.10	nd	17.2
0.003	100	0.096	0	0	19.9
0.013	460	0.094	0	0	18.0
0.023	820	0.093	0	0	17.5
0.033	1200	0.092	0	0	16.9
0.052	1800	0.091	0	0	18.3
0.098	3500	0.086	0	0	16.0
0.185	6500	0.084	0	0	11.8

(a) Aqueous phase is 2.1M $Mg(NO_3)_2$—0.3M $Ca(NO_3)_2$—0.1M HNO_3.
(b) nd = not determined.

Process Selected

From these tests, a process was designed that included the following steps:

1. Removal of salt from water-insoluble debris by leaching with water.
2. Metathesis of the water-insoluble debris with aqueous ammonium carbonate to remove sulfate.
3. Dissolution of the water-insoluble debris in nitric acid.
4. Clarification of the solution of dissolved residue.
5. Adjustment of the solution to proper concentration for feed to solvent extraction.
6. A first cycle of solvent extraction to separate actinides and rare earth elements from gross debris, and to reduce process volume.
7. Evaporation of solvent extraction product solution to reduce process volume further.

8. A second cycle of solvent extraction to separate the actinides from residual ionic impurities and to obtain additional volume reduction.

9. Evaporation to produce a final product concentrate that contains >85% of the actinides in a small volume.

DISSOLUTION OF DEBRIS

Sample Description

Samples of debris from the Gnome Test, conducted in December 1961 at the Carlsbad, N. M., site adjacent to the proposed Coach Test site, were obtained from the Lawrence Radiation Laboratory at Livermore, California, for process development studies. The samples were designated B, E, F, and Drift Composite, according to their original location in the test site. The samples consisted of whole drill corings and grey powder with radiation levels from 100 to 500 mr/hr. Some of the corings from Sample F showed two distinct zones—a gray, radioactive, cinder-like material and a pink crystalline salt with negligible radioactivity. The gray material was debris that had been melted by the explosion, and the crystalline coring was the natural salt formation. The samples contained 80 to 96% water-soluble salts, NaCl plus a small amount of $MgSO_4$.

The radioactivity in the Gnome debris samples was mainly unburned plutonium from the nuclear device and fission products produced in the explosion. Curium-242 tracer was added to the device before detonation to assist development studies. The activity level of the samples varied about a factor of five between samples of the crude debris, but only varied by a factor of two to three between samples of the water-insoluble fractions (Table IV).

TABLE IV

Radioactivity of Gnome Debris Samples

Sample	Water-Insoluble Fraction, wt % of sample	Alpha Activity,(a) dis/(min)(g)		Fission Product *Gamma* Activity, counts/(sec)(g)	
		Raw Sample	Water-Insoluble Fraction	Raw Sample	Water-Insoluble Fraction
B	5.2	1×10^5	2×10^6	6×10^4	1.4×10^6
E	3.6	3.3×10^4	9.2×10^5	4.6×10^4	10^6
F	9.2	1.5×10^5	1.9×10^6	3.5×10^4	3×10^6
Drift Composite	5.8	6.5×10^4	1.1×10^6	1.3×10^5	3.8×10^6

(a) 99.9% mixed plutonium isotopes.

The Drift Composite was different from Samples B, E, and F. In general, the water-insoluble fractions of Samples B, E, and F were predominantly calcium sulfate, but the Drift Composite was much higher in silicates and iron, and relatively low in sulfates. A comparison of the calculated components of Sample F and the Drift Composite is shown in Table V. Minor constituents of the water-insoluble fraction of the debris are shown in Table VI.

TABLE V

Calculated Composition of
Water-Insoluble Fractions of Gnome Samples

	Sample F	Drift Composite
$CaSO_4$, wt %	62	11
$MgSO_4$, wt %	16	-
Olivine (combined Mg_2SiO_4 and $MgFeSiO_4$), wt %	20.5	40
SiO_2 (excluding olivine), wt %	-	43
NaCl, wt %	-	5
Fe, wt %	2.5	10

TABLE VI

Minor Components of
Water-Insoluble Fractions of Gnome Samples

Sample	Minor (0.1-3%)	Trace (<0.1%)
B, E, and F	Fe, Al, Pb, Cu	Ti, Cr, Ni, Mn, Mo
Drift Composite	Al, Pb, Cu	Ti, Cr, Ni, Mn, Ag

The large amount of silicates present—over 80% of the water-insoluble fraction of the Drift Composite—was a major cause of difficulties in the feed preparation steps. The removal of salt by water leaching and sulfate metathesis was less effective on this material than on Samples B, E, and F, and the inclusion of some salt and sulfates with the silicate minerals is presumed to be responsible.

Water Leaching

Random samples (B, E, F) were crushed, ground to a fine powder, and leached with boiling water for several hours. The pH of the leach water increased from 5.6 to 7.0 during these tests, suggesting the presence of basic oxides.* The results of water leach tests, shown in

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*Powdered samples of the debris reduced dilute ceric solution. It is presumed that FeO is responsible for this effect.

Table VII, indicate that the leaching is more effective on those fractions that were ground to -50 mesh. Distilled water dissolved considerably more of the debris than did the Culebra water obtained from the Carlsbad test site. Culebra water is relatively impure (Table VIII) and is nearly saturated in calcium sulfate. Leaching with distilled water was more effective because of the greater solubility of calcium sulfate. However, the large amount of leach water needed for a large-scale process at the Carlsbad site virtually requires the use of Culebra water.

TABLE VII

Water Leach Tests on Gnome Samples

(Solids boiled 2 to 4 hours)

Sample	Mesh	Type Water	Total ml H_2O/g Sample	% Water Insoluble
B	+50	Culebra	14	11.5
	-50	Culebra	7.5	8.8
	-50	Distilled	5.1	6.0
E	-50	Culebra	8.9	5.3
	Ungraded	Distilled	10	3.6
F	+50	Culebra	10	26
	-50	Culebra	10	20
	-50	Distilled	5.5	11
Drift Composite	-50	Culebra	3.7	9-12

TABLE VIII

Composition of Culebra Water

Constituent	Concentration, M
NaCl	0.021
$CaSO_4$	0.015
$MgSO_4$	0.0052
Fe^{3+}	<0.001

The only major activity found in the water leach solution was ^{137}Cs. Loss of alpha activity to the solution was on the order of 0.2% or less. The ratio of ^{242}Cm to plutonium in the water waste was the same as in the water-insoluble residue, implying that neither was leached selectively from the insoluble residue.

The quantity of residual chloride is important in assessing the corrosion potential for stainless steel equipment during processing of the water-insoluble fraction of the debris. The amount of chloride retained in the debris after dissolving the salt and washing the residue was determined as a function of the particle size of the original debris. Sample B was crushed and dry-screened to obtain approximately 50-gram portions of debris in different particle size ranges. The salt in each portion was treated with 500 ml of hot, distilled water, and the insoluble residue was washed repeatedly in 250 ml of boiling water for 1-2 hours. After each wash a sample of the wash solution was analyzed for chloride. The final residue was dissolved with 6M HNO_3 in a closed system with a nitrogen sweep through the system and an alkali scrubber to collect the HCl that was evolved during the dissolution. Results of the experiments are shown in Table IX.

TABLE IX

Chloride Removal Tests on Water-Insoluble Residue

(50-g portions of Sample B)

Sample size (mesh, U. S. Standard Sieve Series):	-50 +100	-100 +200	-200
Water-insoluble residue, wt % of debris	1.8	3.5	5.3
Chloride, wt % of residue			
After salt dissolution in 500 ml of hot H_2O	2.6	1.8	0.25
After 1 wash in 250 ml of hot H_2O	0.61	0.28	0.22
After 5 washes of 250 ml each	0.54	0.22	0.17
Wt % of washed residue dissolved in 6M HNO_3	67	40	72
Chloride in final HNO_3 solution, ppm	7	5	14
% of chloride evolved during acid dissolution of residue	82	87	70

These data demonstrated that 99.4% of the chloride present in the debris was removed by dissolution and a single wash step, and that the chloride can be decreased further by about a factor of three by crushing the original debris to -200 mesh. The leaching experiments also showed that no significant reduction in chloride content was observed after the first wash. The majority of the residual chloride was volatilized during the nitric acid dissolution, and the final chloride content of the solution was at an acceptable level. The amount of chloride evolved indicates that alkali absorbers may be necessary to protect a plant ventilation system. A surprising observation from these experiments is that the water-insoluble material was concentrated in the finer fraction. This result can be explained by assuming that salt particles including a second solid phase are more easily crushed than pure salt particles.

Sulfate Metathesis

Preliminary tests of the dissolution of water-insoluble residue in nitric acid showed that precipitation of calcium sulfate from the nitric acid solution would ensue. This $CaSO_4$ could cause fouled equipment or plugged transfer lines during large-scale processing. Since Culebra water is saturated with $CaSO_4$, the removal of $CaSO_4$ from the water-insoluble residue would be still less effective under processing conditions at Carlsbad. This consideration led to the investigation of methods for leaching $CaSO_4$ from the water-insoluble residue prior to dissolution.

A survey of the available solubility data(8) for $CaSO_4$ indicated that the normal solubility of 2.08 g/l in water is exceeded in solutions of ammonium salts by factors of 5 to 10. To verify these data, samples of Gnome debris from Sample F were leached with Culebra water, and portions of the water-insoluble residue were leached with solutions of NH_4NO_3, $NH_4C_2H_3O_2$, NH_4Cl, and $(NH_4)_2CO_3$. After leaching, the samples were rinsed with water. The insoluble residue was analyzed for sulfate by infrared absorption before and after leaching, and the leach and rinse solutions were analyzed for plutonium alpha activity. The results are shown in Table X.

TABLE X

Removal of $CaSO_4$ by Ammonium Salts(a)

	NH_4NO_3	$NH_4C_2H_3O_2$	NH_4Cl	$(NH_4)_2CO_3$
Concentration, g/l	600	210	200	180
Pu loss, %	11	5	6	1
Residual SO_4^{2-}, wt %(b)	15	20	27	3.6

(a) Water-insoluble fraction of Sample F stirred 1 hour at 25°C in 10 ml of salt solution per g.
(b) Initial SO_4^{2-}: 38 wt %.

Treatment with ammonium carbonate was superior in sulfate leach performance to treatment with the other salts. Additional tests with $(NH_4)_2CO_3$ solutions showed that:

- Better than 95% of the sulfate was removed by 0.3 gram of $(NH_4)_2CO_3$ per gram of Sample B.
- Curium and plutonium maintained the same ratio in the leach solution as in the solid residue.
- The loss of alpha activity was low.

Some results are shown in Table XI. The curium loss to the $(NH_4)_2CO_3$ solution was about 1%, and, as stated, no significant selectivity for curium over plutonium was observed. The superiority of $(NH_4)_2CO_3$ over the other salts is attributed to different mechanisms of sulfate removal: $(NH_4)_2CO_3$ metathesizes $CaSO_4$ to $CaCO_3$, removing only the sulfate, whereas the removal of $CaSO_4$ by other ammonium salts depends upon increasing the solubility of $CaSO_4$.

TABLE XI

Removal of Sulfate by $(NH_4)_2CO_3$ Metathesis[(a)]

Amount of $(NH_4)_2CO_3$, g/g of residue	SO_4^{2-} Removed, %	Pu Loss to Filtrate, %
0.055	56	~0.1
0.112	55	~0.1
0.166	78	1
0.305	95	1
0.918	97	1

(a) Water-insoluble fraction of Sample B (11 wt % SO_4^{2-}) stirred 1 hour at 25°C in 5.0-5.3 ml of solution/g.

In an integrated demonstration test to remove the water-soluble fraction and metathesize the sulfate with $(NH_4)_2CO_3$, 1 kg of the non-radioactive fraction of Sample F of Gnome debris was processed. The Culebra-water-insoluble residue was 12.1 wt % and contained 23 wt % of sulfate. Two consecutive treatments with 1-liter portions of 180-g/l $(NH_4)_2CO_3 \cdot H_2O$ (300% of the stoichiometric equivalent) reduced the sulfate to 1 wt %. This metathesized residue after acid leach (described below) yielded a feed solution that was concentrated to 173 ml and contained 417 g of residue per liter.

Dissolution of Water-Insoluble Residue

In preliminary tests, nitric acid was an effective reagent for removing plutonium from the water-insoluble residue. Small samples of the water-insoluble fraction of Sample B were tested by boiling in 1.7M K_2CO_3, 10M NaOH, and 8M HNO_3 and by fusion with Na_2CO_3 followed by water leaching. These treatments, except for that with 8M HNO_3, dissolved less than 13% of the plutonium in the samples, as shown in Table I.

Further tests confirmed that most of the water-insoluble residue* dissolved in hot HNO_3 at concentrations between 1 and 8M (Table XII).

TABLE XII

Nitric Acid Dissolving Tests

Water-Insoluble Fraction of Sample B
Samples boiled in HNO_3 1-2 hours

HNO_3, M	1	2	6	8
Ml of acid/g of sample	60	40	30	45
Residue dissolved, wt %	71	78	72	71
Plutonium dissolved, %	71	65	87	85

Samples of the water-insoluble residue from the Drift Composite were dissolved in nitric acid under varying conditions of temperature, time, and acid volume to determine optimum dissolving conditions and the effect of these conditions on the production of a clarified feed solution for solvent extraction. Test results are shown in Table XIII. Boiling the residue in 6M HNO_3 dissolved the bulk debris and leached the plutonium more efficiently than treatments at room temperature. Boiling in 6M HNO_3 for periods longer than two hours did not improve the dissolution significantly, but from the evidence of other tests aided the coagulation of hydrated silica.

TABLE XIII

Effect of Dissolving Conditions on Performance

Water-Insoluble Fraction of Drift Composite Sample

HNO_3, M	6	6	6	6	6	3	3	4
HF, M	0	0	0	0	0	0	0	0.6
Acid volume, ml/g	50	10	5	5	10	5	5	10
Temperature	Ambient	Ambient	Ambient	Boiling	Boiling	Boiling	Ambient	Ambient
Time, hr	26	6	288	2[a]	6	2[b]	2	4[c]
Water-insoluble residue dissolved, wt %	43	40	41	48	52	40	43	41
Pu dissolved, %	32	40	52	86	89	42	22	49
Settling Rate,[d] in/hr	300	0.1	0.1	0.5	1	-	0.1	-

(a) A second 2-hour treatment dissolved an additional 5 wt % and 12% of Pu.
(b) A second 2-hour treatment dissolved an additional 12 wt % and 35% of Pu.
(c) A second 4-hour treatment dissolved an additional 19 wt % and 25% of Pu.
(d) Sample B settled 0.2 in/hr after 1 hour in 6M HNO_3 at 65°C.

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*Treatment of the acid-insoluble residues with boiling 5M HCl dissolved less additional residue and plutonium than further HNO_3 treatment.

FEED CLARIFICATION

General

During the dissolving tests on samples of high silicate content, unusual difficulties were experienced in clarifying the solution sufficiently for solvent extraction. The dissolver solutions contained small particles of flocculent, hydrated silica that were removed only after repeated centrifugations. Attempts to filter the slurry failed from pluggage of the filter. Also, the filtrate still contained some colloidal and dissolved silica, which interfered with solvent extraction operations by forming emulsions with the organic extractant and by coagulating at the aqueous interface. The majority of the silica was dispersed during the initial contact of the water-insoluble debris with acid. Subsequent acid treatments on the same sample produced solutions that were considerably easier to filter.

Several methods were tested to develop an efficient technique for clarification of the dissolver solutions, including refluxing the solutions in strong nitric acid to coagulate the silica, diluting the dissolver solution to accelerate filtration and settling rates, coagulating with gelatin, and dissolving the silica with hydrofluoric acid.

The most effective procedure for feed clarification involved (1) extended boiling in 6M HNO_3, (2) decantation of the clear supernate, (3) recovery of the remaining solution by dilution and decantation, (4) evaporation, and (5) precipitation of silica from the evaporated solution with gelatin. Boiling in 6M HNO_3 coagulated most of the silica during dissolution, permitting decantation of a large fraction of the solution as clear supernate. The gelatin[8] treatment precipitated the suspended or colloidal silica remaining in the solution. This procedure was developed initially on a small scale, and the test described in the following section validated adequate performance on a larger scale.

Dissolution and Clarification Demonstration

A 1-kg batch of Drift Composite was used to prepare solvent extraction feed according to the flowsheet shown in Figure 2. The water-insoluble residue was leached with two portions of boiling 6M HNO_3 for 6 hours. The first leach solution was allowed to stand for 16 hours; then all the clear supernate (350 ml) was decanted, and the procedure was repeated with a second portion of 6M HNO_3. The dissolver contained about 700 ml of solution after the second decantation—the upper 150 ml was quite turbid from suspended white solids above a larger layer of heavier, gray solids. The solids were rinsed twice by agitation with

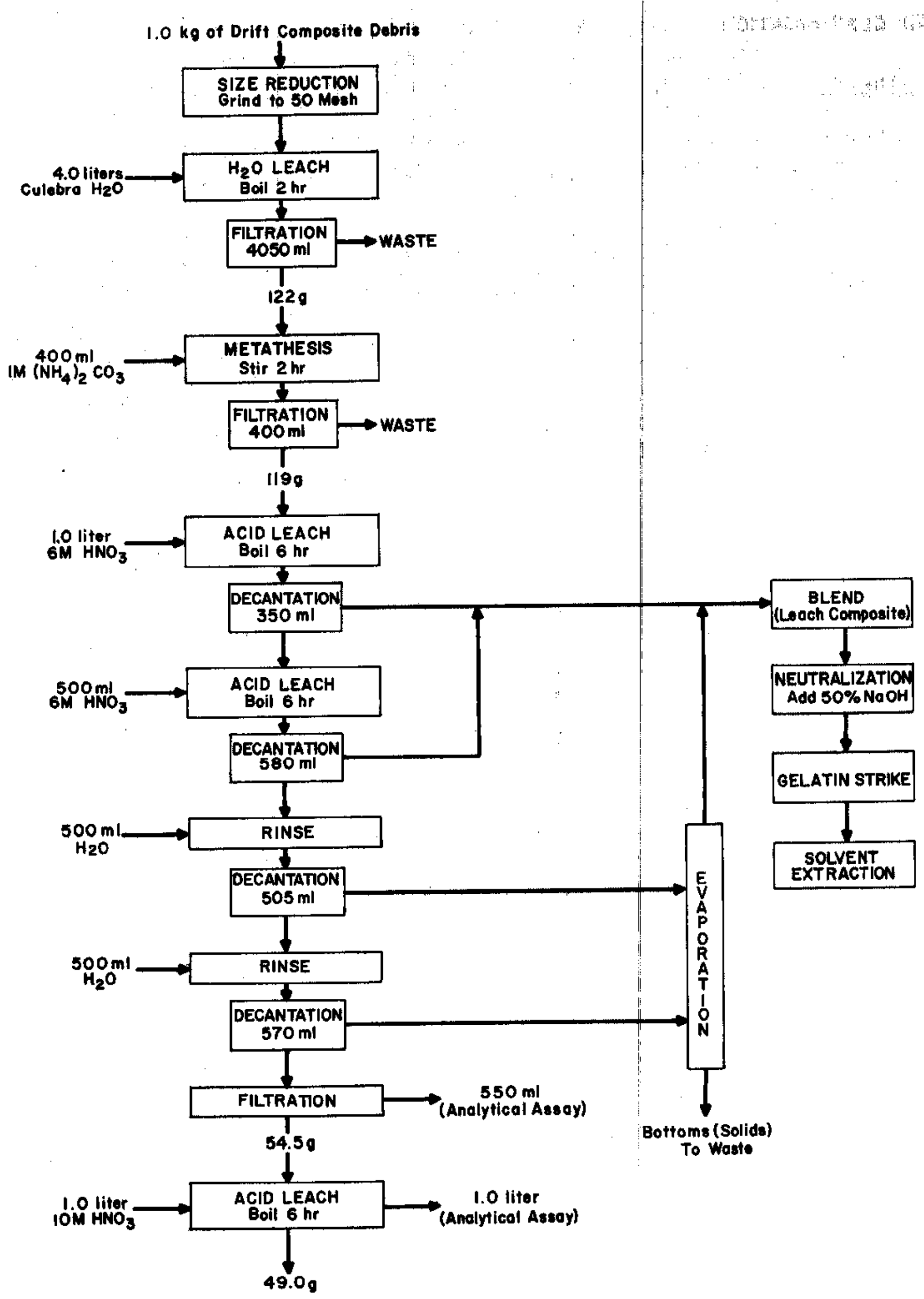


FIG. 2 FEED PREPARATION TEST FLOWSHEET

500 ml of distilled water and allowed to settle for 2 hours each time; then the supernate was decanted. The rinses were turbid with suspended solids, but during evaporation of the rinses the solids coagulated and settled from the concentrated solution. The clear supernate was decanted and blended with the acid leach composite. The coagulated solids from the rinse concentrate were small in quantity compared to the acid-insoluble residue and were discarded.

The 6M HNO_3 dissolved 54% of the water-insoluble residue; the leaching of the actinides was virtually complete after this treatment, as demonstrated by dissolution of the remaining residue by successive treatments with 10M HNO_3, concentrated HF, concentrated HCl, and 9N H_2SO_4. About 10% of the residue that did not dissolve in 6M HNO_3 and 1.6% of the total actinides dissolved in the 10M HNO_3. Most of remaining residue was dissolved by the HF treatment, and only 0.4% remained after the H_2SO_4 treatment. The tests showed that only 1% of the total plutonium remained in the nitric-acid-insoluble residue.

Analysis of the solutions showed that 97% of the plutonium was leached from the debris by the 6M HNO_3 and that 89% of the plutonium was collected in the leach composite solution. The major loss of plutonium resulted from incomplete separation of the acid solution from solids by decantation. Vacuum filtration, which would be required to remove an additional 8% of the product, is not considered practical for a large-scale process. A summary of the results is given in Table XIV. Less than 1% of the plutonium was lost during the water leach and $(NH_4)_2CO_3$ metathesis, and less than 3% was retained in the

TABLE XIV

Radioactivity of Process Fractions

	Gross Alpha[(a)]		Gross Gamma	
Fraction	dis/min	%	cts/min	%
H_2O leach	0.4×10^6	0.3	8.0×10^6	4.3
$(NH_4)_2CO_3$ supernates	0.8×10^6	0.6	0.9×10^6	0.5
6M HNO_3 supernates	85.5×10^6	63	104×10^6	55
Rinses	35.1×10^6	26	42×10^6	23
Filtrate (Vacuum)	10.9×10^6	8.0	18×10^6	9.6
10M HNO_3 leach	2.2×10^6	1.6	8.9×10^6	4.7
Residue	1.5×10^6	1.1	6.2×10^6	3.3
Total	136×10^6	100	188×10^6	100

(a) Alpha pulse height analysis indicated that >99% of the alpha radiation was due to isotopes of plutonium.

solids after treatment in boiling 6M HNO_3. The small additional loss in weight and recovery of plutonium from the residue with 10M HNO_3 attest to the efficiency of boiling 6M HNO_3 as a leaching agent.

Treatment of the leach composite solution with 100 ppm of gelatin coagulated the suspended solids and clarified the solution to a degree sufficient for use as a solvent extraction feed solution. The leach composite was adjusted with 50% NaOH solution to 6.3M NO_3^-—0.14M HNO_3, and 3 ml samples were treated with gelatin, as shown in Table XV. After 1% gelatin solution was added, the leach composite samples were agitated at 70°C for one hour and centrifuged to remove coagulated silica. The supernate was then mixed thoroughly with an equal volume of 30% TBP, and the time necessary for formation of an interface was measured. A trace of interfacial solids collected in the sample that was not treated with gelatin, but none formed in the other tests. However, the results indicated incomplete coagulation and formation of transient emulsions in tests with less than 50 to 100 ppm of gelatin. The remaining leach composite solution was treated with 100 ppm of gelatin, heated at 70°C for one hour, filtered, and extracted with 30% TBP in a 12-stage miniature mixer-settler. No hydraulic difficulties were observed after five hours of operation. The normal interfacial foam that flows from the mixing section occupied about one-third of the settling section, and no accumulation of interfacial solids was observed. This test demonstrated a practical dissolution and feed clarification procedure that can be applied to large-scale processing.

TABLE XV

Feed Clarity Tests

Gelatin Added,(a) ppm	Coagulated Solids, vol %	Breaking Time,(b) sec
0	trace	90
20	trace	65
50	0.6	35
100	1	30
500	1	40
1000	1	30

(a) Solutions agitated 1 hour at 70°C.
(b) Time for formation of interface after mixing with an equal volume of 30% TBP.

Dilute Acid Dissolution

Dissolution of the water-insoluble residue in dilute acid was tested to determine whether a large volume and a lower salt concentration would facilitate clarification of the solution. Drift Composite debris was used for these tests, which are described in the Appendix; acid dissolving was tested at 75°C with 1.5M HNO_3 (three consecutive treatments) followed by two treatments with 3M HNO_3, and a final treatment with 6M HNO_3 (see Table XXVI in Appendix). The initial contact of nitric acid with the debris dissolved about half the total material, but the product solution was difficult to filter. Evaporation of this solution resulted in a paste-like slurry of silica that was even more difficult to filter. Less difficulty was incurred during subsequent dissolving steps, but the dissolution of actinides was incomplete after treatment with 1.5M HNO_3 (Table XXIII). Moreover, two gelatin precipitations were required before the solution was free of silica. In general this over-all procedure was concluded to be unsatisfactory for large-scale processing.

HF Dissolution

Dissolution of the water-insoluble residue with HNO_3-HF was tested as a means for avoiding the problems associated with feed clarification. Dissolution in 4M HNO_3—0.6M HF proceeded smoothly at room temperature, and the undissolved solids were easily filtered from the solution. The filtrate was stable toward precipitation for at least 14 days, indicating that the silica was dissolved as the SiF_6^{2-} complex ion, rather than as a colloidal species.

Unfortunately, when the excess acid was neutralized to ~0.1M H^+ to produce a solution suitable for feed to the solvent extraction step, a major portion of the silica precipitated. Solvent extraction treatment of the solution, after centrifugation, resulted in further precipitation at the interface between the aqueous and organic (30% TBP) phases. When this precipitate was removed and a second attempt made to extract the actinides, a fresh precipitate of silica appeared at the interface between the two phases.

In a parallel test aluminum nitrate was added to the acid leach filtrate before the acid concentration was adjusted. No silica precipitate was observed in this test after acid adjustment; however, when a sample of the adjusted solution was mixed with 30% TBP, a precipitate appeared, as before, at the interface and also in the aqueous phase. In addition, extraction factors for curium from both solutions (Table XVI) were low. Dissolving with HNO_3-HF was thus not considered further in developmental studies.

TABLE XVI

Curium Extraction from Fluoride Solutions

Aqueous Phase Composition				$E_{o/a}$[(a)]	
NO_3^-	HNO_3	F^-	Al^{3+}	Pu	Cm
4.2M	0.11M	0.2M	0.9M	16	3.3
4.4M	0.13M	0.6M	0	1.9	1.7

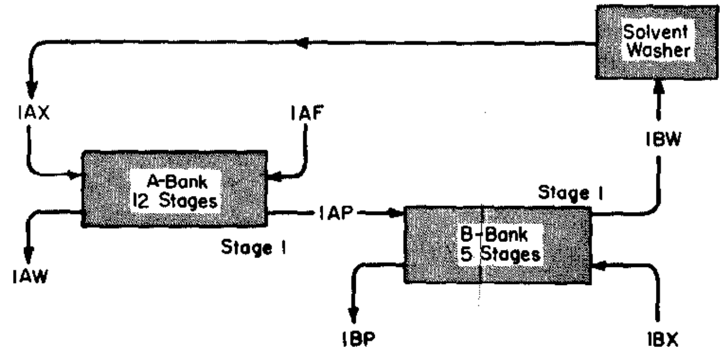
(a) Extractant is 30% TBP containing 0.15M HNO_3.

FIRST SOLVENT EXTRACTION CYCLE

General

The objectives of the solvent extraction process were to separate the actinides from other elements in the dissolver solution and to concentrate the product solution for subsequent processing. The process relies upon extraction of the actinides from a strong nitrate—low acid feed solution with 30% TBP under conditions unfavorable to the extraction of Fe^{3+}. A demonstration of the process in continuous solvent extraction equipment with a feed solution prepared from Gnome debris showed (1) a curium loss of only 1%, (2) separation factors of $\sim 10^3$ for the major cation impurities, and (3) a concentration factor of 16 in one solvent extraction cycle. About 40% of the gamma-emitting fission products were coextracted with the curium product, including essentially all of the lanthanides. Seven solvent extraction runs were made—six tests with synthetic feed solutions for process development and the final test with feed prepared with Gnome debris to demonstrate curium recovery from an actual feed solution.

Two miniature mixer-settler banks, an A-bank of 12 stages and a B-bank of 5 to 7 stages were used in the tests. Actinides were extracted from the aqueous to the organic phase (1AX) in the A-bank, and were stripped into a second aqueous phase (1BX) in the B-bank. The process was operated at room temperature; runs required 2 to 3 hours to reach steady-state for the A-bank and 4 to 5 hours for steady-state in the B-bank. The flow allowed about a one-minute residence time per stage for the feed solution, and stage residence times for other streams were in proportion to their relative flow. A flow diagram for the solvent extraction tests is shown in Figure 3; relative flows and composition of the feed solutions are tabulated in Table XVII. Curium tracer was added to the feed solution in all tests; ^{144}Ce tracer was added for Run 3 and ^{147}Pm tracer for Run 4.



IAF	Feed to A-Bank
IAX	Extractant to A-Bank (diluted TBP)
IAW	Aqueous Waste from A-Bank
IAP	Organic Product from A-Bank
IBX	Strip Solution to B-Bank
IBP	Aqueous Product from B-Bank
IBW	Spent Organic from B-Bank

FIG. 3 SOLVENT EXTRACTION FLOW DIAGRAM

TABLE XVII

Solvent Extraction Test Results

Extractant (1AX): 30% TBP
Strip (1BX): 0.10M HNO_3

Run:	1	2	3	4	5	6	7(a)
Feed (1AF) Composition							
Mg^{2+}, M	3.5	3.5	2.1	2.1	0.58	0.94	0.81
Ca^{2+}, M	0.2	0.2	0.2	0.2	0.12	0.28	0.16
Na^{+}, M	0	0	0	0	2.6	3.0	2.9
Fe^{3+}, M	0.1	0.1	0.06	0.07	0.31	0.36	0.36
HNO_3, M	0.15	0.15	0.15	0.09	0.11	0.12	0.12
NO_3^-, M	7.8	7.8	4.9	4.9	5.1	6.6	6.1
Extractant (1AX) Composition							
HNO_3, M	0.02	0.08	0.02	0.001	0.001	0.001	0.001
Relative Flows							
1AF	100	100	100	100	100	100	100
1AX	100	100	33	44	34	34	34
1BX	0	0	0	10	10	6.5	6.1
A-Bank Stages	12	6	12	12	12	12	12
Cm Loss							
To 1AW, %	<1	1.4	0.5	0.35	13	2	1
To 1BW, %	-	-	-	0.20	0.01	-	0.01
Other Tracers	-	-	^{144}Ce	^{147}Pm	-	-	fission products
Loss to 1AW, %	-	-	1.6	0.10	-	-	48
Loss to 1BW, %	-	-	-	0.05	-	-	12
Fe in Product, M	0.036	0.03	0.001	0.0015	-	0.0043	0.0067

(a) Gnome feed solution, also contained 0.04M Cl^-, 0.07M SO_4^{2-}, and 0.004M Cu^{2+}.

Preliminary Tests

Preliminary runs (Runs 1 and 2) were characterized by high iron extraction. In Run 1, about one-third of the total iron in the feed was extracted. The strongly salted system also extracted acid to such an extent that ferric hydroxide precipitate formed in the last three stages of the extraction contactor. Adjustments in the acidity of the extractant and in the number of stages in Run 2 eliminated precipitation (but not extraction) of iron. The recovery of curium in these runs was nearly complete, but losses were difficult to measure because of the presence of precipitated ferric hydroxide in the aqueous waste stream.

Tests with more dilute (lower NO_3^-) feed solutions and lower extractant flow rates decreased the extraction of iron and also avoided precipitation of ferric hydroxide. Runs 3 and 4 (Table XVII) showed excellent recovery of the curium, ^{147}Pm, and ^{144}Ce tracers. Recovery was not directly affected by reducing the extractant flow rate in the 1A bank. Higher acid concentration in the feed (0.15M) in Run 3 did not lead to appreciable curium loss because of the 12 extraction stages (Figure 4). However, Run 4 demonstrated that the same recovery can be

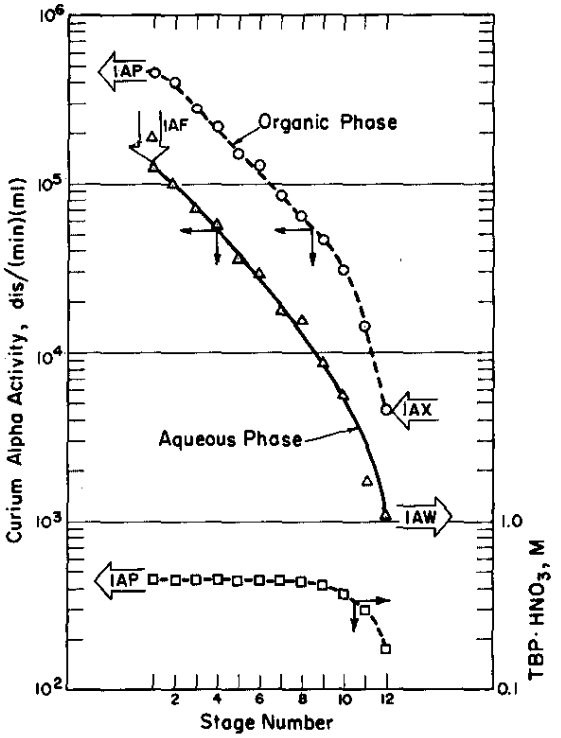


FIG. 4 STAGE CONCENTRATIONS OF CURIUM AND NITRIC ACID IN RUN 3

achieved in only 5 to 7 extraction stages as long as the process is controlled to maintain 0.1M HNO_3, or less, in the 1A bank (Figure 5).

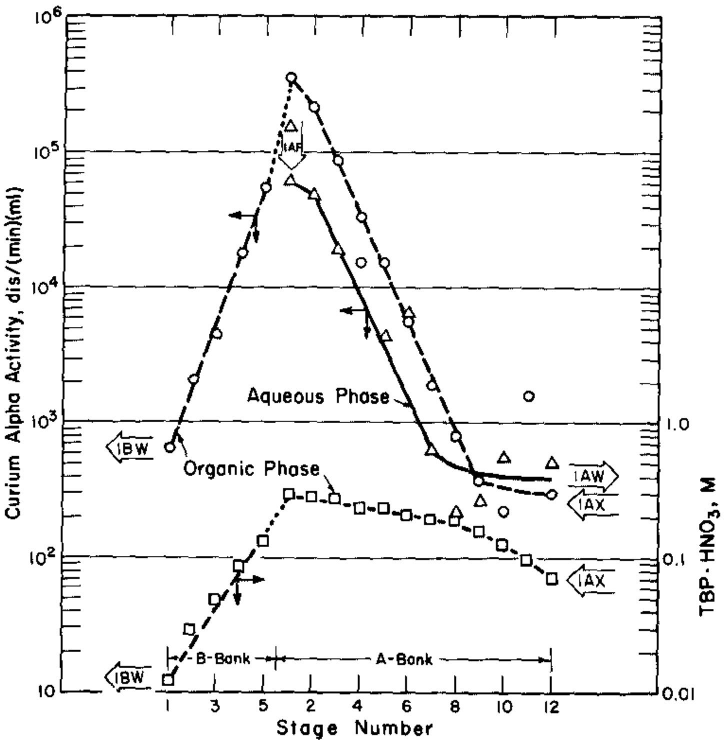


FIG. 5 STAGE CONCENTRATIONS OF CURIUM AND NITRIC ACID IN RUN 4

The solvent extraction process extracts both nitric acid and actinides, but the nitric acid is extracted better ($E_{o/a}$ = ~10^2) than the actinides ($E_{o/a}$ = ~14). Essentially all the acid is extracted, and the extraction of actinides is decreased because of the TBP consumed by the $TBP\cdot HNO_3$ complex (actinides extract as $Ac(NO_3)_3\cdot 3TBP$). Stage data from Run 3 indicate that when the concentration of $TBP\cdot HNO_3$ reaches 0.4M, the loss of actinides after 7 extraction stages is about 10%, an excessive amount. The acidity of the organic phase can be controlled either by restricting the acidity of the feed, or by regulating the flow of the organic phase to maintain the acidity of the organic phase below 0.4M. Of these two methods, restricting the feed acidity is the more effective; matching the organic phase flow to the feed acidity can correct an excess of acid, but with the penalty that the organic-to-aqueous flow ratio in the B (stripping) bank is increased. Since this ratio is already near the practical hydraulic limit to obtain the maximum product concentration, hydraulic problems in the B-bank will probably result unless aqueous flow is increased, which would reduce the concentration of the product. Thus, for satisfactory operation, the acidity of the feed stream is a major variable that should be carefully controlled to achieve both good recovery and maximum product concentration.

The feed solutions for Runs 5 and 6 more closely approximated the expected process composition (based on analysis of Gnome debris). The equipment operated satisfactorily during Run 5, but the loss of curium to the aqueous waste (1AW) stream was 13%. The loss was assumed to result from insufficient salting; the tests with 5M NO_3^- (Runs 3 and 4) solution showed acceptable losses (<1%) but with Mg^{2+}, rather than Na^+, as the major cation (2.1M). Apparently, the lower concentration of divalent ions in this feed decreased the salting strength and was responsible for the high curium loss. When the feed (Run 6) was adjusted to 6.6M NO_3^-, however, the loss of curium decreased to 2%.

Tests with Gnome Debris

Solution prepared from Gnome debris was used as feed for Run 7. The composition is shown in Table XVII, and the details of the feed preparation are given in the Appendix. During operation of the miniature solvent extraction equipment, end streams from the banks were analyzed each hour to determine the approach to steady-state operating conditions. Based on alpha activity, the A-bank reached steady-state in 1 hour (~4 bank throughputs of 1AF), and the B-bank required 4 hours (~5 bank throughputs of 1BX). After attainment of steady-state conditions, operations were stopped and samples of the aqueous and organic phase in each stage were withdrawn for analysis. The analytical data for the end streams at steady-state are shown in Table XVIII. Figures 6, 7, and 8 display curium, plutonium, gross gamma, and acid concentrations in the organic and aqueous phases of the contactors. Separation of the curium tracer from other cations is shown in Table XIX.

TABLE XVIII

End Stream Analyses in Run 7[(a)]

	1AW	1AP	1BW	1BP
Relative flow	100	34	34	6.1
Gross alpha, dis/(min)(ml)	1.9×10^4	4.86×10^6	2.47×10^5	2.62×10^7
Gross alpha, %	1.1	99	5.1	96
Cm alpha, %	1(b)	99	0.01	99
Pu alpha, %	2(b)	98	63	35
Gross gamma, cts/(min)(ml)	1.17×10^5	3.74×10^5	8.85×10^4	1.60×10^6
Gross gamma, %	48 (Ru + Ag)	51	12 (Ru)	39 (Ru + Ce)
Fe^{3+}, M	0.36	0.0027	0.0015(b)	0.0067
HNO_3, M	-0.023(c)	0.40	0.087	1.59

(a) 1AF: 1.66×10^6 alpha dis/(min)(ml) [92% Cm, 8% Pu]; 2.47×10^5 gamma cts/(min)(ml) [^{106}Ru, ^{144}Ce, ^{110}Ag].

(b) Estimated from mass balance.

(c) Acid deficient due to the presence of $Fe(OH)^{2+}$ and similar species.

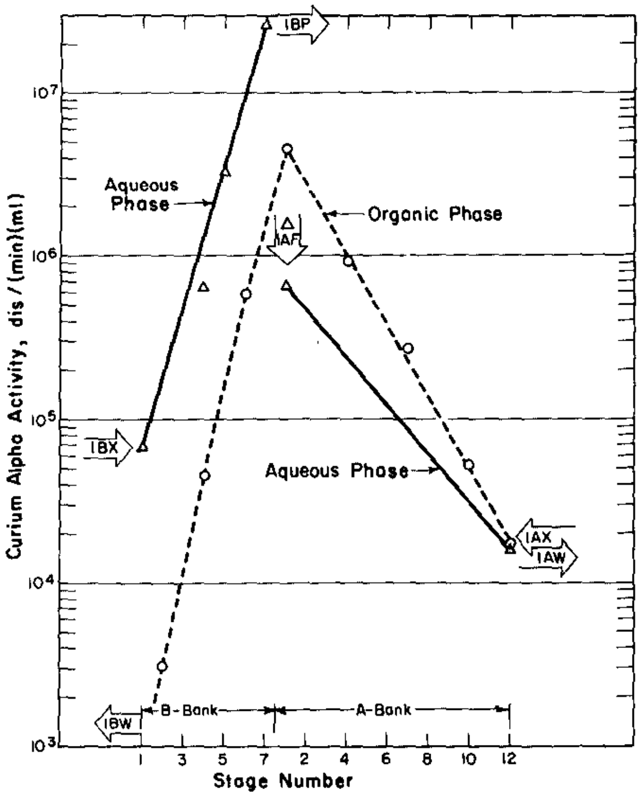


FIG. 6 STAGE CONCENTRATIONS OF CURIUM IN RUN 7

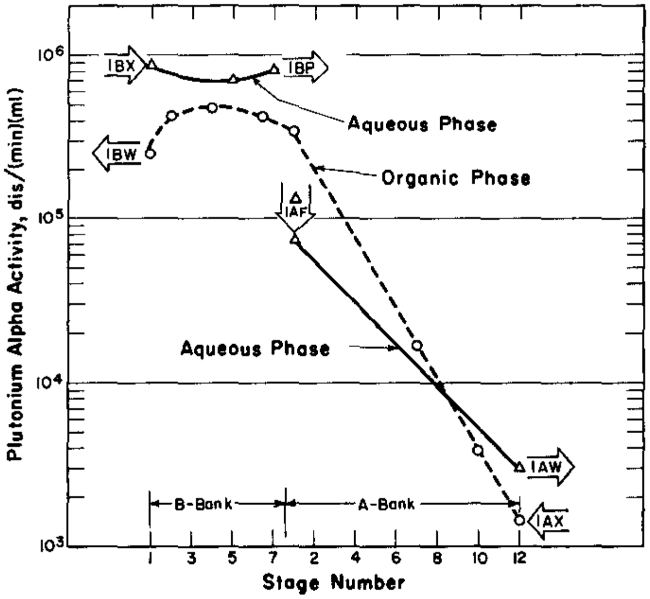


FIG. 7 STAGE CONCENTRATIONS OF PLUTONIUM IN RUN 7

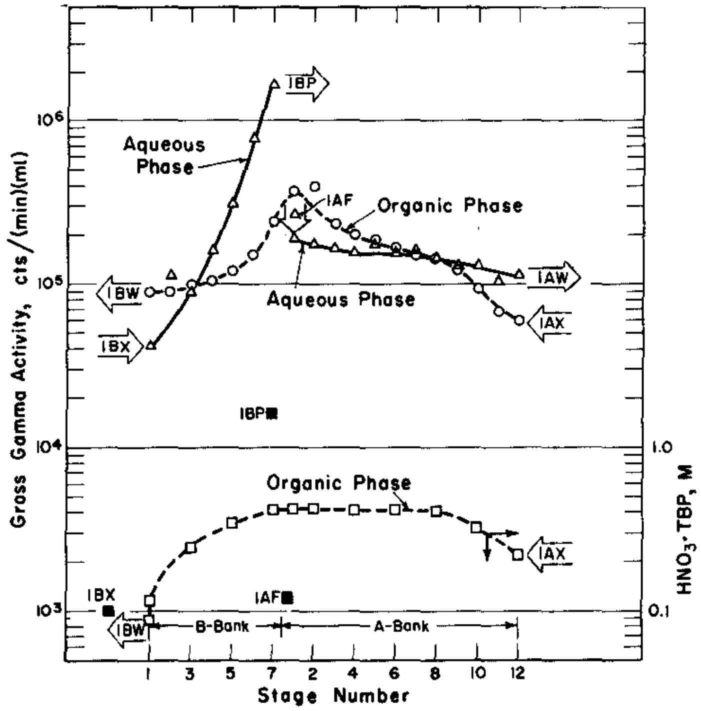


FIG. 8 STAGE CONCENTRATIONS OF FISSION PRODUCTS AND NITRIC ACID IN RUN 7

TABLE XIX

Separation of Cations from Curium

Cation	Concentration in 1BP, ppm	Separation Factor
Fe	380	850
Ca	1060	1000
Mg	56	5600
Na	2000	530
Cu	24	190

The results of Run 7 show excellent extraction of curium and plutonium in the A-bank, and complete stripping of curium in the B-bank. The partial separation of plutonium and curium in the B-bank was unplanned, but may be desirable to reduce the nuclear hazard potential in later processing. Calculations indicate that an increase in the acidity of the 1BX stream from 0.1M to 0.3M HNO_3 would increase the separation factor between plutonium and curium in the B-bank from 3 to 10 without affecting the stripping of curium. The extraction of acid in the A-bank produced an acid-deficient 1AW stream, but no ferric hydroxide precipitated in either the contactor or in the collected waste over a 10-day period.

The separation factors between curium and other major cations present in the feed solution were quite satisfactory (Table XIX), and the product solution was evaporated without difficulty to a volume suitable for feed to the second solvent extraction cycle.

SECOND SOLVENT EXTRACTION CYCLE

The objectives of the second cycle of solvent extraction were the same as those for the first cycle, viz., to separate actinides from ionic impurities and to reduce the scale of processing. The process was essentially the same, except sodium nitrate was the salting agent instead of a mixture of calcium, magnesium, and sodium nitrates. A demonstration of the second cycle process with synthetic feed showed a curium loss of 0.3%, a concentration factor of 14, and separation factors of 600 for Fe^{3+}, 150 for Ca^{2+}, and 1400 for Mg^{2+}. As in the first solvent extraction cycle, control of the feed acidity at 0.1M HNO_3 or less is required for proper operation of the process.

Batch distribution data demonstrated that curium was readily extracted from sodium nitrate solutions of 5M or greater with 30% TBP, as long as the acidity of the system was maintained at about 0.1M. Results of the distribution coefficient measurements (Figure 9) showed

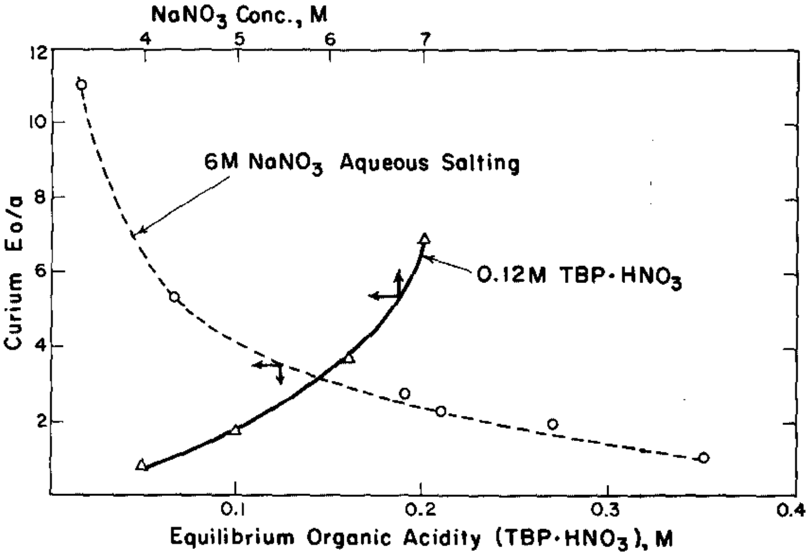


FIG. 9 CURIUM EXTRACTION FROM HNO_3-$NaNO_3$ BY 30% TBP

that curium extraction was decreased by an increase in nitric acid concentration in the organic phase. A test of a process designed from these data was made with a synthetic feed solution whose composition was adjusted to simulate the solution that would result from a tenfold evaporation of the first solvent extraction product followed by addition of sodium hydroxide to produce a sodium nitrate concentration adequate for aqueous phase salting. Two mixer-settler banks were used, an A-bank of 12 stages and a B-bank of 7 stages, and the flow diagram was identical to that for the first cycle (Figure 3). Steady-state operating conditions were achieved after about four hours of operation. Table XX gives the flowsheet for the test, Table XXI lists the concentrations of significant species in the end streams at steady-state conditions, and Figure 10 shows the concentration of curium alpha activity in both the aqueous and organic phases in each stage. No operating problems were encountered from the high organic-to-aqueous flow ratio in the B-bank. The flow ratio used is near the operating limit for miniature mixer-settler equipment, but plant-scale equipment will operate satisfactorily at double this ratio.

TABLE XX

Second Cycle Flowsheet

	2AF	2AX	2BX
Relative flow	100	31	6.9
Flow rate, ml/min	4.6	1.4	0.32
Composition	0.085M HNO_3, 7.0M NO_3^-, 6.3M Na^+, 0.077M Fe^{3+}, 0.18M Ca^{2+}, 0.022M Mg^{2+}, 0.0096M Cu^{2+}, 1.09×10^6 Cm dis/(min)(ml)	0.0013M HNO_3, 30 vol % TBP, 70 vol % "Adakane 12"	0.32M HNO_3

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TABLE XXI

Second Cycle End Stream Concentrations

	2AW	2AP	2BW	2BP
Cm, dis/(min)(ml)	2.9×10^3	3.56×10^6	1.7×10^2 (a)	1.52×10^7
HNO_3, M	-0.007 (b)	0.30	0.083	1.15
Fe^{3+}	0.077M	20 ppm	<1 ppm	105 ppm
Ca^{2+}	0.18M	140 ppm	<1 ppm	660 ppm
Mg^{2+}	0.022M	~1 ppm	<1 ppm	6 ppm
Cu^{2+}	0.0096M	5 ppm	<1 ppm	16 ppm

(a) Also contained 3.2×10^3 dis/(min)(ml) of ^{238}Pu daughter.
(b) Acid-deficient due to $Fe(OH)^{2+}$ and similar species.

CONCEPTUAL PLANT-SCALE PROCESS

The chemical flowsheet developed in these studies defines the necessary operations and the total material balance for the process. The operating details of each processing step, however, cannot be defined without decisions on the type of equipment and the desired processing rate. This section outlines a suggested method of operation, with the assumption that capital costs for a processing plant must be minimized.

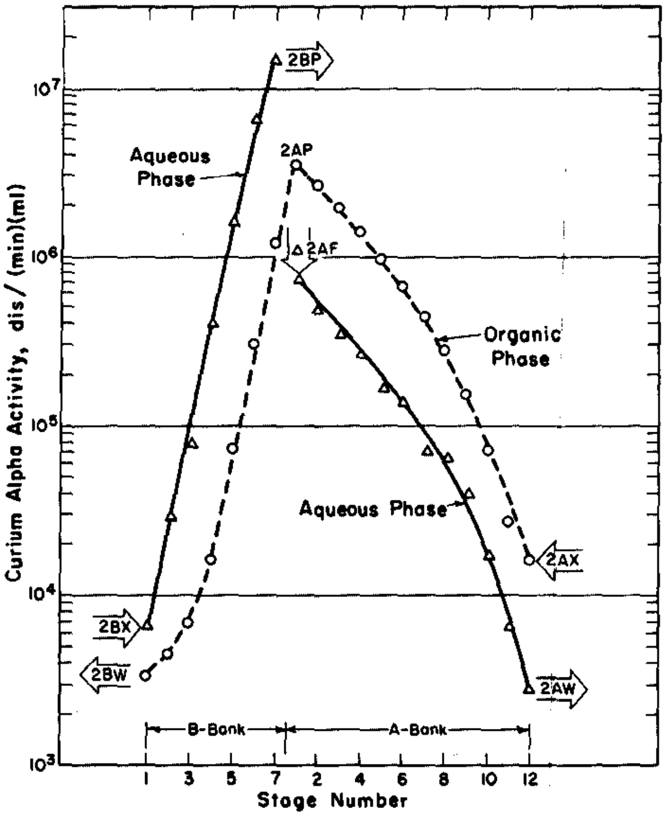

FIG. 10 STAGE CONCENTRATIONS OF CURIUM IN SECOND CYCLE

Feed Preparation

Salt removal, ammonium carbonate metathesis, and nitric acid dissolution can all be carried out in the same vessel. Debris, ground to -50 mesh, would be charged to this vessel and agitated with Culebra water to dissolve the salts. The waste salt solution would be discharged, a second charge of debris would be added, and the water leach would be repeated. Up to 10 charges of debris could probably be desalted before the vessel would reach its capacity for solids. Metathesis of the water-insoluble charge would follow; two consecutive treatments with excess $(NH_4)_2CO_3$ solution will achieve an efficient metathesis of sulfates to carbonates. A chloride-free water rinse of the metathesized solids will recover $(NH_4)_2CO_3$ from the slurry. The waste $(NH_4)_2CO_3$ solutions and the water rinse would next be evaporated to recover the excess $(NH_4)_2CO_3$, and the evaporator bottoms, a slightly radioactive solution of ammonium sulfate, would be discarded as low-level waste.

Following these steps, the metathesized residue would be dissolved by adding 6M HNO_3 and boiling for six hours. The dissolver solution would be transferred to a settling tank, a second batch of acid charged, and the dissolving repeated. Successive dissolvings would be made until the acid-soluble residue is exhausted. The acid-insoluble residue would be rinsed with chloride-free water; then the insoluble solids would be suspended by violent agitation in a second water addition; and the slurry would be transferred to waste. The discarded solids will be essentially all silica.

Performing these three steps in a single vessel avoids the awkward operation of transferring solids from one vessel to another during processing, and requires only basically simple equipment. The major uncertainty is corrosion of the vessel (presumably stainless steel) by sodium chloride, ammonium carbonate, and nitric acid solutions.

The nitric acid solution and dissolver rinses would be combined in a settling tank, to allow fine particles to settle from the solution. The supernatant solution would be evaporated to increase the nitrate concentration, and to recover water and a part of the excess nitric acid. Suspended silica is also coagulated during evaporation. After evaporation, the solution would be adjusted to 6M NO_3^-—0.1M HNO_3 by adding the required amounts of 50% NaOH and water; residual silica would be precipitated by adding gelatin (100 ppm) to the feed solution and heating to 70°C for one hour. After filtration, this feed solution would be processed by solvent extraction.

Solvent Extraction

The feed solution for solvent extraction would contain 85-98% of the actinides, 85-95% of the rare earth fission products, and about 90% of the total fission product activity, plus essentially all the calcium, magnesium, iron, and other impurities in the original debris. Solvent extraction processing would separate the actinides and rare earths from most of the impurities of the debris, and, combined with evaporation, would concentrate the solution to a small final volume. The suggested method of processing is to operate the first solvent extraction cycle, evaporate the product solution to a small volume, and store this solution. When the storage volume is exhausted, solvent extraction equipment could be used for the second solvent extraction cycle, and the second cycle product solution could be evaporated and stored. The final product would be a small volume (~100 gal) of a feed solution satisfactory for the operations required to separate actinides from rare earths and to isolate the individual actinide fractions.

Use of the same equipment for both solvent extraction cycles and for the product evaporation would effect a considerable reduction in cost. From the proposed concentration factor, operating the first solvent extraction cycle for 75 days would provide enough feed solution to operate the second solvent extraction cycle for 1 day.

APPENDIX

Dissolution of Debris with Dilute Nitric Acid and Clarification of Feed for Solvent Extraction

A large-scale test of the residue treatment and acid dissolving procedure was made on a sample of Gnome Drift Composite debris to test performance and to follow the paths of the constituents. The results are shown in Tables XXII through XXVII (pages 45-47). The processing procedure was as follows:

Crushing and Water Leach

The composite sample of Gnome debris (dark gray in color) was pulverized and sieved to -50 mesh. Total sample weight was 3.1 kg. The radiation level was 60 mr/hr measured 3 inches from the surface. The debris was leached successively for two periods of 1 hour each with 7.5 and 3.9 liters of hot Culebra water. A brown residue weighing 290 g remained. Pertinent data from the water-leaching steps are listed in Tables XXII through XXV.

Sulfate Removal

Sulfate was removed from 280 g of the water-insoluble residue as ammonium sulfate by two consecutive treatments with 855 ml and 305 ml of 1.84M ammonium carbonate solution, a combined ratio for the two treatments of 4.1 ml of $(NH_4)_2CO_3$ solution per initial gram of residue. After rinsing to remove excess $(NH_4)_2CO_3$ and drying, 262 g of residue remained, retaining only 11% of the initial sulfate. Residual sulfate was higher than observed in earlier tests, but still low enough to prevent precipitation of sulfates in the final feed solution. Data are listed in Tables XXII through XXV.

Acid Dissolution

The residue, now composed mainly of silicates and carbonates, was decomposed by six successive treatments with nitric acid—the first three treatments with ~1.5M HNO_3, the next two with ~3M HNO_3, and the final treatment with 6-8M HNO_3. For the first five treatments, the solid residue was stirred in the acid solution for one hour at 75°C; then a 1% gelatin solution was added, and the solution was stirred for an additional 30 minutes as the solution cooled. The undissolved solids were filtered, rinsed, dried, and weighed after each acid treatment. The solution produced by the initial acid treatment was extremely turbid, and could be filtered only with difficulty. Solutions from subsequent acid treatments were easier to filter.

After five treatments with acid, the solids were brown, indicating that iron silicates were not completely decomposed and suggesting that an appreciable quantity of actinides remained associated with the undecomposed silicates. The remaining solids were boiled in 8.1M HNO_3 at a ratio of 5.2 ml/g for four hours; then the solution was adjusted to 6M HNO_3, and the residue was boiled with this solution (~19 ml/g) for two additional hours. After this treatment with nitric acid, about 60 g of gray-white residue remained. Data are given in Tables XXII through XXVI.

Feed Adjustment

The filtrates from each nitric acid treatment were evaporated separately to concentrate the solutions for feed adjustment. A substantial quantity of hydrated silica precipitated during evaporation of the first filtrate. The silica was filtered and washed with dilute nitric acid, and the filtrate and wash solution were evaporated further. The weight of dry silica was 55 g. During evaporation of filtrates from the last five acid treatments, very little silica precipitated.

The silica in each of the evaporated solutions was coagulated by a second addition of 1% gelatin solution followed by heating at 70°C for one hour and then removed by filtration. A total of about one gram of solids was removed from all solutions by this final step. The filtrates were combined, diluted with water to about 5M NO_3^-, and neutralized with 50% NaOH solution. After the neutralization, the nitrate concentration was adjusted to 5.1M with solid $NaNO_3$. Data pertinent to this operation are listed in Tables XXII and XXVII.

Solvent Extraction Tests

The ability to recover actinides from the adjusted feed solutions by solvent extraction was confirmed by equilibrating a small aliquot containing added curium tracer with an equal volume of 30% TBP. The distribution coefficient for curium between the extractant and the adjusted feed solution was 4.4, compared to a value of 4.1 for a synthetic solution. After mixing, the phases separated normally, and no precipitate formed at the interface, indicating that the solution was satisfactory for a test of continuous solvent extraction.

TABLE XXII

Content of Solutions

Solution	Fe, g	Mg, g	Ca, g	Na, g	Cl, g	SO_4^{2-}, g	Cu, g
Water Leach							
Total	0	6.1	6.8	1091	1684	42	0.06
Initial Culebra water	0	1.5	7.2	5.6	8.6	23	0
Net Leach	0	4.6	0	1085	1675	19	0.06
$(NH_4)_2CO_3$ Supernates							
First	0.002	0.011	0.055	1.9	5.4	28	0.028
Second	0.001	0.009	0.009	0.13	1.1	2.6	0.042
Total	0.003	0.020	0.064	2.0	6.5	31	0.070
Nitric Acid Dissolvent							
First	10.8	24.2	6.0	2.77	-	3.48	0.31
Second	3.0	1.25	0.41	0.08	-	1.76	0.020
Third	1.9	0.32	0.57	0.02	-	0.18	0.006
Fourth	4.1	1.44	1.10	0.05	-	0.18	0.005
Fifth	1.7	0.65	0.50	0.02	-	0.13	0.001
Sixth	7.2	0.94	0.57	0.03	-	0.40	0.002
Total	28.7	28.8	9.15	3.0	3.3	6.13	0.34

TABLE XXIII

Dissolution of Radioactivity

	Gross Alpha		Gross Gamma	
	dis/min	%	cts/min	%
Solutions				
Culebra water leach	2.4×10^5	0.1	1.7×10^7	4.3
$(NH_4)_2CO_3$ treatments	3.1×10^5	0.1	5.5×10^6	1.4
Nitric acid dissolutions				
First	8.2×10^7	30	9.9×10^7	25
Second	5.6×10^7	21	3.7×10^7	9.3
Third	0.25×10^7	0.92	3.6×10^7	9.0
Fourth	6.7×10^7	24	7.9×10^7	19.8
Fifth	2.5×10^7	9.2	3.9×10^7	9.8
Sixth	3.1×10^7	11.3	8.7×10^7	21.7
Total	26.4×10^7	96.6	40.0×10^7	100.3
Acid-Insoluble Residue	0.91×10^7	3.3	-	-

TABLE XXIV

Curium-Plutonium Analyses

	Gross Alpha Activity, dis/min	Alpha Activity, % of total			Pu/Cm	Curium Alpha Activity, dis/min
		Pu	Cm	U(a)		
Water Leach	2.4×10^5	-	-	-	-	-
$(NH_4)_2CO_3$ Supernates						
First treatment	1.2×10^5	72	2.9	25	25	3.5×10^3
Second treatment	1.9×10^5	87	0.4	13	220	0.8×10^3
Composite Feed Solution	2.64×10^8	99.4	0.6	-	165	1.6×10^6
Acid-Insoluble Residue	9.12×10^6	99.4	0.6	-	165	5.5×10^4
Silica Precipitate	2.85×10^6	99	1	-	99	2.9×10^4

(a) Alpha activity at 4.8 Mev, probably due to ^{237}Np or ^{233}U, either of which could have resulted from contamination of the samples.

TABLE XXV

Trace Element Analyses(a)

	Cation, mg						
	Pb	Al	Ti	Ni	Cr	Mn	Ag
Solutions							
$(NH_4)_2CO_3$ Supernates	20	<10	<5	<10	<10	<5	-
Nitric Acid Dissolvent							
First	3700	4100	80	170	170	80	<8
Second	300	800	90	20	<20	10	4
Third	70	1000	50	10	10	10	1
Fourth	70	2000	50	10	30	20	5
Fifth	30	500	50	0	10	10	2
Sixth	60	1100	80	0	30	30	8
Total	4230	9500	400	210	250	160	20
Composite Solution (Volume: 1.7 l)	5600	8500	260	130	260	110	17

Acid-Insoluble Residue

Constituent	wt %
Fe	1.25
Mg	0.75
Al	0.75
Ca	0.25
Ti	0.25
Mn	0.025
SO_4^{2-}	0.5

Major fission products: ^{125}Sb, ^{106}Ru, ^{95}Zr

(a) Initial sample: 3.1 kg of Gnome debris.

TABLE XXVI

Nitric Acid Dissolution

Treatment number:	1	2	3	4	5	6
Nitric acid						
Concentration, M	1.53	1.54	1.54	3.61	3.14	6.0
Volume, ml	3600	800	350	425	450	1500
Ml acid/g residue	14	7.0	3.5	4.5	5.4	19
Volume of 1% gelatin solution, ml	180	15	4	10	10	-
Weight of water-insoluble residue, g	116	100	95.1	83.2	77.6	60.2
Wt % dissolved(a)	55	6.0	2.0	4.6	2.2	6.8
Water-insoluble residue, g per liter of acid	34	13	11	28	13	11
Final nitric acid						
Concentration, M	0.44	0.83	0.87	2.12	2.56	5.05
Volume, ml	4140	1165	450	430	445	1600
Millimols HNO_3 consumed per g of residue dissolved	26	17	31	52	49	53

(a) Initial weight: 257 g

TABLE XXVII

Composition of the Adjusted Acid Leach Composite

Volume: 1.7 liters

Constituent	Concentration, M
Na^+	2.40
Fe^{3+}	0.30
Mg^{2+}	0.68
Ca^{2+}	0.13
H^+	0.10
NO_3^-	5.1
Pb^{2+}	0.016
Cu^{2+}	0.003

Trace amounts of Al, Si, Cr, K, Ni, Mn, Ti and Ag were detected by emission spectrographic analysis. Major fission products were ^{106}Ru, ^{144}Ce, ^{110}Ag.

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