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Thorium-Plutonium Chemical Separation Process

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THORIUM-PLUTONIUM
CHEMICAL SEPARATION PROCESS

by

David G. Clifton and Thomas W. Blum

ABSTRACT

A new chloride anion exchange process is described, which separates thorium from plutonium yet eliminates corrosive HCl fumes and consequent gas scrubbing equipment. Process flow sheet and experimental testing results are presented.

Plutonium product yields of over 90% with <0.025 wt% thorium were obtained with single-pass processing of plutonium feed solutions contaminated by up to 46 wt% thorium.

I. INTRODUCTION

Within the DOE complex thorium-plutonium materials are amassed from which plutonium should be recovered. This task may be accomplished by several processes that have been used intermittently over the years, but each process has shortcomings.

- Solvent extraction processes, based on small differences in extraction coefficient values, normally require multistage equipment, such as pulsed columns, which are complex to operate and expensive to install. Existing facilities are committed primarily to separation of fission products, uranium, and plutonium, with none actually dedicated to thorium-plutonium separation.
- A chromatographic anion exchange method using nitric acid solutions relies on a small difference in distribution coefficient values for the two species and the consequent slow displacement of resin-bound thorium by plutonium. This gives a fractionation of species in the output stream with one material following the other, preventing clean-cut separation because of common boundary overlap.
- A frequently used chemical method is based on oxidation of plutonium to Pu(VI) by sodium chromate in an acid solution, with subsequent precipitation and thorium separation as ThF_4 and plutonium oxalate precipitation from the filtrate after the plutonium is reduced to Pu(III). Good plant-scale separations have not been obtained because of difficulties in maintaining plutonium as Pu(VI), incomplete thorium precipitation leaving the plutonium product contaminated by thorium, and large plutonium losses to the thorium precipitate resulting from coprecipitation, absorption, and/or occlusion.
- Perhaps the most successful process for a clean thorium-plutonium separation is chloride anion exchange from strong (4-8 M) HCl solutions.[1,2] The Pu(IV) forms a complex, $PuCl_6^{=}$, which is sorbed on the resin, and Th(IV), which doesn't form the chloride complex, passes through the resin column.

- Unfortunately, this process produces HCl fumes that interact with other glove box atmospheric components to cause severe corrosion of steel glove boxes and their ventilation systems. Off-gas scrubbing equipment and special alloy or plastic construction equipment are possible solutions to the problem, but they are almost prohibitively expensive.

When the thorium-plutonium problem and known separation processes were reviewed, we concluded that chloride anion exchange warranted closer study.

II. NEW FLOW SHEET FOR THORIUM-PLUTONIUM SEPARATION

To lessen problems of conventional chloride anion exchange processes, the HCl fumes must be managed. Because HCl partial pressure varies directly as its concentration in solution (which, in turn, is involved in several shifting equilibria), the pressure can be reduced by lowering either the hydrogen or chloride ion solution concentration. The latter, necessary in complex formation for the process, may be supplied at needed concentrations from any readily soluble chloride salt, with a noninterfering cation, so the remaining option is reduction in the hydrogen ion concentration.

Exploratory experiments testing this concept were positive and established a basis for the generalized thorium-plutonium separation flow sheet of Fig. 1.

There are several novelties and advantages in this process.

- A chloride salt, preferably NaCl, in ~1 N HNO_3 is used to give chloride ion concentrations (~4-5.5 M) high enough to transform Pu(IV) into the complex $PuCl_6^=$ and to cause it to stick onto the chloride form of a strongly basic anion exchange resin, rather than strong (4-8 M) HCl solutions.
- Heretofore, chloride anion exchange processes for this separation had the major disadvantage of emitting corrosive HCl fumes that attack glove box enclosures and equipment. (In the new process, the maximum HCl solution concentration is ~1 N. At room temperature, pure HCl solutions at ~1 N have an HCl vapor pressure of only ~1.5×10^{-4} mm of mercury, whereas that for 8 M HCl is 3000 times more, or ~0.5 mm of mercury. This essentially eliminates corrosive fumes and obviates off-gas scrubbing.)
- All exiting column streams are immediately neutralized by adding strong aqueous base, preferably NaOH, in appropriate quantities. Resulting hydrous oxides filter out and give discardable caustic filtrates containing NaCl, $NaNO_3$, and NaOH.
- The wash stream of the first sorption column also passes through a second anion resin column of the chloride form to almost completely clean up the low concentration of plutonium that will be in the wash effluent. The second column's effluent and wash combine with the first column's effluent for eventual discard; its eluate combines with any eluate from the first column.

Other process features include use of 1 N HNO_3 in the feed to prevent hydrolysis of Pu(IV) and Th(IV), addition of $NaNO_2$ to adjust Pu(III) to Pu(IV), and elution with 0.5 N HCl, leaving the resin ready for reuse in the chloride form.

III. EXPERIMENTAL PROCEDURES

A. Feed Preparation

Feeds containing various thorium-plutonium ratios were made by mixing appropriate volumes from two nitric acid stock solutions of known composition, one with thorium, the other with plutonium. Feed samples assayed for thorium and plutonium compared favorably with values calculated from stock mixing. In this report, weight per cent frequently designates composition in terms of plutonium and thorium. The value is based on total plutonium and thorium metal in a sample; in other words, the value is 100 times the result obtained by dividing the weight of thorium (or metallic plutonium) by the sum of

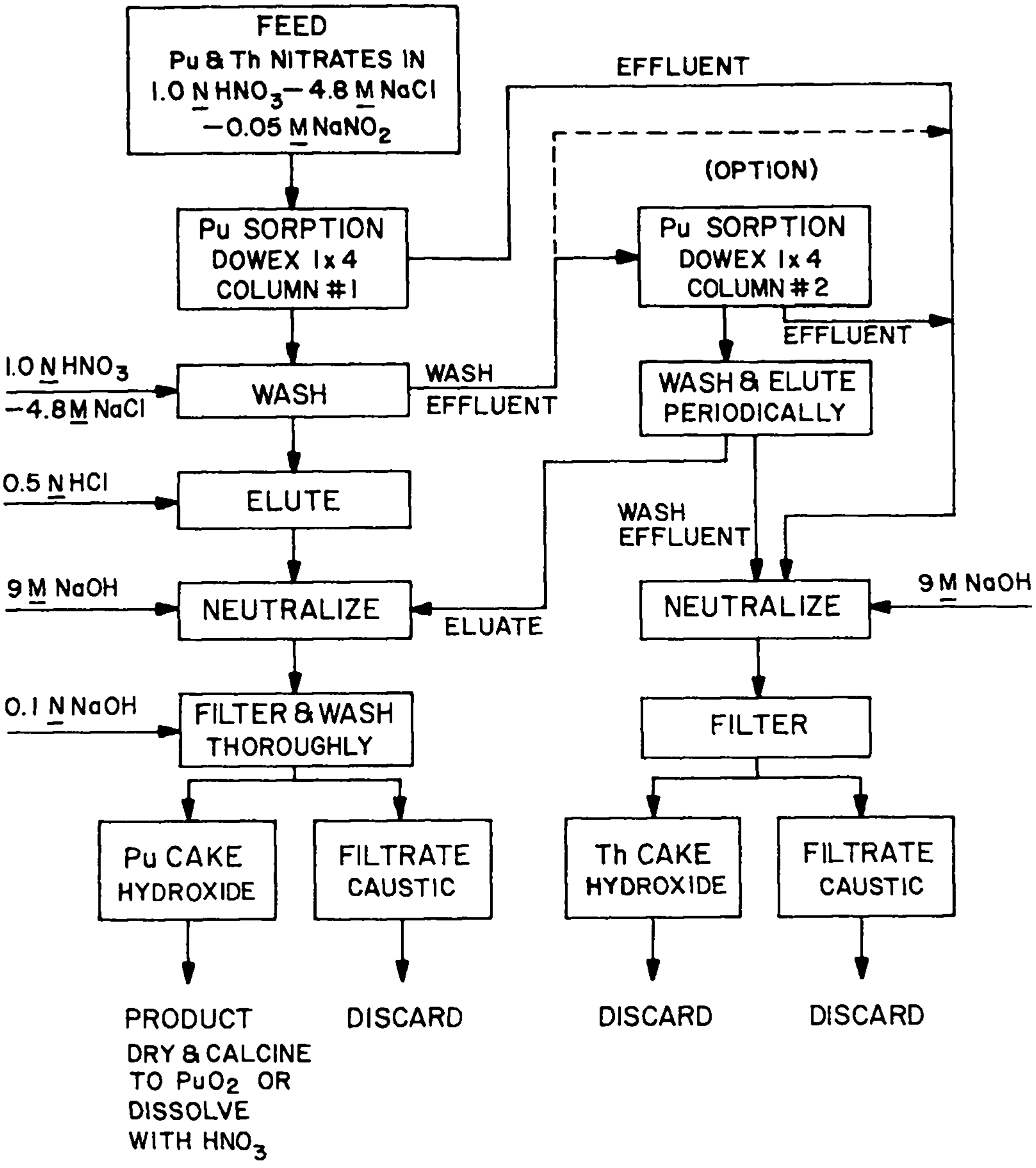

Fig. 1. Thorium-plutonium separation flow sheet.

the plutonium and thorium weights in the assayed sample. For consistency, all reported compositions are based on assay results rather than on values calculated from known stock mixing, unless we specifically state otherwise.

Appendix A details the stock solutions, chemicals used, resin treatments, assay methods, and resin column construction.

After stock solution aliquots were mixed to a desired thorium-plutonium blend, the acidity was calculated and enough 0.1 N HNO_3 was added to dilute this solution to ~1 N HNO_3. (Volumeadditivity was assumed here.) To this solution, ~310 g NaCl and ~3.4 g $NaNO_2$ per liter of 1 N HNO_3 solution were added. (This chosen quantity of NaCl was determined empirically from testing its ease of dissolution in 1 N HNO_3 while stirring at room temperature.) Feed solution volume increases ~10% when the NaCl dissolves, so the resulting calculated concentrations are ~4.8 M NaCl and ~0.05 M $NaNO_2$. The sodium chloride dissolves slowly, and occasionally, if the feed plutonium and thorium loading is high, all of the salt corresponding to the above recipe may not dissolve. If this occurs, the supernatant may be decanted and processed.

All reported tests had feeds of ~20 to 25 g plutonium/ℓ or were ~0.08 to 0.105 M in plutonium, and ~0.05 M $NaNO_2$ was used for valence adjustment. This choice of quantity for the nitrite ion was arbitrary; no experimental attempts verified whether changes in its concentration would affect the results. We assume that a decrease of 2 to 5% in the quantities of NaCl and $NaNO_2$ would not cause extreme perturbations in the process. If solubility problems arise, we would decrease the quantities added.

B. Wash and Eluant Preparation

The wash solution, 1 N HNO_3 with 4.8 M NaCl, contained ~310 g NaCl in 1 ℓ of 1 N HNO_3. Because dissolution increases volume, the resulting solution is less than 1 N HNO_3; however, this is ignored in the flow sheet.

The eluant, 0.5 N HCl, was concentrated HCl diluted with H_2O. Note that using this eluant for plutonium removal readies the resin for reuse in the chloride form. Resin may sit conveniently in the column in 0.5 N HCl when the system is not in use. In contrast, allowing the column to sit with wash solution in it causes considerable salt crystal deposition near the liquid surfaces.

C. Plutonium Sorption and Effluent Collection

1. **Column Conditioning.** Before feed was introduced to the resin bed, approximately one-third column volume of 1 N HNO_3–4.8 M NaCl (the wash solution) passed through the column. Thus, HNO_3 was in the column fluid, so the first feed increments tended not to convert to Pu(III). (The term, column volume, c.v., here means the total resin bed volume from the top resin surface to its bottom restraining system, including the void volume.)

2. **Feed Sorption.** After the liquid level of the conditioning wash reached within ~0.6 cm of the resin bed top, feed solution flowed into the column's reservoir volume above the resin. Column flow was adjusted at the stopcock at the bottom to 1 to 2 mℓ/min, as determined by collecting measured volumes for 5-10 min. This rate corresponds to ~0.7 to 1.1 mℓ/min-cm^2, based on the cross-sectional area of 1.77 cm^2 for the column used in the small-scale tests.

These smaller tests processed ~60 to 75 mℓ of feed that loaded ~1.25 to 1.86 g plutonium onto ~12 g "dry" resin or ~30 mℓ wet resin. (See Appendix A.)

3. **Effluent Collection and Sampling.** All effluent from feed processing was collected, its volume measured, and samples taken for thorium and plutonium analyses. To easily identify samples taken here, they were labeled EF samples. A compilation of sample assay results is given in Appendix B. In early experiments, an occasional grab sample of flowing effluent was taken to compare these assays with later ones taken of the combined total effluent.

The effluent, 1 N HNO_3–4.8 M NaCl containing thorium, was neutralized by incremental addition of 9 M NaOH, causing precipitation of thorium (and any plutonium that may have come through with the thorium) as hydrous oxides. The precipitate was filtered through a finely fritted glass funnel, and the filtrate was collected and assayed for plutonium. These samples were called Fil-EF samples.

The thorium cake (possibly plutonium contaminated) was redissolved with a minimum of concentrated HNO_3 and a little H_2O; its volume was measured and then assayed for plutonium and thorium. Such samples were called EF-PPTD.

4. **Column Washing.** As feed processing was ending, the liquid level was lowered to ~0.6 cm above the resin bed top and wash solution was introduced. This solution is essentially feed minus the plutonium and thorium.

The wash flow rate was about the same as that of the feed, and its total volume was 2.5 to 3 c.v.'s.

The wash removes all thorium left in the resin column. Void volumes are filled with plutonium-depleted, thorium-containing, residual feed; also, the beads have been invaded, so this residual material must be transported through the bead, its wall, and surface film to the bulk of the wash solution. Because transport processes are driven by concentration gradients, appreciable time is required. Any unwashed thorium will later be eluted directly into the product; accordingly, thorough washing is essential.

During washing, grab samples were tested for thorium by dropping in 9 **M** NaOH; in these, formation of $Th(OH)_4$ was observed, which led to the recommendation of washing with at least 2.5 to 3 c.v.'s.

A second aspect of washing was observed: because the wash solution has no plutonium initially, it will tend to pick up plutonium in highly loaded regions and distribute it to the cleaner resin areas. Thus it will carry out some plutonium in the wash effluent, prompting the use of a second column to recover this plutonium.

Wash effluents were passed through a second column similar to column #1. The plutonium concentration of the total collected effluent from this second column was 1/10 the plutonium concentration of the feed material (wash effluent from column #1). This second column accommodates many wash effluents from column #1 before elution is necessary because of the low plutonium values involved.

During the experiments, wash effluent of column #1 was collected, its volume measured, and samples taken for plutonium and thorium assay. Samples were designated WEF1. These data, combined with the EF samples, determined how the thorium splits between feed and wash effluents. Also, the plutonium numbers helped estimate plutonium losses in the wash.

Collected wash effluent was next passed through column #2 to clean up some of the wash plutonium. The column #2 effluent was collected and assayed for plutonium. These samples were called WEF2.

For disposal purposes, we neutralized the column #2 collected effluent with 9 **M** NaOH, thereby precipitating any thorium and plutonium as hydroxides. These were filtered through a finely fritted funnel. The filtrate was sampled, as Fil-WEF2, and was assayed for plutonium to check whether to discard it or not. The hydroxide cake, dissolved in minimal quantities of HNO_3, was sampled, labeled WEF2-PPTD, and assayed for plutonium and thorium, thus providing values for the plutonium amount discarded with the thorium cakes.

5. **Product Elution.** After washing ended with the liquid level lowered to within ~0.6 cm of the resin bed top, we added the eluant of 0.5 N HCl to the column and started elution.

Eluate flow rate was set the same as feed flows; occasionally, it was accelerated 20 to 40%, where heavy elution was evidenced by the dark color in the stream. Here again, some time is required for plutonium diffusion into the system, so flows should not be too fast. The volumes used were 2 to 2.5 c.v.'s.

Because plutonium is deep green to black in this solution, we could see when most of the plutonium left the column. However, tests showed that although the eluate would become colorless, there were still appreciable plutonium concentrations in the stream; therefore, the recommended eluant volumes are 2 to 2.5 c.v.

Total eluate was collected, its volume was measured and sampled as EL samples, and it was assayed for plutonium and thorium. With drop-by-drop addition of 9 **M** NaOH, the solution was neutralized and spinach-green plutonium hydroxide was formed. Filtration left the plutonium on a finely fritted funnel from which it was dissolved in a minimal concentration of HNO_3 with small amounts of H_2O wash. This volume was measured and sampled as EL-PPTD samples and was sent for plutonium and thorium assays. The collected filtrate from the hydroxide cake, Fil-EL, was assayed for plutonium.

IV. RESULTS AND DISCUSSION

A. Early Tests

In testing the effectiveness of the thorium-plutonium separation process, we used one figure of merit extensively, the decontamination factor (D.F.), defined as the weight per cent of thorium in the feed plutonium divided by thorium's value in the product, or the weight percent of thorium contaminating the processed plutonium.

Early tests of processes in the flow sheet (Fig. 1) loosely followed the above operating procedures, but they had overly fast feed flows and inadequate wash volumes before product elution, yet even these gave encouraging results. For example, test PTX1 showed an average D.F. of 15 for two eluate stream samples, and PTX2 gave a D.F. of 55 on an eluate grab sample but 27 for the total collected eluate. Other tests showed very obvious quantities of thorium in the effluent and wash streams, extremely high-quality plutonium hydroxide cakes, and discardable filtrates.

One test, PTX5, used $AlCl_3 \cdot 6H_2O$ to get ≥ 5.6 M chloride concentrations, a higher value than that obtainable with NaCl at room temperature because of its solubility limit. Amphoteric aluminum will be discarded eventually in the filtrates. Plutonium loading of the resin was sharp and neat, but washing aluminum from the resin column was very difficult; in fact, in this test the wash was incomplete. Downstream, the aluminum caused problems, too, in that upon neutralization, precipitation, and dissolution of the aluminum hydroxide in excess base, the bulkiness of the initial precipitate requires care in handling. Excess base used for the dissolution seemed to change the character of the thorium precipitate so that it was very hard to filter. Although this system may have some value, if investigated more thoroughly, we decided to concentrate upon the simpler NaCl system for further tests.

B. Test Results

The input parameters and results for the tests that demonstrated the efficacy of the thorium-plutonium separation process are listed in Table I.

1. **Feeds and Products.** The PTX series of experiments used 1.5-cm-i.d. columns containing ~30 mℓ of wet resin. The B-1 experiment was done on a 7.62-cm-i.d. by ~20.3-cm-long resin bed containing ~930 mℓ of wet resin.

Tests PTX6 and 9 show reproducibility using 35.8 and 32.6 wt% thorium feeds, respectively. PTX9 showed lower thorium levels and a higher yield, but this is attributed to better technique because of experience. Of primary concern are the obtainable product yields and purities.

Plutonium product yields in Table I are expressed as percentages of the total feed plutonium remaining in the product. All reported yields exceeded 90%, and some have approached 95%, a value which will probably prevail.

In Table I, plutonium product purity measurements are inferred from the weight per cent of thorium, to be compared with the corresponding feed values for the weight per cent of thorium.

Decontamination factors are very good, ranging from 358 to 4600. This spread in values may result from certain experimental features and constraints. (See the later discussion on assays.) Actually, we judge these reported cleanup values to be conservative.

The Table I thorium values are for samples in which both plutonium and thorium were assayed and multiple samples were averaged. In PTX experiments, samples of the total collected eluate volumes were assayed; then, solution samples were obtained by dissolving the plutonium hydroxide cake precipitated from these same eluates. Both sets of data agreed well.

The values of <0.015, <0.036, and <0.033 wt% thorium for tests PTX7, 8, and 9, respectively, are given in this way because the analytical report stated that sensitivity limits had been reached

TABLE I. Experiments and Data

EXPERIMENTAL PARAMETERS OR RESULTS	EXPERIMENT NO.				
	PTX6	PTX7	PTX8	PTX9	B-1
FEED:					
Total Pu Processed, g	1.34	1.86	1.25	1.40	28.9
Pu conc. g/ℓ	20.4	26.5	20.9	19.4	21.9
Th conc., g/ℓ	11.4	1.6	5.3	9.4	19.0
wt%, Th	35.8	5.7	20.2	32.6	46.0
Pu PRODUCT:					
wt%, Th	0.10	<0.015	<0.036	<0.033	0.01
Decontamination Factor	358.	>380.	>561.	>988.	4600.
Yield, % of Feed Pu	∼91.	>93.	---	∼95.	>90.
THORIUM SPLIT:					
Amount in Effluent, %	∼32.	∼46.	50.	59.	---
Amount in Wash, %	∼34.	∼48.	60.	42.	---
MASS BALANCES:					
Pu, % deviation from feed	−8.	+3.	+16.	+1.	+2.
Th, % deviation from feed	−34.	−6.	+12.	+2.	---
FILTRATES:					
Pu conc. in g/ℓ for					
Pu cake,	0.00016	0.0002	0.00001	0.0001	combined
Th cake of effluent,	---	0.003	0.0015	0.0001	were
Th cake of wash eff.	0.00052	0.005	0.0017	0.0001	discardable
Pu IN THORIUM STREAMS:					
Effluent, wt%	1.9	30.	4.6	0.3	combined
Col. #1 wash eff., wt%	---	64.	48.	23.	was
Col. #2 wash eff., wt%	<1	4.8	∼1.	0.3	<1.0

corresponding to these values. The sensitivity limits were dependent on the sample size, so larger or more concentrated samples may result in lower weight per cents for thorium. The PTX6 result of 0.1 wt% thorium, highest of the lot, came from one plutonium and thorium assay done on a solution sample of dissolved plutonium hydroxide cake.

The B-1 test product gave an admirable D.F. of 4600, which reflects the thorium analysis showing only 100 ppm. The assayed sample of ∼5 g resulted from drying the plutonium hydroxide cake and calcining it at ∼500°C for 2 h; both plutonium and thorium were obtained in the assay. A second substantiating assay, performed on a sample obtained by dissolving part of the hydroxide cake before it was dried and calcinated, gave 0.0134 wt% thorium or 134-ppm thorium, based on thorium-plutonium content.

Note in Table I that the PTX tests loaded from 1.25 to 1.86 g plutonium onto the resin, and the 1.86 g of PTX7 seems to have overloaded the resin, because high plutonium values were found in both feed and wash effluents.

Feed for the big B-1 test was from typical thoria-plutonia taken from the vault supply of such materials routinely processed in the plant. Material dissolved in a stock solution was assayed as ∼134 g plutonium/ℓ, ∼113 g thorium/ℓ, and $H^+ = 5.0$ N with a total volume of ∼1.75 ℓ. About 220 mℓ of this solution, containing ∼29 g plutonium, was diluted with 0.1 N HNO_3 to 1.0 N HNO_3; ∼360 g NaCl and

$\sim$4 g $NaNO_2$ were added to the feed for the test. The remaining stock solution was used later to process other batches of $\sim$29 g plutonium, but these results are not reported here because assays are incomplete. Partial results from three such batches confirm the B-1 results in that the products all had <0.025 wt% thorium.

2. **Mass Balances and Filtrate Solutions.** Thorium and plutonium assays and total stream volume measurements for feeds, effluents, washes, and eluates gave data needed for mass balances in most tests. Results for these balances are listed in Table I as per cent deviation of the mass of materials in effluents and eluates over (+) or under (−) the mass of those materials introduced as feed. Considering the precision in all relevant measurements, these reported balances demonstrate no gross systematic errors and generally validate the experiments.

Of major significance to the process is the ease and convenience in disposing of the filtered caustic solutions as discardable waste. Table I lists plutonium concentrations found in the various filtrate solutions. The highest concentration found was 5 mg plutonium/ℓ ($\sim 8.2 \times 10^8$ alpha counts/min-ℓ) so in *all* experiments the filtrates were discardable.

During the experiments the main thorium stream was divided into feed effluent, wash effluent from column #1, and wash effluent from column #2 (Fig. 1). These volumes were collected, sampled, assayed, and precipitated separately.

3. **Thorium Split and Plutonium in Thorium Streams.** The thorium split information in Table I expesses the percentage of the total feed thorium going into effluent and wash streams for each experiment. These estimates are based on single-sample thorium assays and should not be considered definitive. Thorium splits almost in half between the feed effluent and the wash, yet the wash volume is two to three times that of the feed effluent, so it is less concentrated in thorium.

Another figure of merit for thorium-plutonium separation processes is the quantity of plutonium discarded as a contaminant in by-product thorium. The allowable plutonium amount is determined somewhat by the recovery costs. In Table I, plutonium weight per cent in thorium streams is based on total thorium and plutonium as metals.

Test PTX7, which had used too much feed and overloaded the resin, shows anomalously high plutonium concentrations in the effluent stream as well as the wash; hence, the warning against resin overloading.

Note that the column #1 wash effluent generally contains appreciable amounts of plutonium, although the weight per cent of plutonium is misleading, because it also reflects the thorium amount in the stream. As the thorium level decreases in absolute value for the feeds with less thorium, the weight per cent of plutonium increases dramatically. Table I data show that plutonium losses to the thorium streams decrease when column #2 is used to treat column #1 wash effluent. This supports the recommendation for column #2's use, although we emphasize that using column #2 is *not* a safety measure to account for overloading column #1, but it will decrease wash effluent plutonium losses.

V. CONCLUSIONS

All our experiments have shown that the thorium-plutonium separation process works very well (Fig. 1).

Plutonium feeds contaminated with 5 to 46 wt% have been processed in one pass through the anion exchange column and have resulted in 90 to 95% plutonium yields with thorium contamination levels consistently in the range of low hundreds of parts per million.

A scale-up factor of 22 for the initial experiments posed no problems, and the product obtained represented >90% plutonium yields with $\sim$0.01 wt% thorium.

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APPENDIX A
EXPERIMENTAL DETAILS: MATERIALS AND EQUIPMENT

I. RESIN

Dowex 1x4, 50-100 mesh, strongly basic anion exchange resin (as it was received) was conditioned to ensure chloride form by washing it with distilled water, decanting off all floating fines, filtering, then equilibrating for ~2 h each with two batches of ~2 N HCl solution. It was washed thoroughly with distilled water until the filtrate showed no signs of cloudiness when $AgNO_3$ solution was added by drops, then dried by aspiration through a filter funnel until the resin was free flowing.

A large measured volume of the dry resin had a density of ~0.519 g/mℓ. Twelve grams of dry resin corresponds to ~30 mℓ of wet resin, that is, resin which is slurried in H_2O.

A dry resin equivalency of 3.9 ± 0.1 meq/g was obtained from three determinations. The chloride form was rinsed with excess volumes of 0.25 M $NaNO_3$ to release chloride ions into the collected effluent. This was titrated with standard $AgNO_3$ solution using K_2CrO_4 as indicator.

Calculations based on this equivalency value and the loading of 1.4 g of plutonium per gram of dry resin, as used in PTX9, show that this loading was only ~25% of this resin's theoretical equivalency.

Resin prepared for production does not require the chloride precipitation test given above for the wash water, which was used to remove excess 2 N HCl.

In experiment B-1, approximately 372 g of dry resin or ~930 mℓ of wet resin was used to load ~29 g plutonium.

II. CHEMICALS

Chemicals such as NaOH, HCl, HF, HNO_3, NaCl, and $NaNO_2$ were commercially obtained and reagent grade per ACS specifications. Water was either distilled or deionized.

Thorium stock solution was made by dissolving reagent-grade $Th\,(NO_3)_4 \cdot 4H_2O$ in water and adding HNO_3 to volume to give ~200 g thorium/ℓ in ~6 N HNO_3. Later titrations and gravimetric assays gave $H^+ = 5.7$ N and Th = 198 g/ℓ for the solution.

Plutonium stock solution was made by dissolving PuO_2 in HNO_3 and adding a few drops of HF. The solution was refluxed for good dissolution, filtered to remove any undissolved material, reduced in volume by evaporation, diluted with 0.1 N HNO_3, and finally adjusted to ~200 g plutonium/ℓ and 6 N HNO_3. Later assay and titration showed the solution to be $H^+ = 6.0$ N and Pu = 192 g/ℓ.

Aliquots of these stock solutions were mixed, then diluted appropriately with 0.1 N HNO_3 to give feed solutions of the desired thorium-plutonium ratio. The final feed compositions, reported in Table I, were determined by assays made directly on feed samples. All PTX feeds were prepared this way.

Preparation of the stock solution and feed used in the B-1 test is described in the body of this report. The final feed assay results are those given in Table I.

III. ASSAYS

All plutonium and thorium samples were assayed by the Los Alamos National Laboratory Analytical Chemistry group. Thorium was determined by a spectrophotometric method after plutonium separation, based upon oxidation of the plutonium to Pu(VI) and thorium precipitation as a fluoride with subsequent dissolution. The chemistry is similar to that described in the introduction but is done quantitatively. Reference 3 describes the procedure in more detail.

The plutonium was determined radioanalytically by standardized alpha-counting procedures.

IV. EQUIPMENT

All experiments other than B-1 used resin bed columns contained between two glass wool plugs in cut-off laboratory burettes. After shortening the burette by cutting off its top, we flared the remaining top for ease of introducing fluids and resin. The Teflon stopcock at the burette's bottom provided good flow control.

With the cock closed, the burette was half-filled with water, a glass wool plug was inserted near the bottom, the desired resin amount in a water slurry was added slowly and allowed to settle, and then the top glass wool plug was inserted. These operations excluded all air bubbles, and as long as the resin bed is not allowed to drain dry, no channeling problems occur.

The PTX experiments used a cut-down 100-mℓ burette, with 1.5-cm-i.d. or 1.767-cm^2 cross-sectional area, and 12 g of dry resin (~30 mℓ wet resin).

The B-1 experiment used ~930 mℓ of wet resin, corresponding to ~372 g dry resin, in a containment vessel made by adding a stopcock to the bottom of a 7.62-cm-i.d. glass tube approximately 34.3 cm long. A Teflon disk, 3.18 mm thick, filled randomly with 3.18-mm-i.d. holes, was a retaining disk for a glass wool plug that supported the resin bead bed. A similar disk was on top of a glass wool plug above the resin bed. This scale-up was based on processing ~30 g plutonium at a loading, ~1.3 g plutonium/12 g dry resin, which is what we found to be successful plus a built-in conservancy factor of 30%.

Other equipment used in the experiments was conventional glassware or polyethylene laboratory ware, such as beakers, filtering flasks, fritted glass funnels, and graduated cylinders.

One must not mix containment vessels used in the thorium line with those of the plutonium line. Otherwise, the cross-contamination will negate all that is accomplished in the procedure.

APPENDIX B
SAMPLE ASSAY RESULTS

TABLE B-I. Sample Assay Results

	PTX6			PTX7			PTX8			PTX9			B-1		
SAMPLE	Pu (g/ℓ)	Th (g/ℓ)	Vol (mℓ)	Pu (g/ℓ)	Th (g/ℓ)	Vol (mℓ)	Pu (g/ℓ)	Th (g/ℓ)	Vol (mℓ)	Pu (g/ℓ)	Th (g/ℓ)	Vol (mℓ)	Pu (g/ℓ)	Th (g/ℓ)	Vol (mℓ)
FEED	20.4	11.4	65.5	26.5	1.6	70.	20.9	5.3	60.	19.4	9.4	72.	21.9	19.	1320.
EF	0.07	3.58[a]	65.5	0.318	0.695	69.	0.121	2.5	63.5	0.0133	5.0	79.5	---	---	---
Fil-EF	---	---	---	0.003	---	---	0.0015	---	---	0.0001	---	---	---	---	---
EF-PPTD	---	---	---	18.0	38.	1.3	1.04	17.9	8.	0.0991	50.8	8.	1.31	48.	---
WEF1	0.0131	---	~100.	1.21	0.405	132.	1.41	1.5	133.	0.642	2.2	132.	---	---	---
WEF2	0.0013	---	---	0.019	---	115.	0.0069	0.79	137.	0.0058	1.5	133.	---	---	---
Fil-WEF2	0.00053	---	---	0.0054	---	---	0.0017	---	---	0.00007	---	---	---	---	---
WEF2-PPTD	0.0254	52.8	---	0.7	14.0	3.	0.24	11.9	8.	0.06	21.7	8.	---	---	---
EL	30.3	0.045[b]	---	21.2	<0.01	72.	18.2	<0.01	69.5	18.1	<0.01	72.5	---	0.01 wt%[c]	---
EL-PPTD	54.9	0.055	~20.	65.2	<0.01	22.	281.	<0.01	---	30.5	<0.01	41.	75.5	0.010	---
Fil-EL	0.00016	---	---	0.0002	---	---	0.00001	---	---	0.0001	---	---	0.0015	---	---

[a] Results for EF are suspect; a sample was salvaged from a spill.

[b] Sample EL was of partially collected eluate.

[c] Eluate was not sampled. The plutonium hydroxide cake was dried and then calcined at 500°C for 2 h. A 5-g sample of the cake showed only 100 ppm of thorium.

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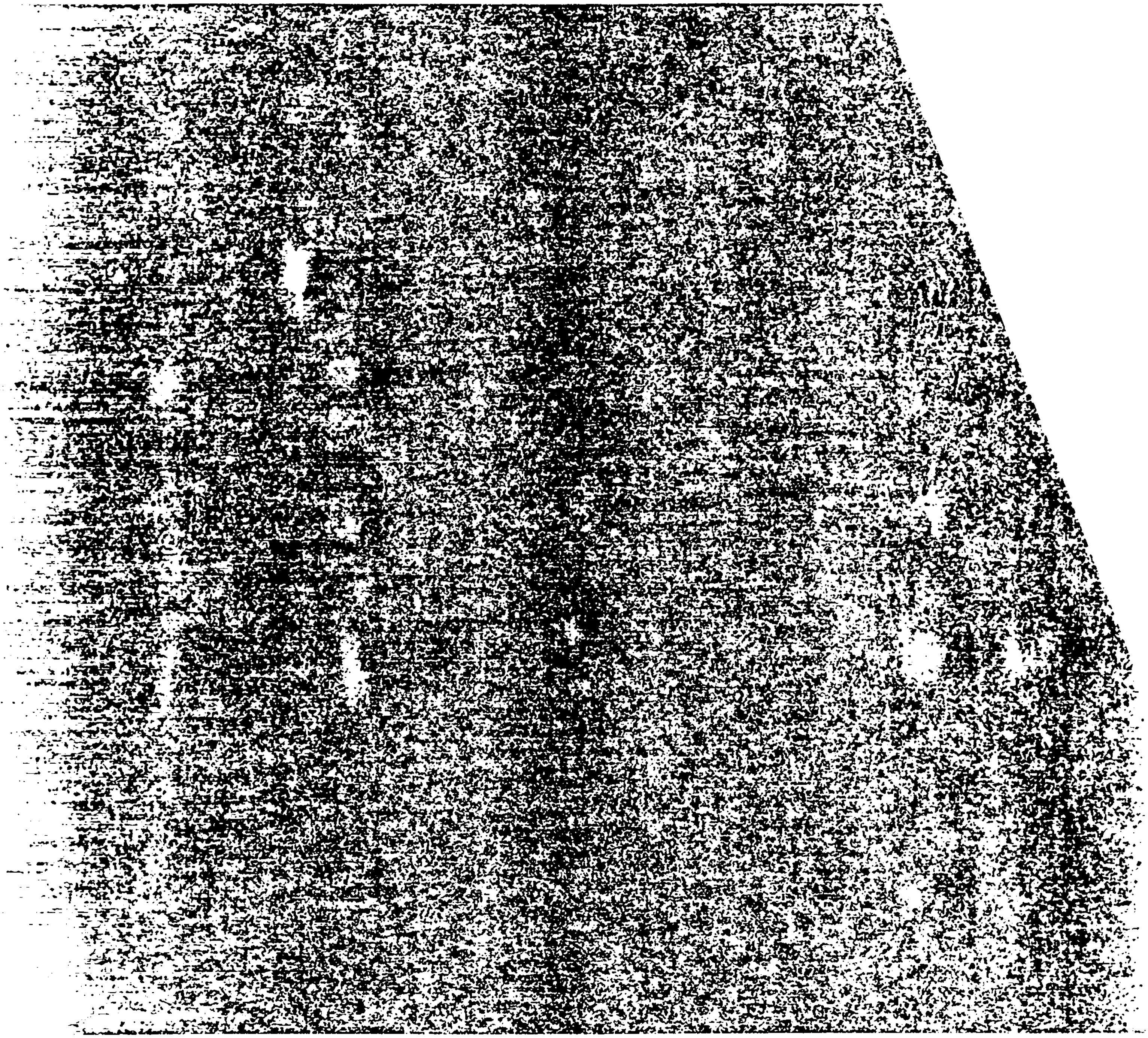

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