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PLUTONIUM ANION EXCHANGE FROM
CONCENTRATED SOLUTIONS

Roy E. Jones

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ROCKY FLATS DIVISION
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PLUTONIUM ANION EXCHANGE FROM CONCENTRATED SOLUTIONS

Roy E. Jones

ABSTRACT. Plutonium purification by anion exchange from nitrate solutions of high plutonium concentration was investigated using 6-inch-diameter by 30-inch-long ion exchange columns. The process was not recommended to replace plutonium purification by hydrogen peroxide precipitation because of relatively poor americium removal and excessive requirements for equipment.

INTRODUCTION

Plutonium purification by anion exchange has been suggested for use in a new plutonium recovery facility being planned for the Rocky Flats Plant. Anion exchange, evaporation, and denitration of the eluate would replace the portion of the current plutonium-recovery process involving hydrogen peroxide precipitation and calcination. Excellent purification has been reported by anion exchange from nitric acid solutions of low plutonium concentration in laboratory-size equipment.¹ Experiments were made to determine the characteristics of anion exchange from nitric acid solutions of high plutonium concentration in production size columns.

SUMMARY AND CONCLUSIONS

Eleven experimental runs were made to determine resin capacity, feed flowrates, wash flowrates, and wash volumes which would provide plutonium purification comparable with that obtained by hydrogen peroxide precipitation. An additional goal was to determine the conditions required to ensure a discardable effluent containing 1×10^{-3} grams plutonium per liter or less.

All runs were made at room temperature using identical feed containing 66 grams of plutonium per liter. Runs at elevated temperatures were not made since experience at Rocky Flats in production equipment indicates no significant advantages are gained. Maximum resin capacity obtained was 0.08 grams plutonium per gram dry resin at feed rates up to 15 liters per hour. Equilibrium conditions were approached under the above conditions. Two empty column volumes of wash at 15 liters per hour followed by

13 column volumes of wash at flowrates up to 50 liters per hour did not remove significant amounts of plutonium from the loaded column.

Plutonium purification obtained from three experimental anion exchange runs at the recommended wash conditions is compared with the 1968 Rocky Flats average for hydrogen peroxide precipitation. Peroxide precipitation appears to remove more americium, aluminum, beryllium, and silicon, whereas anion exchange removes more total impurities, copper, chromium, iron, gallium, nickel, and lead.

Three columns used as backup to the load column produced an effluent containing an average of 1×10^{-3} grams plutonium per liter. Total plutonium discard would be about 0.04% of the feed when 15 column volumes of wash is used.

Equipment sizing calculations based on 1,000 kilograms of plutonium per month fed to anion exchange columns show that approximately 76 columns and 576 valves would be required.

Ion exchange purification is not recommended to replace hydrogen peroxide precipitation in the new plant because of relatively poor americium removal and excessive equipment requirements for anion exchange.

DISCUSSION

Equipment and Procedure

A sketch of the equipment used is shown in Figure 1. The equipment consists of a bank of 4 glass columns, 6-inches diameter and 30-inches long (empty volume = 13 liters), a three micron Fulflo® feed filter, a pump, a rotameter, and tankage. The columns were connected in series with Tygon® tubing. Flows were controlled with stainless steel valves. Each column was filled with 8400 grams of Dowex® 1-X4 (50-100 mesh) resin.

One column was used as the load column with three backup or stripping columns. Feed, wash, and reconditioner flows were from the bottom to the top of each column. Elution flows were from the top to the bottom of each loaded column. Flowrates were measured by a rotameter.

FIGURE 1. Sketch of Experimental Equipment.

At the beginning of the experiment, the columns were conditioned with 7N nitric acid. Each test run consisted of the following steps:

1. Loading — adsorption of plutonium hexanitrate anions from 7.2N HNO_3 solution.
2. Washing — flushing of non-adsorbed impurities from the loaded resin with 7N HNO_3 .
3. Elution — desorption of purified plutonium from the resin with 0.35N HNO_3 .
4. Reconditioning — filling the column with 7N HNO_3 in preparation for the next run.

During loading and washing, the load column was connected to the backup columns. The load column was disconnected from the backup columns after washing and was eluted and reconditioned by itself.

Column effluent and eluate samples were taken directly from the connecting tubing to prevent contamination from tankage. All runs were made at room temperature.

Column Feed

One batch of 7.2N nitric acid feed containing 66 grams of plutonium per liter was used for all runs. Two grams of ferrous sulfamate was added to ensure that plutonium was in the plus four valence state. The total cationic impurities measured in the feed were approximately 124,000 parts per million parts plutonium as shown in Table I.

Column Reconditioning

An average of 5 empty column volumes of 7N nitric acid reconditioner per column was required to recondition a column previously containing 0.35N nitric acid.

Column Loading

It was observed that when over 660 grams of plutonium was fed at a feed flowrate of 5 liters per hour, loaded resin just began to appear at the bottom of the first backup

column. Using 660 grams as a load on a column containing 8400 grams dry resin results in a resin capacity of 0.08 grams plutonium/gram dry resin. Resin capacities of 70 to 120 grams of plutonium/liter of resin or about 0.1 to 0.18 grams plutonium/gram dry resin have been reported in the literature.¹

Feed flow rates of 5—, 10—, 15—, and —20 liters per hour were tried to determine the maximum flowrate at which 660 grams can be fed with no observed loading of the first backup column. At feed rates over 15 liters per hour, plutonium loading on the first backup column was observed.

At a load rate of 15 liters per hour, the resin system must have been near equilibrium since the addition of a second column-load of feed (660 g plutonium) to a loaded column which had "soaked" for eight hours completely loaded the first backup column.

TABLE I. Significant Impurities in Column Feed.

Element	Parts Per Million Parts Plutonium in Column Feed
Am	1,650
Al	1,000
Bc	30
Cr	3,000
Cu	400
Fe	100,000
Ga	5,000
Ni	10,000
Pb	3,000
Si	300
Total	124,380

Plutonium Losses in Column Effluents

Plutonium concentrations in each column effluent as a function of the cumulative volume of feed and wash fed to the load column are shown in Figures 2, 3, 4, and 5. The accuracy of the data and the limited amount of data available do not support theoretical examination and are used only to show general trends. Graphical integrations of the curves show the approximate percentages of feed in the total effluent from each column and the average plutonium

concentration in the third backup column effluent which is discarded. (See Table II.)

Curve (2) in Figure 5 shows a relatively high percentage of plutonium lost in column effluent as the result of poor reconditioning of the columns prior to the run.

Plutonium discarded in the third backup column effluent should not exceed an average of 1×10^{-3} gram Pu per liter for a total of about 0.04% of plutonium fed to the system when the following conditions are met:

1. Three load column volumes of resin are used to backup the load column.
2. The column system is reconditioned adequately.
3. The maximum feed flowrate is 15 liters per hour.
4. The first 2 column volumes of wash are fed at, or below, the maximum feed flowrate.

Column Elutions

No attempt was made to optimize elution conditions since column elution is independent of feed concentration and flow rate. Elution has been studied extensively elsewhere.¹ During elution, the first 1.5 empty column volumes of eluate were recycled and 1.5 column volumes of eluate at an average plutonium concentration of 30 grams per liter were collected. Eluate samples for impurities were taken from the column exit midway through the elution to prevent contamination from tankage.

Recycle

The amount of recycle is primarily dependent on the elution cycle and is independent of the feed concentration and flow rate. Operating experience on low-level-feed anion

TABLE II. Estimated Plutonium Losses in Column Effluents

Run No.	Feed Flow Rate (l/hr)	Wash Flow Rate (First two Col. Volumes) (l/hr)	Percent of Feed from Load Column	Percent of Feed from 1st Backup	Percent of Feed from 2nd Backup	Percent of Feed from 3rd Backup	Average Grams Pu/l from 3rd Backup
1	5	30	6	2	0.1	—	—
2	10	10	2	0.2	0.2	0.1	3.3×10^{-3}
3	15	15	4	0.8	0.04	0.04	8×10^{-4}
4	20	20	16	0.1	0.08	0.005	1.6×10^{-4}

FIGURE 2. Grams Pu Per Liter in Load Column Effluent vs. Cumulative Liters of Feed and Wash Fed to the Load Column.

FIGURE 3. Grams Pu Per Liter in First Backup Column Effluent vs. Cumulative Liters of Feed and Wash Fed to the Load Column.

FIGURE 4. Grams Pu Per Liter in Second Backup Column Effluent vs. Cumulative Liters of Feed and Wash Fed to the Load Column.

FIGURE 5. Grams Pu Per Liter in Third Backup Column Effluent vs. Cumulative Liters of Feed and Wash Fed to the Load Column.

exchange systems at Rocky Flats indicates that a plutonium recycle of about 10% of the feed can be expected.

Column Washing

Experiments were made to determine the wash volume required to produce eluate containing no more impurities, on a plutonium basis, than are present in current-production calcined peroxide cake. During all runs, after Run 1, the first two-column volumes of wash were fed at the feed flowrate to minimize the passage of plutonium to the first backup column. Three methods of final washing were investigated:

1. Continuous wash at 30 and 50 liters per hour
2. Continuous wash interrupted with air sparging of the loaded column resin
3. Draining and filling the loaded column with fresh wash, with and without air sparging of the resin

Table III lists the impurities measured for production control of peroxide cake found in (1) the column feed, (2) eluate from each run, (3) the average of eluates produced under the recommended washing conditions, and (4) the

1968 process average for Rocky Flats-produced calcined peroxide cake. It must be noted that eluate data are for a limited number of runs, whereas the peroxide cake data cover a year's production. These materials (except americium) were analyzed by emission spectroscopy.

WASHING OF PARTIALLY OR FULLY LOADED FIRST BACKUP COLUMN — During Runs 2, 5, 8, and 11 (see Table III, the first backup column was partially or fully loaded along with the load column. "A" designates the load column and "B" designates the first backup column.

During Runs 2, 5, and 8, the load columns and first backup column were washed in series. As shown in Table III, the eluate from the first backup column (B) contained considerably more impurities than eluate from the load column (A). Considering the first backup column as a simple extension of the load column, the data indicate better purification would be expected when short load columns are used.

CONTINUOUS WASH OF THE LOAD COLUMN — Runs 1, 2, 3, 4, 5, 6, 7, 8, and 11 (Table III) were made using continuous wash. No correlation between column volumes of wash and impurities in the eluate is evident.

TABLE III. Significant Impurities in Column Feed — Column Eluates — Denitrated Oxide and Peroxide Cake (Parts Per Million Parts Plutonium)

Element				Am	Al	Be	Cr	Cu	Fe	Ga	Ni	Pb	Si	Total
Anion Column Feed				1650	1000	30	3000	400	100,000	5,000	10,000	3,000	300	124,380
Anion Column Eluates														
Run No.	Feed Flow Rate (1/hr)	Column Volumes of Wash	Air Sparge During Wash											
1	5	7	No	26	70	0.5	25	1	100	10	10	10	NR	252
2A	10	11	No	26	120	0.05	21	3	75	16	15	10	75	361
2B		11	No	41	140	0.25	30	2	154	35	10	50	240	702
3	15	11	No	34	95	0.05	23	0.5	125	37	5	10	50	380
4	20	15	No	28	2	0.05	17	3	62	33	8	50	42	245
5A	15	15	No	38	70	0.05	17	3	60	10	6	12	67	273
5B		15	No	29	100	0.25	62	20	285	200	90	77	62	925
6	15	15	Yes	24	55	0.20	15	4	232	15	15	65	65	490
7	15	15	Yes	27	250	0.10	15	3	242	35	13	50	50	695
8A	15	15	Yes	34	130	0.05	9	2	51	20	6	3	59	314
8B		15	Yes	43	215	0.05	50	10	440	225	400	3	107	1493
9	15	15	Yes	32	215	0.05	60	6	357	75	10	25	116	896
10	15	7	No	37	50	0.05	23	1	95	18	5	20	24	272
11A	15	15	No	26	61	0.05	7	3	40	3	6	10	32	188
11B		15	No	24	90	0.05	11	2	45	3	7	2	40	224
Avg. of Runs 4, 5A, and 11A				31	44	0.05	14	3	56	15	7	21	50	241
1968 Process Avg. on Peroxide Cake				10	19	1.0	28	11	128	46	36	25	23	327

CONTINUOUS WASH OF THE LOAD COLUMN WITH AIR SPARGING OF THE RESIN — In Runs 6, 7, and 8, (Table III), the load column resin was air sparged three times during each wash to break up any channels in the resin and thereby improve wash efficiency. The impurity levels in the eluates were considerably higher when air sparge was used, suggesting that channels were formed by the air sparge where none existed before.

LOAD COLUMN WASH BY DRAINING AND REFILLING — It was thought that less wash volume would be required if the solution in the loaded column were repeatedly drained out and the column refilled with fresh acid since continuous wash is somewhat a process of dilution. In Run 9, 2 column volumes of wash were fed continuously at the feed rate, and 8 column volumes were fed at 30 liters per hour. At this point, it was decided to drain and fill each column five times with an air sparge after each filling. In Run 10, 2 column volumes of wash were fed continuously, followed by draining and filling the load column five times. The impurity level in Run 9 eluate was considerably higher than the level in Run 10 eluate; apparently this was caused by the air sparge used in Run 9.

Washing the load column by draining and filling with fresh acid is not attractive since considerable difficulty is encountered in air removal during each column filling.

RECOMMENDED WASH CONDITIONS — To yield elute of the highest quality, the following wash conditions are recommended using the highest wash volume (15 empty column volumes) as a safety precaution:

1. Two column volumes of wash fed continuously at the feed flowrate.

2. Thirteen column volumes of wash fed continuously at 30 to 50 liters per hour.
3. No air should be allowed to enter the resin bed.

Plutonium Purification

As shown in Table III, total impurities in the eluates produced under the recommended wash conditions (Runs 4, 5A, and 11A) are lower than in peroxide cake; however, americium is three times higher in the averaged eluates. Since americium removal is one of the prime objectives in the plutonium purification process, it is very doubtful that anion exchange in production scale columns using a reasonable amount of wash would provide adequate purification.

EQUIPMENT SIZING

Equipment requirements for 1000 kg per month, calculated from operating conditions determined from the experimental runs (see Appendix) are 36 banks of columns. Each column bank consists of one load column backed up by one column equivalent to three load columns. Total columns required is 72. Each column requires 8 valves for a total of 576 valves. Fewer valves would be needed if the banks were connected in gangs; however, experience at Rocky Flats indicates that each bank should have its own flow control.

Because of the large number of columns and valves required for ion exchange, the process is not recommended to replace peroxide precipitation for the new plant.

REFERENCES

- ¹ J. L. Ryan and E. J. Wheelright, *The Recovery, Purification and Concentration of Plutonium by Anion Exchange in Nitric Acid*, Hanford Atomic Products Operation, HW 55903 (1959)

APPENDIX

Equipment Sizing – Conditions and Calculations

The following operational conditions, based on the experimental runs and the proposed operation of the new plant, were used to calculate the columns required to process plutonium in high level nitrate solution.

1. Column operating time per month = (24 hours/day) 5 days/week) (4 weeks/month) (80% operating time) $\cong$ 380 hours per month.

2. Columns must contain 0.35N nitric acid over the idle weekend to minimize fire hazards.

3. Each bank of columns contains one load column and three backup columns all of equal volume.

4. Five empty column volumes of 7N nitric acid are required to recondition one column.

5. Reconditioner flow rate is 100 liters per hour.

6. Loading rate for feed containing 60-grams plutonium per liter is 15 liters per hour.

7. Kilograms of plutonium loaded per liter per column volume per load = $\frac{0.66 \text{ kg Pu}}{13 \text{ liters/column volume/load}}$
 $= 0.05 \text{ kg Pu/liter/column volume/load}$

8. First wash is 2 column volumes at 15 liters per hour.

9. Second wash is 13 column volumes at 50 liters per hour.

10. Total elution volume is 3 column volumes, one-half of which is recycled.

11. Elution flow rate is 20 liters per hour.

12. Production rate is 1,000-kg plutonium per month.

13. Recycle from reconditioning and elution is neglected.

Let C = the number of loads per bank of columns per month

$$\text{Let } X = \frac{\text{Liters}}{\text{Column Volume}}$$

Hours for startup reconditioning =

$$\left(\frac{4 \text{ columns}}{\text{month}} \right) \left(\frac{4 \text{ times}}{\text{month}} \right) \left(\frac{5 \text{ column volumes}}{\text{column}} \right) \left(\frac{X \text{ liters}}{\text{column volume}} \right) \left(\frac{\text{hr}}{100 \text{ liters}} \right) = 0.80X \text{ hours/month}$$

Hours for load =

$$\frac{(C) (0.05) \text{ kg } (X) \text{ L } \text{ L Hr}}{\text{L } 0.06 \text{ kg } 15 \text{ L}} = 0.0625 \text{ CX}$$

$$\text{Hours for 1st wash} = \frac{(C) (2X) \text{ L Hr}}{15 \text{ L}} = 0.133 \text{ CX}$$

$$\text{Hours for 2nd wash} = \frac{C(12X) \text{ L Hr}}{50 \text{ L}} = 0.260 \text{ CX}$$

Hours for (C-4) elutions =

$$\frac{(C-4)(1.5X) (2) \text{ L Hr}}{20 \text{ L}} = 0.150 \text{ CX} - 0.6X$$

Hours for (C-4) reconditions =

$$\frac{(C-4) (5X) \text{ L Hr}}{100 \text{ L}} = 0.050 \text{ CX} - 0.2X$$

Hours for shutdown elution =

$$\left[\frac{(3) (5X) + (1) (3.5X)}{\text{L}} \right] (4) \text{ L Hr} = \frac{0.74 X}{0.656 \text{ CX} + 0.74X}$$

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Total operating hours per month = $0.656 CX + 0.74X$

$$0.656 CX + 0.74X = 380$$

$$X = 380 / (0.656 C + 0.74)$$

Kg Pu/bank·Mo =

$$\left(\frac{0.05 \text{ kg Pu} \cdot \text{Column Volume}}{\text{Liter Load}} \right) \left(\frac{X \text{ Liters}}{\text{Column Volume}} \right) \left(\frac{C \text{ Loads}}{\text{Bank} \cdot \text{Month}} \right) = 0.05 C X$$

Number of banks required =

$$\left(\frac{1000 \text{ kg Pu}}{\text{Mo}} \right) \left(\frac{\text{Bank} \cdot \text{Mo}}{0.05 CX \text{ kg Pu}} \right) = 20,000 / CX$$

C(cycles/mo) X(liters/col) Kg Pu/Bank Month No. Banks

4	112.8	22.6	45
8	63.5	25.1	40
16	33.8	27.0	37
20	27.4	27.4	37
24	23.0	27.6	37
28	19.9	27.8	36
32	17.5	28.0	36
36	15.6	28.1	36
40	14.1	28.2	36
44	12.8	28.2	36
48	11.8	28.3	36

Using 40 cycles per month, 36 banks of columns would be required.