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ABSTRACT

A cation exchange technique was developed for the separation of plutonium from laboratory solutions containing either Pu(III) or Pu(III) - Pu(IV) mixtures in acidic solutions containing chloride ions. The procedure consists of adjusting the acid concentration to less than one molar and adjusting the valence of the plutonium ion to the (III) state, if necessary. The adjusted solution is fed to a cation exchange column and washed with distilled water to remove residual chlorides from the column. Plutonium is then eluted from the column with 5M nitric acid containing 0.34M sulfamic acid. This procedure was used to separate plutonium from 1.2M chloride solution on a production-scale column. Typical plutonium recovery was 99.97%, while greater than 96% of the original chloride was rejected.

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CATION EXCHANGE PROCESS FOR RECOVERY OF PLUTONIUM FROM LABORATORY SOLUTIONS CONTAINING CHLORIDE

INTRODUCTION AND SUMMARY

At the Savannah River Plant (SRP), 6M to 12M hydrochloric acid is used to dissolve samples of plutonium metal prior to analysis. After diluting to a known volume with distilled water, aliquots are removed for individual determinations, such as for uranium and plutonium isotope content. These procedures generate two types of solutions. One solution contains about 1.2 to 1.6M Cl^-, <0.15M H^+, and 65 g Pu/L. The other solution contains about 0.06 to 0.08M Cl^-, 3M HNO_3, and 15 g Pu/L. These solutions are returned to the plant production recovery facility for plutonium recovery.

SRP routinely has processed these laboratory solutions by first removing the chloride by addition of silver nitrate, and then adjusting the resulting solution to Pu(IV) and 7 to 9M HNO_3. This adjusted solution was then fed to an anion exchange column along with other solutions generated in recovery operations. The anion column was stripped with 0.34M HNO_3 and transferred to the second plutonium solvent extraction cycle of the Purex process. This material then followed the normal processing routes for concentration, precipitation, and conversion to plutonium metal. However, silver chloride, which is the removal form of chloride, is a very good carrier for plutonium. Therefore, the coprecipitated plutonium must be recovered from the AgCl or the material must be stored as retrievable waste. Attempts to recover plutonium from precipitated AgCl frequently generate corrosive mixtures (aqua regia) that are detrimental to the stainless-steel glove-box surface and the processing equipment. Therefore, an alternative method that will minimize corrosion to the process equipment and glove-box surfaces was sought.

Cation exchange resin has a high absorption of plutonium[1-3] ($K_D \approx 10^4$) on cation resin in addition to a negligible absorption of chloride. Utilization of this technique has resulted in a process which provides nearly chloride-free plutonium solutions that can be introduced directly into the normal recovery streams.

The solutions are initially adjusted to $\leq$ 1M acid, and the plutonium valence adjusted to Pu(III) (if necessary) by the addition of hydroxylamine nitrate. The solutions are then passed through a bed of cation resin (*Dowex*® 50W X 12, acid-form). To remove the chloride containing solution from the column, the resin is washed with 2.5 to 3.5 bed-volumes of water. The plutonium is eluted using 3 bed-volumes of nitric acid containing 0.34M sulfamic acid.

This purified solution can then be introduced to the Purex process at any convenient point. At SRP, this solution is combined with other solutions generated in recovery facility operations. The combined solution is fed to the anion exchange column and then transferred to the second plutonium cycle of the Purex process.

EXPERIMENTAL

Cation exchange experiments were conducted either in 25-cm-long by 1.0-cm-diameter columns or 18-inch-long by 6-inch-diameter columns. The small columns contained 13 mL of 50 to 100 mesh *Dowex*® 50W X 12 resin. The large column contained 2L of the same type resin. The feed rate was controlled by controlling the column effluent. Loading, washing, and elution were all downflow at 0.5 mL/(cm^2-min).

The behavior of the plutonium was monitored both visually and by gross-alpha counting. The chloride behavior was monitored by specific ion electrodes and by titration with silver nitrate solution.

The smaller of the columns was used for development work on 1M HCl feed solution only and for experiments with Pu-Cl solution. For the full-volume production demonstration experiments, the 6-inch-diameter column was used.

In each set of experiments, the columns were conditioned by passing two bed-volumes of 5M HNO_3-0.34M NH_2SO_3H solution through the column, followed by two bed-volumes of distilled water. The feed solution was fed through the resin bed at a rate of 0.5 mL/(cm^2-min). For the small columns, fractions were collected for each one-half bed-volume. For the large column, fractions were collected in 138-mL bottles (0.069 bed-volumes) for the feed portion of the experiment, and 1.0L-fractions (one-half bed-volume) for the remainder of the experiment.

®Trademark of Dow Chemical Co., Midland, Michigan.

RESULTS AND DISCUSSION

Typical data obtained from the HCl solutions fed to the column are given in Table 1. Approximately 83% of the chloride had traversed the column during the feed cycle. At the end of the first bed-volume of water wash, the total chloride eluted was about 97%; at the end of the third bed-volume wash, the total chloride eluted had increased to 99.5%. On another run, with only one-half the feed volume of the experiment in Table 1, only 98.7% of the chloride had eluted from the column at the end of the third bed-volume of wash.

Two experiments were then made with both normal laboratory-generated recoverable Pu-Cl solutions and the small columns. These experiments showed that plutonium losses could be maintained at less than 0.1%. However, chloride was not eluted from the column as fast as with the clean HCl solutions. After a 2.5 bed-volume wash, only 95% of the chloride fed to the column had been eluted. Most of the remaining chloride (95%), however, was removed in the first one-half bed-volume of plutonium eluate. For this reason, all production demonstration runs used three full bed-volumes of water to wash the column before elution of product began.

The necessity of reducing all oxidized Pu ions to Pu(III) before feeding the column was demonstrated with a mixture of Pu(III) and Pu(IV) in a mixed $HCl-HNO_3$ solution. With this feed solution, only 75% of the chloride fed to the cation column was eluted after 3 bed-volume washes with water. The differences in chloride behavior between the Pu(III) - Cl and Pu(III) - Pu(IV) - Cl solutions are explained as follows. Only two Pu(III) - chloride complexes were identified in aqueous media: $PuCl^{2+}$ in solutions containing chloride concentrations of 2M and above, and $PuCl_2^{+}$, which is predominant at concentrations of chloride exceeding 8M. At the chloride concentrations in these experiments (1.2 to 1.6M), clearly only a portion of the Pu(III) was complexed by chloride as $PuCl^{2+}$. This resulted in broadening of the bands in the column. Also, more chloride was retained on the column during the feeding portion of the cycle than with the unmasked chloride experiments.

Tetravalent plutonium, however, forms chloro complexes even in chloride solutions with concentrations as low as 0.3 to 0.4M.[1,4-8] As the chloride ion concentration is increased, successive chloro complexes are formed until the highest, $PuCl_6^{2-}$, results. Because the Pu(IV) - Cl complexes are more stable than Pu(III) - Cl complexes[1,9], one would expect chloride ion to be more difficult

TABLE 1

Typical Chloride Elution from Cation
Column with No Chloride Masking Agents

		Chloride Conc. in Effluent		
Fraction Number	*Total Bed Volumes through the Column*	*Chloride Fraction, mM/mL*	*Accumulative, mM Cl*	*Accumulative Cl in Feed, % of Total*
1	0.5	0.135	1.35	1.67
2	1.0	0.845	9.80	12.10
3	1.5	0.850	18.30	22.59
4	2.0	0.935	27.65	34.14
5	2.5	0.965	37.30	46.05
6	3.0	0.990	47.20	58.27
7	3.5	0.995	57.15	70.56
8 ↑ Feed	4.0	1.000	67.15	82.90
9 ↓ Wash	4.5	0.975	76.90	94.94
10	5.0	0.175	78.65	97.10
11	5.5	0.115	79.80	98.52
12	6.0	0.035	80.15	98.95
13	6.5	0.030	80.45	99.32
14	7.0	0.015	80.60	99.51
15	7.5	0.015	80.75	99.69
16	8.0	0.015	80.90	99.88
17	8.5	0.010	81.00	100.00
18	9.0	0.010	81.10	100.12
19	9.5	0.010	81.20	100.24
20	10.0	0.010	81.30	100.37

to remove from Pu(IV) than from Pu(III) solutions. This expectation was proven by the recovery of 25% of the chloride from the column containing both Pu(III) and Pu(IV), whereas >96% of the chloride was removed from the Pu(III) solutions when the columns were washed with 2.5 bed-volumes of water.

The necessity to maintain sulfamic acid in the elution solution was demonstrated by an attempt to elute a loaded cation column with 5M HNO_3. Gassing in the column, due to the oxidation of Pu(III) to Pu(IV) and the accompanying reduction of NO_3^- to NO_x, resulted in poor column behavior.

Typical data obtained from the production demonstration experiments are shown in Table 2. Only about 36% of the chloride in the feed had eluted by the end of the feeding step. This compares with the 60 to 80% in the unmasked straight HCl solution. However, the chloride was rapidly stripped from the column as about 96.5% of the chloride had been eluted after three bed-volumes of water wash. Again, most of the residual chloride was removed during the first one-half bed-volume of product elution. Typically 3 bed-volumes of elution with 5M HNO_3 - 0.34M NH_2SO_3H was necessary to remove greater than 99.9% of the plutonium from the column.

After the elution step, the column was washed with one bed-volume of water to remove the residual nitric acid from the column. Failure to remove the nitric acid before feeding of the next batch of Pu(III) - Cl solution resulted in partial oxidation of Pu(III) to Pu(IV).

During periods of inactivity, the resin should remain covered with water.

Although a 2-L bed-volume in a 6-inch-diameter column was used for the experiments, a 1-L bed-volume column would be sufficient. The 2-L bed-volume column was designed on the basis of work at Rocky Flats.[2] Solutions used in the Rocky Flats work, however, had a much higher concentration of mono- and divalent cations than the laboratory-generated solutions at SRP. The recommended column then is a 4-inch-diameter glass column containing 1L of cation exchange resin.

TABLE 2

Typical Chloride Elution from Cation Column with Plutonium as a Chloride Masking Agent

Fraction Number	*Total Volume through Column, mL*		*Chloride Conc., mg/mL*	*Accumulative Cl through Column, g*	*Accumulative Cl in Feed*, % of total*
1	138		< 0.01	< 0.00138	0.002
2	276		< 0.01	< 0.00276	0.004
3	414		3.54	0.4913	0.719
4	552		29.4	4.5485	6.659
5	690		29.3	8.5919	12.578
6	828		26.4	12.2351	17.911
7	966		26.4	15.8783	23.244
8	1104		29.3	19.9217	29.164
9	1242	↑ Feed	33.8	24.5861	35.992
10	2242	↓	23.0	47.5861	69.662
11	3242		7.70	55.2861	80.934
12	4242		7.70	62.9861	92.206
13	5242	Water Wash	2.30	65.2861	95.573
14	6242		0.30	65.5861	96.012
15	7242	↑	0.30	65.8861	96.452
16	8242	↓	2.30	67.8861	99.379
17	9242		0.30	68.1861	99.819
18	10242	Elute Prod.	0.30	68.4861	100.258
19	11242		0.10	68.5861	100.404
20	12242		0.10	68.6861	100.551

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* Total chloride in feed = 68.310 g.

CONCLUSIONS

The results show that plutonium ions can be separated from chloride ions in laboratory-generated solutions by using a cation exchange procedure. The plutonium valence must be adjusted to the (III) oxidation state and the free acid concentration to less than one molar for good column performance. Once the acid is diluted, either ferrous sulfamate, hydroxylamine sulfate, or hydroxylamine nitrate can be used to reduce any Pu(IV) ions to Pu(III) ions. Because the Fe(III) would compete with the Pu(III) for resin sites, the hydroxylamine sulfate or nitrate treatment is preferred. After loading, the cation column is washed with three bed-volumes of water to elute the residual chloride. The product is then eluted with three bed-volumes of 5M nitric acid containing 0.34M sulfamic acid.

After assay for total plutonium, the waste solutions containing recoverable plutonium are added to normal recovery-generated solutions to return the plutonium to normal Purex processing streams. At SRP, the most convenient point to introduce this solution is to the feed-adjustment tank just before the anion exchange recovery column. In this tank, the plutonium valence is adjusted to oxidation state (IV) and the nitric acid concentration is adjusted to 7 to 9M HNO_3. After loading, the anion column is washed with 7M HNO_3 and then eluted with 0.34M HNO_3. The eluate is then transferred to the second plutonium cycle of the Purex Process. The proposed process is shown in block-diagram form in Figure 1.

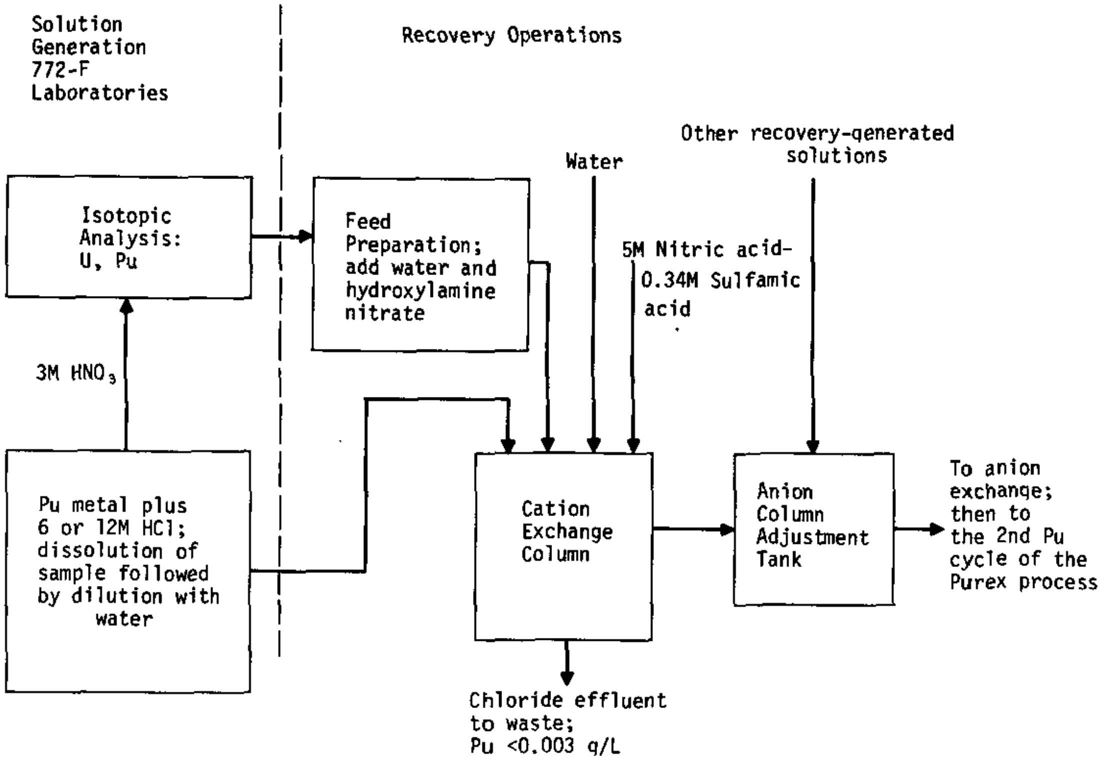

FIGURE 1. Plutonium-Chloride Separations Process

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