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**CHLORIDE ANION EXCHANGE COPROCESSING FOR
RECOVERY OF PLUTONIUM FROM
PYROCHEMICAL RESIDUES AND Cs_2PuCl_6 FILTRATE**

A. C. Muscatello

M. E. Killion

SUBJECT DESCRIPTORS

Chloride Anion Exchange Coprocessing
DOR Residue Salt
ER Residue Salt & Scrapeout
Dicesium Hexachloroplutonate Filtrate Recovery

EG&G ROCKY FLATS, INC.
ROCKY FLATS PLANT
P. O. BOX 464
GOLDEN, COLORADO 80402-0464

PREPARED UNDER CONTRACT DE-AC04-90DE62349
FOR THE
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A. C. Muscatello and M. E. Killion

ABSTRACT

Continuing studies of plutonium recovery from direct oxide reduction (DOR) and electrorefining (ER) pyrochemical process residues show that chloride anion exchange coprocessing is useful and effective. Coprocessing utilizes DOR residue salt as a reagent to supply the bulk of chloride ion needed for the chloride anion exchange process and to improve ER residue salt solubility. ER residue salt and ER scrapeout can be successfully treated, either alone or together, using coprocessing. In addition, chloride anion exchange at 2.0M acidity results in improved process performance by greatly reducing disproportionation of plutonium(IV), eliminating restrictions on oxidation time compared to operation at 1.0M acidity. Laboratory-scale experiments show that below-discard effluent plutonium losses are obtained. Resin capacity was 30 g Pu/l or greater.

Furthermore, it is feasible to perform chloride anion exchange recovery of plutonium from filtrate resulting from precipitation of dicesium hexachloroplutonate (Cs_2PuCl_6 , an oxidant salt to be used in the molten salt extraction process) and integration of its preparation with recovery of DOR salts.

INTRODUCTION

In our previous study,¹ we described continuing efforts to define a process to recover plutonium from direct oxide reduction (DOR), electrorefining (ER) residue salts, and other pyrochemical residues. The DOR process is the reduction of plutonium oxide to metal using calcium metal in a molten calcium chloride matrix. Electrorefining produces ultrapure plutonium metal using an

equimolar sodium chloride/potassium chloride molten salt. These two processes at Rocky Flats have produced a large backlog of salts requiring treatment before disposal.

Our previous results indicated that chloride anion exchange is suitable for recovering plutonium from the DOR and ER salts. However, some difficulty was encountered in the form of limited resin capacities when the two residues were mixed to reduce hydrochloric acid usage and increase ER salt throughput. This report details results of further research into chloride anion exchange coprocessing, producing improved resin capacities and operating conditions.

In addition, a new oxidant salt will be introduced into Rocky Flats molten salt extraction (MSE) operations to eliminate magnesium from the plutonium buttons. The magnesium, which arises from the magnesium chloride oxidizer added to extract americium, interferes with foundry casting operations. Dicesium hexachloroplutonate (Cs_2PuCl_6 or DCHP) was suggested as an alternative oxidizer by the Rocky Flats Plant Pyrochemistry Technology group. DCHP is produced by precipitation from hydrochloric acid, resulting in an above-discard chloride filtrate. Previous studies showed that DCHP can be dissolved in the presence of anion exchange resin.² Consequently, chloride anion exchange was a natural choice to render the filtrate discardable.

EXPERIMENTAL

Residues

The DOR residue salts (90% CaCl_2 , 9% CaO , 0.5% Ca , and 0.5% Pu) were ground to uniformity

Table 1. Impurity Analysis of ER Scrapeout. All results in ppm (W)

Spectrometry Results			
Atomic Absorption		Emission	
Fe	377	Ta	<10
K	71549	W	>5000
Mg	21483	Zr	<10
Na	53892		
Photographic Emission			
Al	10	B	25
Be	2.5	Ca	50
Cr	250	Cu	5
Ga	500	Mn	<5
Mo	5	Ni	500
Pb	<2	Si	10
Sn	5	Ti	10

before use. The ER residue salts (53% KCl, 42% NaCl, and 5% Pu) were also ground to uniformity before use. ER scrapeout, which results from holdup in Tilt-Pour ER furnaces periodically scraped, was calcined at 400 °C to oxidize any plutonium metal and ground to a free-flowing powder. The ER scrapeout contained 51.3% plutonium and 0.0967% americium. Table 1 shows a detailed analysis of the ER scrapeout used in this study.

Oxidation

Sodium nitrite and calcium hypochlorite were each used as oxidizers and were added to the feed and wash solutions at concentrations noted in the text. All chemicals were reagent grade.

Anion Exchange

The 50-mℓ anion exchange columns were 1.8 cm i.d. × 30 cm long and were filled with 50 mℓ of Lewatit[®] MP-500-FK (40-70 mesh) from Mobay Chemical Co. The one-liter column (5.0 cm i.d. × 61.0 cm long) was filled with one liter of MP-500-FK. This resin is currently used in Rocky Flats nitric acid-based production columns and gives superior plutonium loading and elution performance in laboratory and full-scale testing.³

The MP-500-FK performed well in the chloride system in our previous study.¹

The 50-mℓ columns were run at flow rates listed in the text or figures. The one-liter column was run at 20 mℓ/min. Both sizes of columns were loaded and washed in the upflow mode and eluted in the downflow mode. All columns were reconditioned and washed with 8M HCl + 0.05M sodium nitrite unless ER salt was a component of the feed. Under this circumstance, the reconditioner solution and the first bed volume of the wash were 3.5M CaCl₂ + 0.05M NaNO₂ + 1M HCl to avoid precipitation of NaCl and KCl when mixing the effluent and wash. Washing continued with 8M HCl + 0.05M NaNO₂. Elution was accomplished with 0.5M HCl. All solutions in these experiments were analyzed for plutonium (radiometrically), americium (radiometrically), hydrogen ion (titrimetrically), and chloride (modified Volhard). All other procedures were the same as our previous study.¹

RESULTS AND DISCUSSION

Coprocessing ER Scrapeout

Solubility Test

The solubility of 20 g/ℓ ER scrapeout was tested with 360 g DOR residue salt/ℓ plus 3.5M HCl and 0.1M sodium fluoride. Preliminary tests showed fluoride was necessary for efficient dissolution of the scrapeout. The components were combined and the mixture was refluxed for 0.5 hour. After filtration, a black residue remained, which comprised 10.8% of the ER scrapeout by weight. This residue contained 30.1% plutonium, leaving 6.3% of the plutonium undissolved. The solution contained 10.41 g Pu/ℓ, 0.0253 g Am/ℓ, a hydrogen ion concentration of 0.61M, and a total chloride concentration of 7.31M.

Chloride Anion Exchange

Unfortunately, chloride anion exchange with the above solution was unsuccessful at 2.5 mℓ/min;

Table 2. Chloride Anion Exchange Coprocessing of ER Scrapeout

Run	Solution	Vol. (mℓ)	Pu (g/ℓ)	Pu (%)	Am (g/ℓ)	HCl (M)	Cl ⁻ (M)
1:1,	Feed	200	12.49	100	0.0268	0.90	7.62
1M	Effluent	200	0.0358	0.29	0.0211	2.82	7.64
Acid	Wash	150	0.280	1.68	0.00839	5.08	7.06
	Eluate	200	11.52	92.2	0.00087	2.02	2.07
	Heart-cut	40	54.05	86.6	0.00429	3.10	3.36
2.5:1,	Feed	200	13.49	100	0.0285	0.87	7.62
1M	Effluent	200	0.00145	0.00	0.0186	2.40	7.53
Acid	Wash	150	0.127	0.71	0.00940	4.69	7.22
	Eluate	200	10.11	74.9	0.00548	1.75	2.13
	Heart-cut	40	47.12	69.9	0.00273	3.10	3.27
2.5:1,	Feed	200	12.80	100	0.0196	2.00	8.07
2M	Effluent	200	0.00310	0.02	0.0152	3.27	8.21
Acid,	Wash	200	0.00577	0.04	0.00685	6.24	7.58
17-hr	Eluate	200	10.74	83.9	0.00083	2.36	2.45
Ox.	Heart-cut	45	41.04	72.1	0.00314	3.70	4.37
2.5:1,	Feed	200	10.5	100	0.0171	2.66	8.77
2M	Effluent	200	0.00160	0.02	0.0123	4.07	8.17
Acid,	Wash	200	0.00132	0.01	0.00449	6.53	7.87
70-hr	Eluate	200	8.35	79.54	0.00053	2.68	2.71
Ox.	Heart-cut	40	40.75	77.62	0.00251	4.48	4.80

the ion column glass frit plugged with sodium chloride, arising from the sodium fluoride (added during dissolution) and the sodium nitrite oxidizer (added 30 min. before the run). The NaCl precipitated because the oxidizer was added at five times the plutonium concentration, which was about 50% higher than in previous coprocessing studies.¹

To alleviate the plugging, calcium hypochlorite was used to oxidize the plutonium to the (IV) state. Unpublished work at Rocky Flats shows this material is an efficient oxidizer in the chloride system. Any calcium salts formed are much more soluble than the corresponding sodium salts. To counter the effect of fluoride (expected to diminish the resin capacity by complexation of the plutonium), aluminum chloride was added in a 1:1 mole ratio to fluoride.

Table 2 shows the results of two runs at a 2.5 mℓ/min flow rate with 1:1 and 2.5:1 mole ratios of calcium hypochlorite to plutonium and at approximately 1M acidity. At a 1:1 ratio, the effluent slightly exceeded the 0.027 g Pu/ℓ discard limit.

At a 2.5:1 ratio, there was no breakthrough during the loading cycle and the effluent was below the discard limit, giving a resin capacity of 40 g Pu/ℓ. No problems with precipitation were encountered. However, some breakthrough was experienced during the wash step, indicating the actual capacity is somewhat less than 40 g Pu/ℓ. Elution results were excellent, yielding heart-cut plutonium concentrations on the order of 50 g/ℓ.

In both runs, oxidation time was restricted to 30 min. as in previous coprocessing runs.¹ To avoid this limitation, chemistry of the disproportionation reaction was examined. According to equations in Cleveland,⁴ the extent of disproportionation of plutonium(IV) is inversely dependent on the fourth power of the hydrogen ion concentration. Consequently, doubling the hydrogen ion concentration would decrease the extent of disproportionation 16-fold. Furthermore, the rate of disproportionation is inversely proportional to approximately the third power of hydrogen ion concentration. Therefore, the rate of disproportionation would be reduced a factor of eight upon doubling the hydrogen ion concentration. These effects should greatly improve stability of plutonium(IV), and enough hydrochloric acid was added to a new batch of ER scrapeout and DOR salt to produce 2.0M acidity after dissolution.

Figure 1 and Table 2 show that chloride anion exchange of the resulting feed at 2.5 mℓ/min was excellent, even with oxidation times of 17 and 70 hours. Based on the feed, the resin capacities were 51 and 42 g Pu/ℓ, respectively. No breakthrough occurred in either the feed or wash step. Peak concentrations of plutonium in the eluate were 41 g/ℓ.

Calcium was efficiently reduced by the process from 3.2M in the feed to only 51 ppm in the heart-cut eluate. However, as expected,¹ iron follows the plutonium into the eluate at 170 ppm, up from 36 ppm in the feed. If initial iron contamination were low, the resulting concentration in the eluate would be at a tolerable level. The americium decontamination factor, D_r , is about 23, similar to our previous results for ER salt processing.¹

Coprocessing ER Residue Salt

Solubility

In light of control being established over disproportionation of Pu(IV) at higher acidity, the coprocessing of ER residue salt was reexamined. Using higher acidity required redetermining the solubility of the salt in the calcium chloride solution. Figure 2 shows the results of titrating 25 ml of 1.5M KCl + 1.5M NaCl + 2.0M HCl (to simulate ER salt) with 4.0M CaCl₂ + 2.0M HCl (to simulate dissolved DOR salt). All combinations of these two solutions are soluble. The resulting maximum solubilities of the salts are only slightly lower than for a similar titration at 1M acidity.¹ A combination giving a total of 7.0M chloride is: 2M HCl + 1.6M CaCl₂ + 0.9M NaCl + 0.9M KCl. Correcting for the approximate concentrations of these salts in the residues results in a prediction that 120 g of ER residue salt plus 175 g of DOR residue salt plus 3.0M HCl would be soluble. (Calcium metal and calcium oxide in the DOR salt neutralize some of the acid.)

Dissolution of such a combination proceeded readily at ambient temperature. Only 0.5 g of residue remained (<0.2%). After analysis, the chloride concentration was 6.6M, somewhat lower than the minimum of 7.0M required for good resin capacity.⁵ Consequently, the HCl concentration was raised to 3.13M, the amount of DOR salt was increased to 179 g/l (48 g/l less than in our previous study¹), and the ER salt was decreased to 115 g/l (only 7 g/l less than previously¹). This combination was soluble as well and resulted in a solution containing 7.34 g Pu/l, 0.016 g Am/l, 1.9M acidity, and 7.08M chloride. These conditions are acceptable for further processing.

Chloride Anion Exchange

The above solution was oxidized with 2.5:1 calcium hypochlorite and allowed to stand overnight (approx. 17 hrs.). A second portion was oxidized and allowed to stand over the weekend (approx. 90 hrs.). The solutions were then passed through 50-ml columns at 2.5 ml/min. The

Table 3. Chloride Anion Exchange Coprocessing of ER Salt at 2M Acidity

Run	Solution	Vol. (ml)	Pu (g/l)	Pu (%)	Am (g/l)	HCl (M)	Cl ⁻ (M)
17-hr Ox.	Feed	200	7.34	100	0.0160	1.70	6.80
	Effluent	200	0.0172	0.23	0.0123	1.64	6.84
	Wash	200	0.0318	0.43	0.00831	5.57	5.30
	Eluate	200	6.97	95.0	0.00059	1.15	2.35
	Heart-cut	40	31.73	86.5	0.00274	4.10	3.98
90-hr Ox.	Feed	200	7.92	100	0.0161	2.07	7.08
	Effluent	200	0.0170	0.22	0.0115	1.50	6.97
	Wash	200	0.0178	0.22	0.00456	4.40	7.38
	Eluate	200	7.26	91.7	0.00054	2.81	2.86
	Heart-cut	40	34.0	85.9	0.00251	4.53	4.68

results of these two runs are shown in Figure 3 and Table 3. Compared to coprocessing at 1.0M acidity,¹ the resin capacity is improved by 50%, even with much longer oxidation times. The resin capacity is about 30 g Pu/l at breakthrough for both runs. The slight loss in ER salt throughput compared to coprocessing at 1M acidity is more than offset by the improved operating conditions. Although the combined effluent and wash plutonium concentration approaches the discard limit of 0.027 g/l for both runs, it does not exceed the limit. Larger columns in production tend to perform better so these conditions should be acceptable.

Calcium impurity reduction in the heart-cut eluate is substantial--to 392 ppm (average) from 1.6M in the feed. The americium D_f is about 26, similar to that found above. However, as with ER Scrapcut Coprocessing, the 170-ppm iron feed impurity follows the plutonium into the heart-cut eluate (875-ppm average). Care should be taken to exclude any gross iron impurities (e.g., rust) from the original salts.

Triple Coprocessing

Solubility

The next logical step is to combine all three residues into a process dubbed "Triple Coprocessing." To improve the resin capacity compared to the above results, a target total

chloride concentration of 7.5M was used. Achievement of this goal requires less ER residue salt and more DOR residue salt because of solubility limitations (Figure 2). In addition, a final acidity of 2.0M is required to control plutonium(IV) disproportionation.

Making these adjustments results in a combination of 228 g DOR salt, 92 g ER salt, and 20 g ER scrapeout per liter of 3.3M HCl. The fluoride source for dissolution was changed to CaF_2 (0.05M) to eliminate the less soluble sodium from NaF. This combination was mixed and refluxed for one hour. The filtered solution contained 17.32 g Pu/l, 0.0407 g Am/l, 1.90M acidity, and 7.28M total chloride. The dissolved plutonium concentration corresponds to 98% dissolution of the plutonium initially in the residues.

Chloride Anion Exchange

The above solution was oxidized with 2.5:1 calcium hypochlorite and complexed with 2:5 aluminum chloride. The aluminum chloride concentration was decreased to eliminate a fine-grained precipitate that appeared in ER scrapeout coprocessing and was difficult to filter. This precipitate was presumably aluminum fluoride, which is sparingly soluble. The solution was run through the column at 2.5 ml/min after both overnight (17 hrs) and weekend (70 hrs) oxidation. Figure 4 and Table 4 show the results of these two runs.

The performance of both runs was virtually identical. In both cases, the resin capacity at breakthrough was 41.5 g Pu/l. The total plutonium loaded was 63 g/l. The runs were repeated with the feed limited to 100 ml to prevent breakthrough. Oxidation time was about two days (42 hrs). Again, performance of the two runs was virtually identical, as seen in Figure 5 and Table 4. Although both runs showed some effluent samples above the discard limit of 0.027 g Pu/l, the average concentration of the combined effluent and wash is below this limit. Based on the feed, the resulting resin capacity is 34.5 g Pu/l, adequate for production usage.

Table 4. Triple Coprocessing at 2M Acidity

Run	Solution	Vol. (ml)	Pu (g/l)	Pu (%)	Am (g/l)	HCl (M)	Cl ⁻ (M)
17-hr Ox.	Feed	200	17.32	100	0.0407	1.90	7.28
	Effluent	200	0.191	1.10	0.0308	1.36	7.12
	Wash	200	0.259	1.50	0.00958	4.45	7.38
	Eluate	200	15.67	90.5	0.00122	2.37	2.69
	Heart-cut	40	73.11	93.1	0.00563	2.37	2.69
70-hr Ox.	Feed	200	17.26	100	0.0416	1.50	7.39
	Effluent	200	0.269	1.56	0.0275	1.30	7.34
	Wash	200	0.288	1.67	0.0116	4.37	7.55
	Eluate	200	15.74	91.2	0.00969	2.41	2.59
	Heart-cut	42	67.89	82.6	0.00430	4.30	4.99
42-hr Ox.	Feed	100	17.28	100	0.0410	1.60	6.84
	Effluent	200	0.0186	0.11	0.0192	1.16	6.74
	Wash	200	0.0203	0.23	0.00950	4.07	7.03
	Eluate	200	8.13	94.1	0.00595	2.50	2.06
	Heart-cut	35	44.13	89.4	0.00315	4.39	4.80
42-hr Dup.	Feed	100	17.19	100	0.0403	1.84	7.39
	Effluent	200	0.0110	0.06	0.0182	1.14	7.28
	Wash	200	0.0308	0.36	0.00983	4.49	7.44
	Eluate	200	7.82	90.9	0.00052	2.91	2.81
	Heart-cut	30	48.16	84.05	0.00343	5.41	5.39

Impurity removal is again very good with calcium reduced to 197 ppm in the heart-cut eluate, down from 2M in the feed. Potassium is reduced from 24,900 ppm to 6 ppm, and sodium is reduced from 13,950 ppm to 224 ppm. Sodium reduction is less because of the 0.05M sodium nitrite oxidizer in the wash solution, which tails into the eluate. Again, iron follows the plutonium into the eluate at 598 ppm, up from 130 ppm in the feed. As with ER Scrapeout Coprocessing, care should be taken to exclude excess iron from the feed. Americium decontamination was very good, averaging 33.4 ± 2.7 .

One-Liter Scale Triple Coprocessing

To prove the validity of Triple Coprocessing on a larger scale, two liters of feed were prepared, oxidized with 2.5:1 calcium hypochlorite, and allowed to stand over the weekend (70 hrs). The undissolved residue weighed 4.6 g (0.68%). The solution was passed through the one-liter column at 20 ml/min, which is the flow rate scaled up from the 2.5 ml/min used for the 50-ml column. The

Table 5. One-Liter Scale Triple Coprocessing

Run	Solution	Vol. (ℓ)	Pu (g/ℓ)	Pu (%)	Am (g/ℓ)	HCl (M)	Cl ⁻ (M)
70-hr	Feed	2.0	17.76	100	0.0436	2.00	7.36
Ox.,	Effluent	2.0	0.421	2.37	0.0271	1.24	7.02
No	Wash	4.0	0.843	9.49	0.00758	5.13	7.01
AlCl ₃	Eluate	4.0	7.73	87.1	0.00065	2.13	2.05
	Heart-cut	0.525	55.18	81.6	0.00456	2.75	3.84
70-hr	Feed	2.0	19.4	100	0.0463	1.70	7.76
Ox.,	Effluent	2.0	0.0173	0.09	0.00648	1.14	5.76
Low Cl	Wash	4.0	5.83	60.1	0.0190	5.33	6.87
Wash	Eluate	4.0	4.08	42.1	0.00040	2.12	2.13
	Heart-cut	0.400	35.23	36.3	0.00298	3.50	3.84
70-hr	Feed	2.0	20.2	100	0.0404	1.70	7.11
Ox.	Effluent	2.0	0.00395	0.02	0.0231	1.08	6.95
	Wash	4.0	0.00144	0.01	0.00690	5.10	6.93
	Eluate	4.0	8.85	87.6	0.00081	2.07	1.81
	Heart-cut	0.700	49.63	85.9	0.00445	2.90	2.65

column had been preconditioned with one liter of 3.5M CaCl₂ plus 1.0M HCl plus 0.05M NaNO₂. Washing and elution were at 40 ml/min to shorten the run time. Three runs were performed, and their results are shown in Figures 6 and 7 and Table 5.

Run 1 shows the deleterious effect of the accidental omission of 0.04M AlCl₃ on resin capacity, reducing it to <20 g Pu/ ℓ . The feed was remade and used in Run 2 including aluminum chloride, but the wash solution was accidentally formulated at only 4.5M total chloride for the first liter, allowing the plutonium to partially elute. More feed was prepared; and in Run 3 (Figure 7), all the parameters were correct and the column performance was excellent. All effluents were below 0.01 g Pu/ ℓ , lower than those of the 50-ml column. Resin capacity was 40 g Pu/ ℓ , with a peak concentration of 49.6 g Pu/ ℓ in the eluate.

Calcium was reduced from 74,500 ppm in the feed to 1082 ppm in the heart-cut eluate. Potassium was reduced from 23,380 ppm to 4 ppm, and sodium was reduced from 16,610 ppm to 98 ppm. Iron followed plutonium as above, rising from 230 ppm in the feed to 315 ppm in the heart-cut eluate. Americium decontamination was slightly less than on the 50 ml column at 26.7 ± 4.0 .

Run 3 demonstrates validity of the Triple Coprocessing concept and shows that scaling up actually improves process performance. Such a system should work very well on a production scale in addition to giving a three-for-one bonus in process throughput compared to processing each residue individually.

Pyrochemical Residue Recovery

Tables 6 and 7 summarize the different conditions and results of this and previous studies^{1,5} for the recovery of Rocky Flats pyrochemical residues using chloride anion exchange. Other pyrochemical residues with high plutonium content, such as anode heel, should behave similarly to the ER scrapeout used in this study.

For sheer bulk throughput, the DOR salt process is superior, but very little plutonium is recovered.

Table 6. Chloride Anion Exchange Processing of Pyrochemical Residues

Residue Processed	DOR Salt (g/ℓ)	ER Salt (g/ℓ)	ERSO (g/ℓ)	HCl (M)	Total Cl ⁻ (M)	Resin Capacity Pu/ ℓ (g)
DOR Salt ⁵	400	-	-	3.0	8.1	20
ER Salt ¹	-	53	-	6.3	6.7	30
ER+DOR	179	115	-	3.0	7.1	30
ERSO+DOR	360	-	20	4.5	8.4	43
ER+ERSO+DOR	228	92	20	3.3	7.3	34

ERSO: ER scrapeout.

ER+DOR: ER salt plus DOR salt.

ERSO+DOR: ER scrapeout plus DOR salt.

ER+ERSO+DOR: ER salt plus ER scrapeout plus DOR salt.

HCl: Concentration of HCl used to dissolve the residues.

Table 7. Chloride Anion Exchange Processing: Feed and Heart-Cut Concentrations

Residue Processed	Feed Pu (g/ℓ)	Heart-Cut Pu (g/ℓ)	Feed Fe (ppm)	Heart-Cut Fe (ppm)
DOR Salt ⁵	2.0	12	5	25
ER Salt ¹	5.0	28	10	94
ER+DOR	7.6	33	175	876
ERSO+DOR	11.6	41	36	170
ER+ERSO+DOR	17.6	46	130	598

Triple Coprocessing is superior for maximizing plutonium recovered in addition to minimizing hydrochloric acid requirements. However, ER salt/DOR salt coprocessing may offer some advantage in that substantial amounts of plutonium are recovered without the need for refluxing residues during dissolution.

As shown in Table 7, the higher the initial plutonium concentration of the feed, the higher the plutonium concentration of the heart-cut eluate. Table 7 also reiterates the fact that iron accompanies plutonium in each of these processes and should be minimized in the feed if there are no provisions made for removing it during subsequent processing.

DCHP Filtrate Recovery

DCHP Precipitation

Ordinarily, DCHP is precipitated from high concentrations of hydrochloric acid.⁶ However, to test an idea for using DOR residue salt as the chloride source, precipitations were made from such a medium. Five hundred grams of DOR salt dissolved per liter of 3.5M HCl, gave 2.29 g Pu/l, 0.00806 g Am/l, 0.219M HCl, and 9.48M total chloride. To increase the plutonium concentration and simulate a proposed production process, 61.3 ml of nitrate eluate (containing 80.38 g Pu/l, 8.50×10^{-3} g Am/l, 2.65M HNO₃, and <1 g chloride/l) together with 38.7 ml of chloride eluate (containing 13.59 g Pu/l, 0.00103 g Am/l, 3.78M HCl, and 3.98M total chloride) were added to 188 ml of the DOR salt solution. The chloride eluate was oxidized with 1:1 calcium hypochlorite. The combined solution contained 23.5 g Pu/l, 6.57×10^{-3} g Am/l, 1.65M total acid, and 7.56M total chloride.

To initiate precipitation, 15 ml of 4M CsCl in conc. HCl was added and the mixture digested for one hour. The precipitate was filtered through a 0.6-micron filter and washed with 30 ml of conc. HCl. Because the filtrate concentration was 10.63 g Pu/l, a second precipitation was performed using 318 ml of DOR salt solution instead of 188 ml to

increase the chloride concentration. This yielded a solution containing 18.3 g Pu/l, 7.07×10^{-3} g Am/l, 1.2M acidity, and 7.45M chloride. A 29-ml aliquot of 3M CsCl was used to initiate precipitation. The change was somewhat successful with the second run giving a filtrate plutonium concentration of 5.70 g/l. These two runs will be referred to as DCHP-1 and DCHP-2, respectively.

DCHP-1 gave 8.1 g of solid after drying at 150 °C for 4 hrs. At a theoretical concentration of 0.3332 g Pu/g, the yield was only 42.2%. DCHP-2 performed somewhat better, giving 12.6 g, a 68.9% yield. Thermogravimetric analysis showed that both precipitates contained <0.1% water. Because the Rocky Flats analytical laboratories had no standards for analyzing DCHP, 1.00 g of the material was dissolved in 10 ml of 1M HCl and analyzed by Atomic Absorption Spectroscopy for calcium, iron, and nickel. DCHP-1 contained 1210 ppm Ca, 627 ppm Fe, and 22 ppm Ni. DCHP-2 contained 168,850 ppm Ca, 847 ppm Fe, and 22 ppm Ni. Both results are corrected to parts per million DCHP solid. Because of the high losses of plutonium to the filtrate and the possibly high concentrations of calcium in the DCHP (perhaps resulting in a hygroscopic precipitate), this method is not recommended for DCHP preparation for MSE usage.

Filtrate Chloride Anion Exchange

Because solubility of DCHP exceeds current discard levels for plutonium even at higher chloride concentrations,^{7,8} chloride anion exchange is necessary to recover the plutonium. After overnight (17 hr) oxidation with 2.5:1 calcium hypochlorite, the filtrates from DCHP-1 and DCHP-2 were pumped through the 50-ml anion exchange column. Figure 8 and Table 8 show that excellent results were obtained at 5 ml/min flow rates. The elution peaks are offset because the DCHP-1 filtrate had less than half the volume of that of DCHP-2. In both cases, effluents are very low in plutonium and are discardable. Resin capacities are also excellent--42.0 g Pu/l for DCHP-1 and 51.3 g Pu/l for DCHP-2, both based on the feed.

Table 8. Chloride Anion Exchange of DCHP Filtrate from DOR Salt Solution

Run	Solution	Vol. (ml)	Pu (g/l)	Pu (%)	Am (g/l)	HCl (M)	Cl ⁻ (M)
DCHP-1	Feed	200	10.5	100	0.00570	2.40	7.39
	Effluent	200	0.000289	0.00	0.00304	3.80	7.43
	Wash	50	0.000315	0.00	0.00440	2.90	6.94
	Eluate	200	9.39	89.5	0.00087	2.48	2.65
	Heart-cut	40	45.02	85.8	0.00375	4.30	4.74
DCHP-2	Feed	450	5.70	100	0.00591	2.20	6.97
	Effluent	450	0.000732	0.01	0.00432	2.66	7.44
	Wash	50	0.00286	0.01	0.00479	2.01	7.56
	Eluate	200	9.91	77.3	0.00088	2.55	2.67
	Heart-cut	40	46.50	72.5	0.00383	4.40	4.91

Americium decontamination factors were about 10 because of the limited wash volume. Although the bulk of the chloride in the filtrate was supplied by DOR residue salt in these runs, chloride anion exchange would be expected to perform as well if the chloride were supplied by HCl, as demonstrated below.

Laboratory-Scale Simulation of Production Operation

In the course of this work, a plan was developed to integrate production of DCHP with the processing of pyrochemical residues because both require chloride-resistant equipment. Using the Kepner-Tregoe decision-making process⁹ resulted in the choice of chloride anion exchange processing of DOR residue salts in the new pyrochemical residue processing facility being built in the Rocky Flats plutonium recovery facility. One of the major criteria was bulk throughput, and this process was a clear choice in this category in addition to being at an acceptable level of development and producing small waste volumes per kilogram of residue processed.

This choice allows preparation of DCHP by substitution of its precipitation for that of plutonium(III) oxalate if the plutonium in the DOR salts is supplemented by dissolution of "non-spec" plutonium oxide in hydrochloric acid plus fluoride. Non-spec oxide is chosen because of its availability

Table 9. Impurity Analysis of Non-Spec Oxide. All results in ppm (W)

LECO[®] Carbon Analysis:

C 14955

Atomic Absorption Spectrometry Results:

Fe 5800 K 1400

Emission Spectrometry Results:

Ta 250 W <10

Zr <10

Photographic Emission Spectrometry Results:

Al	2500	B	<1
Be	5	Ca	5000
Cr	250	Cu	250
Ga	5000	Mn	100
Mo	5	Ni	250
Pb	<2	Si	2500
Sn	5	Ti	<10

and high concentration of plutonium. Table 9 shows an analysis of the oxide used in this study. Precipitation of DCHP offers some decontamination from impurity elements¹⁰ so this should be an acceptable feedstock. The chloride eluate and the dissolved oxide are then combined and precipitated with cesium chloride. The DCHP is filtered and dried; then the filtrate, along with more dissolved DOR salt, is recovered by chloride anion exchange. The cycle is then repeated.

Consequently, this process was demonstrated on the laboratory scale using proportions estimated to give sufficient DCHP for production usage in MSE. Using procedures developed previously,⁵ 400 g DOR salt/l of 3M HCl was dissolved and passed through the 50-ml column after oxidation. A working resin capacity of 12 g Pu/l was used for both the DOR salt and the combined DOR salt plus filtrate because production-scale tests of chloride anion exchange showed this capacity. Figure 9 and Table 10 show excellent performance was obtained. The eluate head-cut and the reconditioner were combined and analyzed. These solutions would be recycled through dissolution of more DOR salt. A combination of 75 ml of reconditioner and 40 ml of head-cut produced a plutonium concentration of

Table 10. Simulation of Production-Scale
DOR Salt/DCHP Filtrate Recovery Process

Run	Solution	Vol. (mℓ)	Pu (g/ℓ)	Pu (%)	Am (g/ℓ)	HCl (M)	Cl ⁻ (M)
DOR	Feed	300	1.78	100	0.00159	1.00	7.64
Salt	Effluent	300	0.000273	0.02	0.00132	2.00	6.98
	Wash	200	0.000234	0.01	0.00041	5.88	7.36
	Eluate	190	5.63	105.4	0.00048	5.11	6.52
	Heart-cut	50	11.00	103.0	0.00093	4.00	6.85
DOR	Feed	260	2.09	100	0.00699	3.10	6.77
Salt+	Effluent	260	0.00130	0.06	0.00542	4.04	6.80
DCHP	Wash	200	0.0104	0.38	0.00171	6.68	7.56
Filt.	Eluate	200	2.97	109.4	0.00127	4.40	3.76
	Heart-cut	50	11.55	106.3	0.00504	4.19	4.12

0.0437 g/ℓ, 1.09×10^{-5} g Am/ℓ, 5.0M acidity, and 4.91M total chloride. The heart-cut eluate volume was deliberately increased to capture most of the eluate plutonium and to eliminate the tail-cut. The small amount of material remaining on the resin is recoverable in the reconditioner.

Next, 8.6 g of non-spec oxide at 0.8023 g Pu/g was dissolved in 55 mℓ of boiling conc. HCl plus 0.1M CaF₂ for one hr. Off-gasses were scrubbed with 6M NaOH. The solution was cooled, its volume returned to 55 mℓ with conc. HCl, and filtered through a 1-micron filter. The resulting solution contained 98.0 g Pu/ℓ, 0.0698 g Am/ℓ, 7.2M acidity, 8.04M total chloride, 8444 ppm Ca, 53 ppm Ni, and 588 ppm Fe. An undissolved residue weighing 1.86 g after drying (21.6% of oxide weight) remained on the filter. Such residues would be recycled into the next dissolution in a production process.

The DCHP was precipitated by combining 40 mℓ each of dissolved oxide and 11 g Pu/ℓ chloride eluate from the DOR salt processing, oxidizing with 0.05M sodium nitrite, and adding 1.5 g CsCl/g Pu in 40 mℓ of conc. HCl. The precipitate was digested for 30 min, filtered through a 0.6-micron filter, and washed with 10 mℓ of conc. HCl. The filtrate volume was 120 mℓ and contained 2.85 g Pu/ℓ, 0.0168 g Am/ℓ, 7.4M acidity, and 7.25M total chloride. After drying in a muffle furnace for

three hours at 150 °C, the DCHP weighed 11.86 g. Analysis showed the DCHP contained 0.3217 g Pu/g and 3.32×10^{-5} g Am/g, for a yield of 87.5%. Based on the filtrate, the yield was 92.2%, in fair agreement. Thermogravimetric analysis showed the DCHP contained <0.1% water. Atomic Absorption Spectrophotometry of the DCHP showed 50 ppm Ca, <22 ppm Ni, and 793 ppm Fe.

Subsequently, 80 mℓ of the filtrate was combined with 180 mℓ of dissolved DOR salt, complexed with 0.025M AlCl₃, oxidized with 0.05M sodium nitrite overnight, and passed through the column. Figure 9 and Table 10 show excellent results for this test as well. Effluents were well below discard level and only 0.44% of the plutonium was lost. Although the americium decontamination factor is only about 10, this should be adequate.

The test was concluded at this point. In actual production, more oxide would be dissolved and combined with the eluate from filtrate recovery to continue the cycle. To prevent excessive buildup of iron (which is expected to follow the plutonium through the cycle), the eluate should be precipitated periodically as plutonium(III) oxalate instead of DCHP. After calcination, the resulting oxide should be recovered using nitrate-based ion exchange, which is selective against the iron. The test described above confirms the validity of a flowsheet that would allow the recovery of hundreds of kilograms of DOR salt per year as well as production of sufficient DCHP for MSE.

SUMMARY

These studies show that chloride anion exchange coprocessing is useful and effective for recovering plutonium from the pyrochemical residues DOR salt, ER salt, and ER scrapeout. With control of plutonium(IV) disproportionation established by using 2M acidity, discardable effluents can be obtained with resin capacities of 30 g Pu/ℓ or greater. In addition, heart-cut plutonium concentrations of 30 g/ℓ or higher can be obtained.

Furthermore, laboratory-scale simulations show that chloride anion exchange can be used to recover

above-discard plutonium in filtrates resulting from precipitation of Cs_2PuCl_6 , which will be used in the MSE process. These tests demonstrate that DOR residue salts can be recovered simultaneously, yielding discardable effluents and that the eluates can be converted into DCHP along with dissolved plutonium oxide.

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ILLUSTRATIONS

(Figures 1 Through 9)

FIGURE 1. ER Scrapeout Coprocessing at 2M Acidity. Flow rate = 2.5 ml/min.

FIGURE 2. Solubilities of NaCl, KCl, and CaCl₂ in 2.0M HCl as Determined by Titration

FIGURE 3. ER Salt Coprocessing at 2M Acidity. Flow rate = 2.5 ml/min.

FIGURE 4. Triple Coprocessing at 2M Acidity. Flow rate = 2.5 ml/min.

FIGURE 5. Triple Coprocessing at 2M Acidity.
Limited feed volume. Flow rate = 2.5 ml/min.

FIGURE 6. One-Liter-Scale Triple Coprocessing at 2M Acidity.
Effect of omission of AlCl_3 and of low chloride in the wash solution.

FIGURE 7. One-Liter-Scale Triple Coprocessing at 2M Acidity.
Chloride in the wash solution and AlCl_3 at proper concentrations.

FIGURE 8. Chloride Anion Exchange of Filtrate from Precipitation
of Cs_2PuCl_6 (DOR Salt Medium). Flow rate = 5.0 ml/min.

FIGURE 9. Laboratory-Scale Simulation of Production Operations: Chloride Anion Exchange Coprocessing of DOR Residue Salt and of DCHP Filtrate Combined with DOR Residue Salt (HCl Medium). Flow rate = 5.0 ml/min.

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