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EVALUATION OF ANION EXCHANGE RESINS FOR PROCESSING PLUTONIUM-NEPTUNIUM RESIDUES

Chemistry Research and Development

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James D. Navratil and Robert G. Leebl

ABSTRACT

An anion exchange process was developed to process miscellaneous residues of plutonium plus 0.5 weight percent neptunium to allow prompt return of the plutonium to a plutonium recovery process. Several macroreticular anion exchange resins were compared to Dowex® 1-X4 for the process. Dowex 1-X4 showed the best performance for the plutonium (III)-neptunium(IV) separation.

INTRODUCTION

A process was needed to recover plutonium from miscellaneous plutonium-neptunium (Pu-Np) residues at Rocky Flats. The plutonium-neptunium residues contained 0.5 weight percent (wt %) neptunium. The residues were generated from Lawrence Livermore Laboratory-Nevada Test Site events, where the neptunium was used as a radiochemical diagnostic tracer.

An ion exchange process was evaluated to process the residues. Macroreticular strong-base and weak-base anion exchange resins were compared to gel-type Dowex 1-X4 resin for the separation process. This comparison was made because of reported advantages of the weak-base macroreticular resins over gel-type (microreticular) resins for neptunium purification. These advantages include improved thorium decontamination, sharper neptunium elution band, and fivefold lower resin cost.[1] Higher actinide loading and faster elution were reported for strong-base macroreticular resins.[2]

EXPERIMENTAL PROCEDURE

Materials

Ferrous sulfamate $[Fe(SO_3NH_2)_2]$ was supplied as a 3M solution from the Shepherd Chemical Company.[*] All other chemicals were reagent grade and were used without further purification.

The mixed actinide solutions were prepared by dissolving mixed oxides in 12.5M HNO_3 (nitric acid)-0.1M HF (hydrofluoric acid). After dissolution, the solutions were filtered, and a stoichiometric amount of aluminum nitrate $[Al(NO_3)_3]$ was added to complex the fluoride ion. Dilution of the stock mixed-actinide solutions was usually made with 0.35M HNO_3.

Weak-base Amberlite® IRA-93 and strong-base Amberlite IRA-900 macroreticular ion-exchange resins were obtained from Rohm and Haas[†] in the chloride form. Dowex® MSA-1, a strong-base macroreticular resin manufactured by Dow Chemical, U.S.A., also was supplied in the chloride form. All macroreticular resins were 20-50 mesh beads.

Prior to use, all resins except Dowex 1-X4 were re-screened and converted from

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[*] Shepherd Chemical Company, 4900 Beech Street, Cincinnati, Ohio.

[†] Rohm and Haas Company, Independence Mall West, Philadelphia, Pennsylvania.

the chloride to the nitrate form with 7$\underline{M}$ HNO_3. Dowex 1-X4 gel resin (macroreticular, 50-80 mesh beads) was supplied in the nitrate form. The resins were checked by microscope for broken or cracked beads prior to use.

Wash solutions for the ion exchange experiments consisted of 7$\underline{M}$ HNO_3-0.2$\underline{M}$ $Fe(SO_3NH_2)_2$ or 5$\underline{M}$ HNO_3-0.66$\underline{M}$ $Al(NO_3)_3$-0.2$\underline{M}$ $Fe(SO_3NH_2)_2$.

Equipment and Procedure

Several ion exchange resins were compared for actinide separations on laboratory-scale columns. The resin bed dimensions were 1.7-cm diameter, 20-cm length for Runs B to E and 1.0-cm diameter, 15-cm length for Runs A and F. The feed being investigated was loaded simultaneously onto a column of each of the four different conditioned resins at a flow rate of approximately 2 $ml \cdot min^{-1} \cdot cm^{-2}$. After loading, the resins were washed with wash solution and then eluted with 0.35$\underline{M}$ HNO_3. Samples of the effluent, wash, and eluate streams were taken periodically and analyzed.

The large-scale anion exchange scheme involved loading neptunium(IV) from a plutonium-neptunium feed solution onto a 15-cm diameter by 76-cm-high column of Dowex 1-X4 from a 5$\underline{M}$ HNO_3-0.66$\underline{M}$ $Al(NO_3)_3$-0.2$\underline{M}$ $Fe(SO_3NH_2)_2$ feed. The plutonium that sorbed on the ion exchange resin was removed from the resin by extended washing with a 5$\underline{M}$ HNO_3-0.66$\underline{M}$ $Al(NO_3)_3$-0.2$\underline{M}$ $Fe(SO_3NH_2)_2$ solution. The neptunium was eluted with 0.35$\underline{M}$ HNO_3.

Analysis

Plutonium concentration was determined radiometrically except for $\geq$10 grams per litre of plutonium solutions, which were analyzed by X-ray fluorescence. The neptunium concentration was determined by radiometric pulse-height analysis. This determination followed separation of the plutonium by an ion exchange or solvent extraction procedure.

The iron(II) normality in ferrous sulfamate was determined by a volumetric ceric sulfate titration. Nitric acid concentrations were determined by acid-base titrations.

RESULTS AND DISCUSSION

Evaluation of Anion Exchange Resins

Macroreticular strong-base (Dowex MSA-1 and Amberlite IRA-900) and weak-base (Amberlite IRA-93) anion exchange resins were compared to a gel-type resin (Dowex 1-X4) for plutonium-neptunium separations. Laboratory-scale runs involved the loading of neptunium from a plutonium(III)-neptunium(IV) feed solution onto four resins simultaneously from either 7$\underline{M}$ HNO_3 or 5$\underline{M}$ HNO_3-0.66M $Al(NO_3)_3$ feed solutions containing 0.2$\underline{M}$ [$Fe(SO_3NH_2)_2$].

Ferrous sulfamate was used by itself as the reducing agent; it reduces Pu(VI) and Pu(IV) to Pu(III), and it reduces Np(VI) and Np(V) to Np(IV). The use of hydrazine to help stabilize the reducing conditions are not permitted in the process because of hydrazine's reactivity. Use of 5$\underline{M}$ HNO_3-0.66$\underline{M}$ $Al(NO_3)_3$-0.2$\underline{M}$ $Fe(SO_3NH_2)_2$ instead of 7$\underline{M}$ HNO_3-0.2$\underline{M}$ $Fe(SO_3NH_2)_2$ feed media provided the most stable separation conditions. The lower acidity prevented significant oxidation [<1% Pu(IV)] of plutonium within one day, and the increased nitrate concentration from $Al(NO_3)_3$ maintained maximum sorption of neptunium(IV). Each of the lab-scale experiments was completed within several hours.

The resins were compared for neptunium breakthrough, elution, and plutonium(III) washing behavior. Table 1 shows the relative resin order of increasing neptunium concentration in the ion column effluent (ICE) for the resins tested. When high plutonium concentrations were present in the feed (Run A), the neptunium concentration was less in the ICE for the macroreticular resins; however, for lower plutonium feed concentrations, the neptunium levels were lowest for the gel resin (Dowex 1-X4). Apparently this is due somewhat to the loading of plutonium(IV), present in equilibrium with Pu(III), in addition to neptunium(IV). Increasing plutonium breakthrough capacities for macroreticular resins was observed with an increase in plutonium feed concentrations.[3] Neptunium breakthrough was <10% (i.e., neptunium concentration in the ICE divided by neptunium concentration in feed = 0.1) for all experiments except Run A (see Appendix I).

For the resins tested, Table 2 shows the relative resin order of increasing neptunium concentration in the wash solutions. (Appendix I shows the actual concentrations.) Since the removal of plutonium(III) requires large volumes of wash solution, the concentration of neptunium in the wash effluent is an important factor in selection of a resin. Results show that the level of neptunium in the wash effluent was lowest for Dowex 1-X4 and very high for the weak-base macroreticular resin (Amberlite IRA-93).

Figure 1 shows the washing profile for plutonium(III) on the anion exchange resins. The difference between the two runs (A and F) can be attributed to the different size columns (bulk column volume of 11.8 versus 45.4 ml), and the different wash solutions. Amberlite IRA-93 gave superior performance over the other resins in relation to plutonium(III) removal by washing. Dowex MSA-1 gave the poorest washing behavior, but it was not much worse than Dowex 1-X4. The results of three other runs (B-D) gave the same washing order as shown in Figure 1.

The neptunium elution data on the resins are shown in Table 3. Complete elution data were obtained on only four of the experiments. The majority of the results shows that the neptunium elution order on the resins was Amberlite IRA-900 > Amberlite IRA-93 > Dowex MSA-1 > Dowex 1-X4 (slowest). As with the plutonium (III) washing results, there are no great differences between the elution behavior of the resins.

In summary, based on the lowest neptunium concentration observed in the ICE and wash, Dowex 1-X4 was superior to the macroreticular resins. This advantage of the gel resin outweighed the better washing and elution characteristics of the macroreticular resins, especially since washing and elution differences were not large. Other batches of some of the resins could give variations in performance. This has been observed by other investigators.[4] The possibility of this variation and its effect should be evaluated prior to large-scale application of any separation process.

Demonstration of the Recovery Process

Three successful demonstration runs of the ion exchange process were made on large-scale equipment. The neptunium(IV) was loaded onto a 15-cm-diameter by 76-cm-high column of Dowex 1-X4 (50-80 mesh) from a 5$\underline{M}$ HNO_3-0.66$\underline{M}$ $Al(NO_3)_3$-0.2$\underline{M}$ $Fe(SO_3NH_2)_2$ feed. Most of the nonsorbable plutonium(III) was allowed to pass through the column in the ICE. The remainder of the plutonium was removed from the resin by extended washing with a 5M HNO_3-0.66M $Al(NO_3)_3$-0.2M $Fe(SO_3NH_2)_2$ solution.

Plutonium in the resultant ICE and wash stream was adjusted to the tetravalent species with sodium nitrate, and the resulting solution was returned to the waste stream for purification by a second ion exchange process. Additional neptunium decontamination of the plutonium was also achieved during the second ion exchange step. The neptunium loaded on the column during the first ion exchange step was eluted with 0.35M HNO_3 and was either recycled or precipitated with 7M potassium hydroxide (KOH), calcined, and stored.

Results of the demonstration runs are shown in Table 4. A large amount of plutonium(III) was removed in the ICE of the first run compared to the second run (53 versus 8 percent). A lower concentration of plutonium in the feed in the first run apparently was responsible for this larger amount. Because of equipment problems, both runs had to be terminated before complete plutonium removal could be achieved by washing. Complete washing was accomplished in the third run, and half the plutonium followed the ICE – apparently because of the larger volume of feed processed.

The large volume of feed (7 column volumes) processed in the third run apparently caused the increase in neptunium concentration in the ICE and wash. The average neptunium concentration in the combined washes and ICE for the other two runs was approximately 0.3 milligram per litre. This was acceptable for return to the waste stream via plutonium purification by anion exchange technology. During the three runs, 63, 75, and 98 percent of the plutonium in the residues was separated and returned to the waste stream. Neptunium losses to the plutonium were not critical since the objective was prompt recovery of the plutonium. Neptunium and plutonium remaining on the columns were eluted with 0.35M HNO_3 and will be reprocessed in subsequent runs on a routine basis.

CONCLUSIONS

Several macroreticular anion exchange resins were compared to Dowex 1-X4 (microreticular resin) for processing miscellaneous residues of plutonium and 0.5 wt % neptunium. Based on the lowest neptunium concentrations observed in the effluents, Dowex 1-X4 was superior to the macroreticular resins. This advantage of the microreticular resin outweighed the better washing and elution characteristics of the macroreticular resins, especially since washing and elution differences were small.

Three successful demonstration runs of the ion exchange process were made on large scale equipment. The developed process effectively separated plutonium (III) and neptunium(IV) from the mixed actinide residues, which allowed prompt return of the plutonium to a plutonium recovery process.

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TABLES

TABLE 1. Relative Resin Order of Increasing Neptunium Concentration in the Ion Column Effluent (ICE)

	Feed		
Run	Pu (g/l)	Np (g/l)	Relative Resin Order for Np in ICE
A	8.3	0.16	900 < 93 < 1 < 1-X4
B	7.6	3.7	900 < 1-X4 < 1 < 93
C	4.3	2.9	1-X4 < 900 < 1 < 93
D	4.8	0.92	1-X4 < 900 < 1 < 93
E	3.3	0.66	1-X4 < 93
F	1.5	0.039	1-X4 < 1 < 900 < 93

Feed media was 5$\underline{M}$ HNO_3-0.66$\underline{M}$ $Al(NO_3)_3$-0.2$\underline{M}$ $Fe(SO_3NH_2)_2$ except for Runs B and D, which were 7$\underline{M}$ HNO_3-0.2$\underline{M}$ $Fe(SO_3NH_2)_2$ feed media.

TABLE 2. Relative Resin Order of Increasing Neptunium Concentration in Wash Solutions

Run	Wash Solution[a]	Relative Resin Order for Np in the Wash
A	II	1-X4 < 1 < 900 < 93
B	I	1-X4 < 900 < 1 < 93
C	II	1-X4 < 900 < 1 < 93
D	I	1-X4 < 1 ≈ 900 < 93
E	II	1-X4 < 93
F	II	1-X4 < 900 < 1 < 93

---

a. Wash solutions:

I — $7\underline{M}$ HNO_3 + $0.2\underline{M}$ $Fe(SO_3NH_2)_2$.

II — $5\underline{M}$ HNO_3 + $0.66\underline{M}$ $Al(NO_3)_3$ + $0.2\underline{M}$ $Fe(SO_3NH_2)_2$

TABLE 3. Neptunium Elution of the Resins

	Column Volumes of $0.35\underline{M}$ HNO_3 Required To Elute 90% of the Neptunium			
Description	Dowex 1-X4	Amberlite IRA-900	Dowex MSA-1	Amberlite IRA-93
A-Eluate	7	5	6	5
B-Eluate	7	4	6	5
D-Eluate	7	4	6	5
E-Eluate	6	-	-	5

TABLE 4. Results of Process Demonstration Runs

	Cumulative Column Volumes[a]	Plutonium C/C_o[b]	Neptunium (mg/l)
ICE[c] (Run 1) Wash	2.2	0.53	0.28
	4.1	0.59	0.48
	6.4	0.63	0.15
ICE[d] (Run 2) Wash	2.3	0.08	0.31
	4.5	0.16	0.81
	6.5	0.22	0.14
	8.5	0.31	0.28
	10.3	0.55	0.16
	12.5	0.75	0.26
ICE[e] (Run 3)	7	0.47	0.73
	15	0.84	0.90
	17	0.98	0.41

---

a. Column volume = 13.9 litres; flow rate = 10 litres per hour.

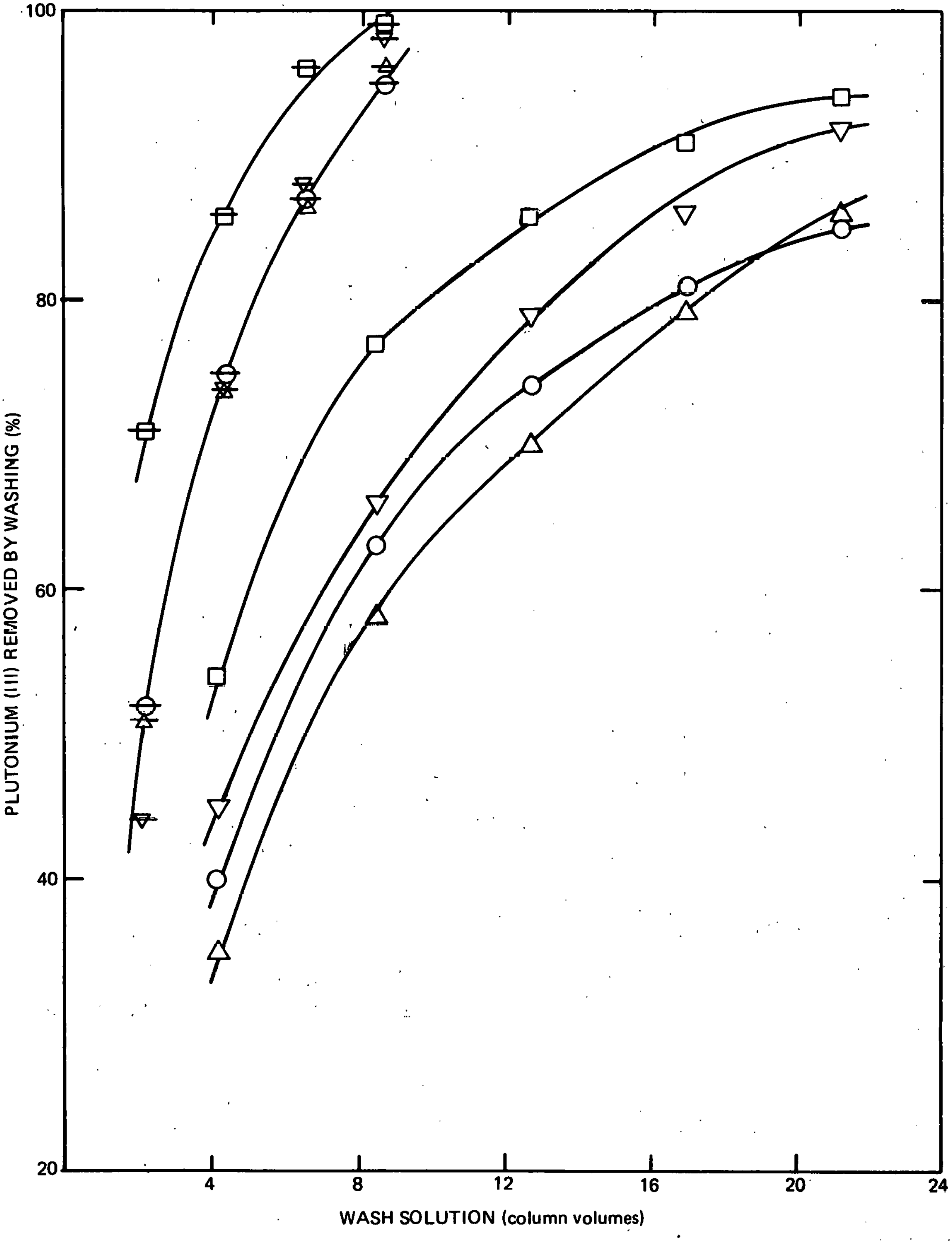
b. C/C_o = concentration of plutonium in ion column effluent (ICE) or wash streams divided by plutonium concentration in feed.

c. ICE using feed containing 2.35 grams per litre of plutonium and 33.9 milligrams per litre of neptunium.

d. ICE using feed containing 7.25 grams per litre of plutonium and 61.9 milligrams per litre of neptunium.

e. ICE using feed containing 6.94 grams per litre of plutonium and 34.6 milligrams per litre of neptunium.

FIGURE 1. Plutonium(III) Washing Profile on Several Resins



APPENDIX I

Neptunium Concentration and Neptunium-to-Plutonium Ratios in Ion Column Effluent and Wash

	Fed to Columns			Dowex 1-X4		Amberlite IRA-900		Dowex MSA-1		Amberlite IRA-93	
Description	Pu (mg/ml)[a]	Np (mg/ml)[a]	Wash[b]	Np (mg/l)	Np/Pu (ppm)	Np (mg/l)	Np/Pu (ppm)	Np (mg/l)	Np/Pu (ppm)	Np (mg/l)	Np/Pu (ppm)
A-ICE	26	0.5	---	76	11,000	24	6,800	72	12,000	43	8,700
A-ICE	62	1.2	---	110	15,000	62	11,000	97	15,000	95	14,000
A-ICE	97	1.9	---	99	13,000	62	11,000	94	15,000	86	12,000
A-WASH	--	---	2.1	4.1	1,800	16	3,200	7.9	2,800	14	3,300
A-WASH	--	---	11	0.58	950	4.0	2,700	3.0	3,000	3.8	5,200
A-WASH	--	---	19	---	---	---		2.2	4,100	0.28	1,100
B-ICE	8	4	---	0.11	20	0.02	300	0.13	200	0.30	500
B-WASH	--	---	6.5	0.06	40	0.10	70	0.36	300	0.78	400
C-ICE	5	3	---	0.02	500	0.03	300	0.26	200	0.44	200
C-WASH	--	---	6.6	0.02	70	0.22	500	7.6	18,000	13	14,000
D-ICE	21	4	---	<0.53	50	1.6	400	2.3	910	5.8	1,200
D-WASH	--	---	8.8	0.20	60	4.4	1,400	3.7	1,200	7.4	2,500
E-ICE	15	3	---	0.03	30	---	---	---	---	2.0	1,300
E-WASH	--	---	8.8	0.75	850	---	---	---	---	31	36,000
F-ICE	23	0.6	---	<0.44	<600	1.3	1,900	1.0	2,000	5.0	6,000
F-ICE	54	1.4	---	2.1	2,800	1.7	2,100	1.3	1,800	8.2	8,000
F-WASH	--	---	6.4	0.30	420	0.52	930	0.87	1,800	2.5	11,000
F-WASH	--	---	15	0.11	240	---	---	1.6	6,300	1.5	31,000

a. Milligrams of plutonium or neptunium fed to columns per millilitre of resin.

b. Bulk column volumes of wash solution fed to columns.