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PROCESSING OF ^{238}Pu AND ^{237}Np WITH MACROPOROUS ANION EXCHANGE RESIN

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PREPARED FOR THE U. S. ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(07-2)-1

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PROCESSING OF ^{238}Pu AND ^{237}Np WITH MACROPOROUS ANION EXCHANGE RESIN

by

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ABSTRACT

"Dowex" MSA-1 macroporous anion exchange was found to be superior to "Dowex" 1 gel-type resin for separation and purification of ^{238}Pu and ^{237}Np . Higher actinide loading per unit of resin is attained, and elution is accomplished in smaller volume. Cross-contamination of the products is lower with macroporous resin, and higher processing rates can be attained. Process performance with different lots of macroporous resin is more consistent than generally obtained with different lots of "Dowex" 1 resin because the high porosity of the macroporous resin facilitates ionic diffusion. The chemical, thermal, and radiolytic stabilities of macroporous and gel-type resins are similar.

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INTRODUCTION

Many kilograms of ^{238}Pu and ^{237}Np have been purified at the Savannah River Plant in the past decade by anion exchange in a nitrate system.¹ The anion exchange/nitrate process has been used to separate neptunium and plutonium from radioactive fission products and from each other.^{2,3} A major problem in plant operation has been variable separation efficiency with different batches of "Dowex"* 1 resin. Conventional resin property measurements such as moisture content and capacity have failed to determine the reason for variation.

The rate determining step in ion exchange is ion diffusion through the polymer matrix.⁴ Since the anion exchange/nitrate process is based on the sorption of bulky hexanitrate ions of the tetravalent actinides, $\text{M}(\text{NO}_3)_6^{2-}$, it was postulated that macroporous anion exchange resin with discrete pores and large surface area might facilitate diffusion and sorption.

This report describes the comparison of macroporous resin, "Dowex" MSA-1, with gel-type resin, "Dowex" 1, for several plant applications: sorption and decontamination of plutonium and neptunium, partitioning of plutonium and neptunium, concentration of neptunium and plutonium, and recovery of plutonium and neptunium from waste streams. The stability of both resins to heat and gamma radiation was also examined.

A previous report⁵ described improved separation of ^{238}Pu and ^{237}Np with small particle gel- and macroporous-type resins in pressurized columns.

*Registered trademark of Dow Chemical, Midland, Michigan.

ANION EXCHANGE PROCESSES AND RESINS

In the present anion exchange process,^{1,2} Np-Pu-Al cermet targets are dissolved in concentrated nitric acid, and the resulting solution is processed through four anion exchange cycles in low-head, gravity-flow columns.

- Cycle 1. *Decontamination.* The dissolver solution is made ~8M in total nitrate, and plutonium and neptunium are adjusted to the tetravalent states by adding hydrazine and ferrous sulfamate and heating to ~50°C. The Pu(NO₃)₆²⁻ and Np(NO₃)₆²⁻ complexes that are formed are subsequently cosorbed on anion exchange resin. After fission products are removed by washing with ~8M HNO₃-0.005M KF, the Np⁴⁺ and Pu⁴⁺ are coeluted with dilute HNO₃.
- Cycle 2. *Partitioning.* The eluate from Cycle 1 is adjusted to ~8M nitrate with concentrated HNO₃, and the hexanitrate anionic complexes are produced by the same valence adjustment used in Cycle 1. After cosorption, Pu³⁺ is selectively eluted with 5.4M HNO₃-0.05M Fe(NH₂SO₃)₂-0.05M N₂H₄; Np⁴⁺ is then eluted with dilute HNO₃.
- Cycle 3. *Concentration.* The plutonium solution from Cycle 2 is adjusted to ~8M nitrate with strong HNO₃ and heated to yield Pu(NO₃)₆²⁻, which is sorbed and eluted as described in Cycle 1. Neptunium from Cycle 2 is similarly concentrated.
- Cycle 4. *Frame Waste Recovery.* Raffinates and washes from Cycles 1-3 are combined with the oxalate filtrates from the precipitation step subsequent to Cycle 3, and residual neptunium and plutonium are cosorbed, washed, and coeluted as in Cycle 1.

Currently "Dowex" 1, a gel-type resin with low surface area and no discrete pores, is used in the plant. While some batches of this resin have performed well, other batches have required additional process cycles to provide adequately purified products. In general, gel-type resins have slow ionic diffusion due to small pore openings, and inefficient separation and slow elution sometimes result.

Macroporous resin differs from gel-type resin in that macroporous resin is copolymerized under special conditions to produce tough, spherical beads with discrete pores and large surface area; larger pores facilitate more rapid diffusion of the hexanitrate complexes of neptunium and plutonium.

Figure 1 shows scanning electron photomicrographs of "Dowex" MSA-1 (macroporous) resin, magnified 11000X; "Amberlite"* IRA-900 (macroporous) resin, magnified 11000X; and "Dowex" 1 (gel-type) resin, magnified 21000X. The porosity of the macroporous resins is very pronounced; no such porosity is evident in the gel-type resin at twice the magnification.

a. Macroporous "Dowex" MSA-1

b. Macroporous "Amberlite" IRA-900

FIGURE 1. Scanning Electron
Photomicrographs of Anion
Exchange Resin

c. Gel-Type "Dowex" 1-X2

* Registered trademark of Rohm and Haas Company, Philadelphia, Pa.

EQUIPMENT AND MATERIALS

Anion exchange tests with simulated dissolver solutions were performed in a 125 ml glass column, 0.75 in. ID x 17 in. long, with a coarse glass frit to support the resin. The column was equipped with a side-arm reservoir to facilitate resin replacement. A solution metering pump with 0 to 20 ml/min capacity fed solutions directly to the column.

All ion exchange resins tested were polystyrene-divinylbenzene resins with quaternary ammonium groups, classified as strongly basic. "Dowex" MSA-1 (macroporous) resin was tested at 20 to 50 mesh and narrower fractions within 50 to 100 mesh. The 20 to 50 mesh was bead form; smaller sizes were granular. Granular resin was obtained by grinding and hydraulically grading bead-form macroporous resin (see Appendix); only bead-form gel-type resin was tested. One partitioning test each on granular 50 to 60 mesh "Amberlite" IRA-900 and IRA-904 macroporous resins was conducted for comparison. The 40 to 60 mesh "Dowex" 1-X2 resins tested consisted of samples of batches used in plant processing. Although this resin contains 2% divinylbenzene, additional methylene bridging is induced during manufacture, giving mechanical properties similar to those of a 3% divinylbenzene resin.

The NO_3^- -form resins were kept in 0.25M HNO_3 when not in use. Before separation tests, the resin bed was preconditioned with $\sim 7\text{M}$ HNO_3 to ensure that the $\text{M}(\text{NO}_3)_6^{2-}$ complexes would be sorbed.

Ferrous sulfamate for neptunium and plutonium valence adjustment was prepared by reacting a sulfamic acid solution with iron powder at $<55^\circ\text{C}$ and filtering to remove unreacted iron.

All test were performed in either a glove box or a shielded cell.

RESULTS

CYCLE 1 - DECONTAMINATION

Five tests of macroporous resin in Cycle 1 (decontamination) are summarized in Table I. Performance of 20 to 50 mesh, bead-form resin (as received) was investigated in Tests 1 and 2; actinides were high in the fission product wash. Actinide breakthrough in Test 1 was attributed to the high mass flow during loading, 0.022 g actinide/(min-cm²), which caused non-uniform loading and low sorption of actinides. Mass flow for Test 2 was ~0.013 g actinide/(min-cm²), ~50% greater than present plant operation. Actinide loading was 64 g/l of resin, almost twice that for Test 1, but actinide breakthrough was still higher than desired.

In Test 3, conditions were similar to Test 2 except 50 to 70 mesh granular resin (from ground and graded 20 to 50 mesh beads) was used. Yields were high and purity was excellent.

In Test 4, 40 to 60 mesh bead-form resin was used; this resin was graded from the nominal 20 to 50 mesh macroporous beads used for Tests 1 and 2. The actinide loading rate was ~50% higher than currently used; loading was 67 g/l of resin. Sorption and wash effluents contained <0.01% each of neptunium and plutonium. >99% of the actinides was eluted with 2 bed volumes of 0.35M HNO₃ at 2 ml/(min-cm²), about double current process flow rates.

Test 5 used 250 ml of plant dissolver solution as feed. Feed composition is given in Table II. The same 40 to 60 mesh bead-form resin used in Test 4 was used in Test 5, but the bed volume was 25 ml instead of 125 ml. Recovery was excellent, and removal of the fission products was similar to that with "Dowex" 1; overall, >99.9% of the gamma activity was removed. Elution was excellent.

TABLE I

Cosorption and Coelution of ^{238}Pu and ^{237}Np
at Ambient Temperature with Macroporous Resin

Resin Bed: Tests 1-4 0.75 in. ID, 17 in. long, 125 ml "Dowex" MSA-1 resin
Test 5 0.30 in. ID, 17 in. long, 25 ml "Dowex" MSA-1 resin

Feed: Tests 1-4 Simulated dissolver solution: 4.0M HNO_3 - 1.2M $\text{Al}(\text{NO}_3)_3$; no fission products; standard valence adjustment
Test 5 Plant dissolver solution - standard valence adjustment

Test	Resin Form and Mesh Size	Feed, g		Flow, ml/(min-cm ²)			Loading Rate, mg/(min-cm ²)	Actinide in Effluent, % feed			
		Np	Pu	Feed	Wash	Eluate		Sorption		Wash	
								Np	Pu	Np	Pu
1	Beads, 20-50	2.2	1	7.5	7.5	2.0	22	0.9	0.5	2	0.4
2	Beads, 20-50	4.1	1	2.6	6.2	2.0	13	0.3	0.2	8	1.5
3	Gran., 50-70	3.5	1	2.1	4.2	2.0	9.3	<0.01	<0.01	0.6	0.3
4	Beads, 40-60	4.4	1.1	2.6	5.0	2.0	15	<0.01	<0.01	0.5	0.3
5	Beads, 40-60	0.66	0.16	2.6	4.7	2.0	8.5	0.08	<0.01	0.4	0.2

TABLE II

Composition of Plant Dissolver Solution

Total NO_3^-	7.8M	^{103}Ru	1.4×10^{10} dpm/ml
H^+ (free acid)	4.3M	^{106}Ru	5.0×10^{10} dpm/ml
Al^{3+}	0.72M	^{137}Cs	4.3×10^8 dpm/ml
^{238}Pu	0.64 g/l	^{144}Ce	7.8×10^9 dpm/ml
^{237}Np	2.64 g/l	^{95}Zr	1.5×10^{10} dpm/ml
		^{95}Nb	1.7×10^{10} dpm/ml
		^{243}Am	2.5×10^8 dpm/ml

CYCLE 2 - PARTITIONING

Table III and Figures 2 and 3 summarize partitioning tests with both macroporous and gel-type resins. Tests 1 through 9 evaluated macroporous resin; particle size and flow of solutions were varied. Tests 10-12 evaluated gel-type resin for comparison.

In Test 1, 20 to 50 mesh, bead-form resin was used as received. The unacceptably high neptunium content of the plutonium product is attributed to: 1) high mass flow during loading, which caused low actinide sorption in the resin and consequently a short stripping section; and 2) maldistribution of flow, probably from the large distribution of resin particle size. (Acceptable purity levels are defined as <1% neptunium in plutonium product and <1% plutonium in neptunium product.)

TABLE III

Partitioning of ^{238}Pu and ^{237}Np at Ambient Temperature

Test	Resin Form and Mesh Size	Feed, g		Flow, ml/(cm ² -min)			Product Purity Ratio, %	
		Pu	Np	Sorption	Elution		Np/Pu	Pu/Np
1	Bead, 20-50	1.0	2.3	6	2.5	2	2.51	0.33
2	Granular, 50-70 ^a	1.0	3.7	2.8	2.5	2	0.18	0.06
3	Granular, 50-70 ^a	1.1	3.6	6	5	4	0.05	0.03
4	Granular, 50-70	1.3	3.7	2.8	2.5	2	0.01	0.10
5	Bead, 50-60	1.2	4.2	3	2.5	2	0.25	0.08
6	Granular, 20-30	1.2	2.7	2.8	2.5	2	0.28	0.06
7	Granular, 30-40	1.2	2.9	2.8	2.5	2	0.15	0.06
8	Granular, 50-60 ^b	c	c	2.8	2.5	2	c	c
9	Granular, 50-60 ^b	1.4	4.0	3	2.5	2	0.09	0.09
10	Bead, 40-60 ^d	1.3	4.1	2.8	2.5	2	3.72	0.26
11	Bead, 40-60 ^d	0.8	2.4	2.8	2.5	2	3.11	0.12
12	Bead, 40-60 ^d	1.2	4.2	2.8	2.5	2	0.18	3.15

a. Same resin used in both Tests 2 and 3.

b. Macroporous resins "Amberlite" IRA-904 and IRA-900 were used for Tests 8 and 9, respectively.

c. Neptunium and plutonium were not partitioned because sorption capacity was very low.

d. "Dowex" 1-X2 resin; all other tests used macroporous resin.

Tests 2 and 3 evaluated 50 to 70 mesh, granular-form resin obtained from the same lot of resin used in Test 1. In Test 3, separation efficiency was similar to that in Test 2, even though flows were double. Both the partition flow [5 ml/(min-cm²)] and elution flow [4 ml/(min-cm²)] were twice the optimum flow used with "Dowex" 1 gel-type resins. A second lot of macroporous resin, ground and graded to 50 to 70 mesh, was used for Test 4. Separation was similar to that in Tests 2 and 3 although the apparent actinide capacity decreased from ~80 g/l of resin to ~70 g/l of resin (visually estimated). Some channeling occurred in Test 4, decreasing the apparent capacity. The 50 to 60 mesh, bead-form resin used in Test 5 was hydraulically graded from the same lot used for Test 4 and also gave excellent results. Tests 6 and 7 were with two additional lots of granular "Dowex" MSA-1 resin and gave excellent partitioning although average particle size was appreciably larger than in previous granular resin tests. The actinide load was lower than in other tests, but actinide capacity was still ~70 g/l of resin.

Tests 7 and 8 evaluated "Amberlite" IRA-900 and IRA-904 macroporous resins ground and graded to 50 to 60 mesh. Performance of IRA-900 was similar to "Dowex" MSA-1. IRA-904, more highly crosslinked than IRA-900, had only ~20% of the capacity of MSA-1 resin for neptunium and plutonium under standard sorption conditions and was not tested further.

For comparison, Tests 10 through 12 evaluated three different lots of "Dowex" 1-X2 gel-type resin. It was planned to use the same loading and flows for these tests as for macroporous resin. However, since resin capacity was much lower in Test 11, loading was discontinued when the actinide band was approximately the same length as for Test 10 (12 inches). Capacity in Test 11 was 26 g actinide/l resin compared to 40 in Tests 10 and 12, and up to 80 for macroporous resins. The loading for Test 11 was only 3.2 g of actinides, compared to 5.4 g of actinides for Tests 10 and 12. Plutonium elution was very good in Tests 10 and 11, and acceptable neptunium product was obtained. Neptunium levels in both plutonium products were unacceptably high (>1%); however, acceptable plutonium product could probably be obtained if actinide loading or sorption and elution flows were decreased. In Test 12 there was apparently very poor diffusion within the resin beads, and plutonium was not eluted adequately in almost twice the bed volumes of partition wash required for most macroporous resin tests. Although the plutonium product was within specifications, this performance is not acceptable in large-scale processing because of increased

FIGURE 2. Elution of ^{238}Pu from Macroporous Resin

FIGURE 3. Elution of ^{238}Pu from Gel-Type Resin

time cycles and larger solution volumes. Tests 10 through 12 point out the significant variation in performance of different batches of gel-type resin.

Neptunium elution was more efficient from macroporous than from gel-type resin. Visually, elution was complete with all resins in 1.4 to 1.7 bed volumes. However, losses to tailing fractions were ten times greater for gel-type resins, so that recovery was ~98% for gel-type versus 99.8% for macroporous resins. Gassing in columns caused by alpha radiolysis of solutions was less pronounced with macroporous resin, resulting in lower pressure drop.

CYCLE 3 - CONCENTRATION

Concentration of neptunium and plutonium (individually) by sorption and elution at 25°C was efficient with a bed (0.75 in. ID x 16 in. long) of 50 to 70 mesh "Dowex" MSA-1 anion exchange resin.

~70 g of Np/l of resin was loaded by feeding 5 g Np/l in 7.5M HNO₃ at ~0.03 g/(min-cm²). The effluent/feed neptunium ratio at the end of loading was 0.005. Despite some channeling in the bottom 2 inches of resin, the sorption effluent contained <0.1% of the neptunium fed for sorption. More than 99.5% of the neptunium was eluted in 1.6 bed volumes of 0.3M HNO₃ at 4 ml/(min-cm²); a 1-bed volume fraction contained 99.5% of the neptunium at ~70 g Np/l.

The same resin bed was used for concentration of plutonium (~81% ²³⁸Pu). About 65 g Pu/l resin was loaded by feeding 5.5 g Pu/l in 7.5M HNO₃ at 0.033 g/(min-cm²). The effluent/feed plutonium ratio at the end of loading was 0.008. Channeling was again observed in the bottom two inches, but the sorption effluent contained <0.1% of the plutonium fed for sorption. More than 99.7% of the plutonium was eluted in 2.5 bed volumes of 0.3M HNO₃ at 4 ml/(min-cm²). A 1-bed volume fraction of the product contained 96.5% of the plutonium at ~63 g Pu/l.

The concentration of neptunium and plutonium (actinide per liter resin) attained on "Dowex" MSA-1 resin at the mass loading rate tested and at ambient temperature is approximately twice the actinide loading attained with "Dowex" 1 or "Dowex" 21K resins for the same conditions. Also, the actinides are eluted more effectively at ambient temperature from macroporous resins than from gel resin; for the test described with macroporous resin, the elution flow rate was more than twice the rate normally used for gel resins.

CYCLE 4 - FRAME WASTE RECOVERY

120 bed volumes of simulated frame waste recovery feed (Table IV) was pumped at $7.5 \text{ ml}/(\text{min}\cdot\text{cm}^2)$, 2.5 times the current plant flow, to a 125-ml bed of 30 to 40 mesh beads of "Dowex" MSA-1 resin. The column was then washed with three bed volumes of 8M HNO_3 at the same flow. Sorption effluent and washes contained $\sim 0.1\%$ of the plutonium and $\sim 0.2\%$ of the neptunium. $>99\%$ of the neptunium and plutonium was eluted in 2.5 bed volumes of 0.35M HNO_3 at $2 \text{ ml}/(\text{min}\cdot\text{cm}^2)$.

The processing rate in Frame Waste Recovery is limited by the flow attainable with the available liquid head in the gravity feed system and the resin particle size, 30 to 50 mesh "Dowex" 1-X3. This test indicates that increased flow rate, which would probably be attainable with larger particle size macroporous anion resin, would not deleteriously affect losses.

TABLE IV

Composition of Frame Waste Recovery Feed

HNO_3	7M	$\text{H}_2\text{C}_2\text{O}_4$	$4 \times 10^{-3}\text{M}$
$\text{Al}(\text{NO}_3)_3$	0.11M	$\text{Fe}(\text{NH}_2\text{SO}_3)_2$	0.055M^a
KF	0.01M	$\text{N}_2\text{H}_4 \cdot \text{HNO}_3$	0.045M^b
$\text{Hg}(\text{NO}_3)_2$	$4 \times 10^{-4}\text{M}$	^{238}Pu	0.02 g/l
Ascorbic Acid	$5 \times 10^{-4}\text{M}$	^{237}Np	0.06 g/l

a. Most of the iron is Fe^{3+} after feed adjustment.

b. Much of the hydrazine reacts before sorption.

RESIN STABILITY

The effect of radiolytic and thermal degradation on the ion exchange capacity and stability of macroporous and gel-type resins was studied. Macroporous and gel-type resins have the same matrix and were found to have similar radiation and thermal stability. The properties of macroporous resin were determined to be consistent with safe plant operation.

Strong base capacity, determined by conventional acid-base titration techniques,⁶ was determined on representative lots of gel-type ("Dowex" 1-X2) and macroporous ("Dowex" MSA-1) resins before and after ⁶⁰Co irradiation (Table V). The decrease in strong base capacity for the two resins was similar.

The specific volume of representative samples of both resin types was also determined before and after ⁶⁰Co irradiation. "Dowex" 1-X2 decreased in volume, but the macroporous resin volume did not change because its higher crosslinkage increases stability (Table V).

Differential thermal analysis of both resins in the nitrate form demonstrated similar thermal stability; both resins char slowly and do not deflagrate or explode. Exothermic and endothermic reactions occur at the same temperatures for both.

TABLE V

Exchange Capacity of Unirradiated and Irradiated Macroporous and Gel-Type Anion Exchange Resins
Initial Volume = 5.0 ml

<i>Exposure, rads</i>	<i>Strong Base Capacity, meq/ml</i>		<i>Final Volume, ml</i>	
	<i>"Dowex" MSA-1</i>	<i>"Dowex" 1-X2</i>	<i>"Dowex" MSA-1</i>	<i>"Dowex" 1-X2</i>
0	0.74	0.90	5.0	5.0
1 x 10 ⁸	0.73	0.77	5.0	4.6
2 x 10 ⁸	0.66	0.63	5.0	4.4
3 x 10 ⁸	0.58	0.57	5.0	4.1

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APPENDIX

RESIN GRADING

Variation in resin particle size distribution can result in high operating pressure and flow maldistribution. These effects are reduced by using particles in a narrow size range, which ensures maximum void volume in the packed resin.

Ion exchange resin is difficult to size with wire sieves. The resins do not flow freely even when dry, and drying causes bead fracturing, particularly with gel-type resins. Resin particles can be separated into size fractions by utilizing their settling velocities in fluid media. A solid particle settles in a fluid at a velocity that is dependent on its size and density as well as on the fluid properties. A particle released into a fluid having a density less than that of the particle will approach a constant velocity that is referred to as the Stokes settling velocity, or the terminal velocity. The terminal velocity of a sphere is defined as⁷

$$V_t = ga^2(\rho_p - \rho_f)/18\mu$$

where

V_t = terminal velocity

g = acceleration due to gravity

a = particle diameter

ρ_p, ρ_f = densities of the particle and fluid,
respectively, and

μ = viscosity

In hydraulic grading, the solid particle is subjected to an upward fluid velocity. If the fluid velocity is greater than the terminal velocity of the particle, the solid particle will be carried along with the fluid stream. Sized fractions can be obtained by varying the flow rate. This type of hydraulic grading was employed to grade resins used in this study. Large particle-size macroporous resin graded quickly (~2 days required); gel-type beads required about one week.

The grading system consisted of five glass columns, 1-1/2 in., 2 in., 2-1/2 in., 3 in., and 4 in. in diameter, 40 in. long with conical bottom sections 7 in., 8 in., 9 in., 11 in., and 16 in. long, respectively; a positive displacement pump delivering 385 ml/min at full stroke; and a surge tank to reduce flow variation due to pumping. "Teflon"* stopcocks at the top and bottom of the columns permitted resin loading and unloading. The stopcocks on the column side arms permitted individual column isolation during loading and unloading procedures. A schematic diagram of the grading system is shown in Figure A-1.

Small quantities of resin were placed in the 1-1/2 in. column. Larger amounts (1 lb maximum) were placed in the surge tank and displaced to the columns. The flow rate was varied to obtain an adequate size distribution in the columns. Grading efficiency was determined by sampling the resin and measuring the particle size and distribution with an optical comparator.

FIGURE A-1. Schematic Diagram of Grading Columns

* Registered trademark of Du Pont.

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