Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Solvent Extraction of Plutonium (IV) Polymer by Dihexyl-N, N-Diethyl-carbamoylmethylphosphonate (DHDECMP)

Anthony C. Muscatello[a]; James D. Navratil[a]; Milton E. Killion[a]
[a] Rockwell International Rocky Flats Plant, Golden, Colorado

To cite this Article Muscatello, Anthony C. , Navratil, James D. and Killion, Milton E.(1983) 'Solvent Extraction of Plutonium (IV) Polymer by Dihexyl-N, N-Diethyl-carbamoylmethylphosphonate (DHDECMP)', Separation Science and Technology, 18: 14, 1731 — 1746
To link to this Article: DOI: 10.1080/01496398308056124
URL: http://dx.doi.org/10.1080/01496398308056124

SEPARATION SCIENCE AND TECHNOLOGY, 18(14&15), pp. 1731-1746, 1983

Solvent Extraction of Plutonium (IV) Polymer by Dihexyl-N, N-Diethylcarbamoylmethylphosphonate (DHDECMP)

ANTHONY C. MUSCATELLO, JAMES D. NAVRATIL, and MILTON E. KILLION

ROCKWELL INTERNATIONAL
ROCKY FLATS PLANT
P. O. BOX 464
GOLDEN, COLORADO 80402-0464

ABSTRACT

The bifunctional organophosphorus compound DHDECMP (dihexyl-N, N-diethylcarbamoylmethylphosphonate) is effective in the extraction of hydrolytic plutonium (IV) polymer from both 0.04 and 7.0M nitric acid. Stripping the polymer is difficult, even with hydrofluoric acid. However, 1.0M sodium carbonate is a very effective stripping agent. The extracted complex contains one to two molecules of DHDECMP per plutonium ion and the plutonium (IV) maintains a polymeric structure.

INTRODUCTION

The extraction chemistry of various carbamoylmethylphosphonates and related compounds is currently under investigation at the Rocky Flats Plant in support of actinide recovery process development and americium purification processes(1-3).

It has long been known that the presence of plutonium (IV) polymer in process streams leads to plutonium losses since ion exchange resins and most solvent extractants do not react with the polymer. Several years ago, Ockenden and Welch(4) studied the extraction of plutonium polymer with dibutylcarbitol, thenoyltri-

 0149-6395/84/1814-1731$3.50/0

fluoroacetone, tributylphosphate (TBP), and dibutylphosphate (DBP), and found that only the latter compound extracts polymeric plutonium. Biggers and Costanzo(5) and Dreze and Duyckaerts(6) also report the extraction of plutonium polymer by DBP. These appear to be the only previous references to successful liquid-liquid extraction of plutonium (IV) polymer.

We have investigated the extraction behavior of plutonium (IV) polymer with two neutral bifunctional organophosphorus compounds. Preliminary experiments indicate that, unlike TBP, DHDECMP and a related compound do extract plutonium (IV) polymer from nitric acid solutions. Possible mechanisms for this extraction will be discussed.

EXPERIMENTAL

Materials

Carbon tetrachloride and mineral acids were reagent grade materials. DHDECMP was obtained as a 63% pure material from Wateree Chemical Company, as a 84% pure material free from acidic contaminants from Bray Oil Company, and as a 98% pure material produced by purification of 84% material by a mercuric salt precipitation procedure described previously(7,8). OØD(IB)CMPO (octylphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide) was kindly supplied by E. P. Horwitz of the Argonne National Laboratory; its synthesis was described previously(9). TOPO (trioctylphophine oxide) was used as received from Kodak Laboratory Chemicals (>95% TOPO, <1% dioctylphosphoric acid).

Ferrous sulfamate was a 2.9M solution from Chemical Sales Company of Denver, Colorado. Hydroxylammonium nitrate was a 1.66M solution from Southwestern Analytical Chemicals, Inc. of Austin, Texas. Distilled, deionized water was used when required.

Fresh plutonium (IV) polymer was prepared by a procedure based on that of Ockenden and Welch(4). A stock plutonium nitrate solution (36.9 g/l, 0.978M HNO_3) purified by anion exchange techniques was obtained from Rocky Flats Plant production facilities. The plutonium stock also contained negligible amounts of americium (1.44×10^{-3} g/l) and iron (0.025 mg/l). A portion of the stock solution was diluted with water to obtain 0.04M HNO_3. This concentration of acid was chosen instead of 0.1M, as used previously(4), because initial dilution attempts appeared to disproportionate rather than polymerize plutonium (IV). Also, Costanzo, et al.(10), have shown that essentially all the plutonium (IV) is converted to the polymeric form after dilution to 0.04M HNO_3 after about 9 hours. The diluted solution was allowed to sit overnight to complete the conversion and was passed through a column of Dowex MSC-1 cation exchange resin (Dow Chemical Co.) (1 ml resin/10 ml solution) to remove any ionic plutonium. In those experiments in which the solution acidity was increased to 7M HNO_3 by adding concentrated HNO_3, the contacts with organic phases were completed within 20 minutes of the dilution so that conversion of the polymer to ionic plutonium was negligible(11,12).

Aged plutonium (IV) polymer was prepared in two ways. A polymer solution was prepared as described above and allowed to age at room temperature for 39 days. Also, a polymer solution was refluxed for 24 hours to simulate longer term aging(11).

Procedures

Distribution ratios (D) were determined using established procedures(13,14) except that vortexing times for plutonium (IV) polymer extractions were 1 minute, instead of 15 seconds, to ensure equilibrium since sampling occurred as soon as the phases disengaged. Preliminary experiments showed that 1 minute is sufficient to reach equilibrium. Equilibrations were carried out at ambient temperatures (25 ± 1 °C).

D-values were calculated by dividing the plutonium concentration in the organic phase by the plutonium concentration in the aqueous phase, or by dividing the initial aqueous plutonium concentration minus the final aqueous concentration by the final aqueous concentration (designated as "by difference").

Analytical Methods

The concentration of plutonium was determined by direct alpha counting of dried samples. The very low concentration of americium obtained after cation exchange did not interfere.

The presence of plutonium (IV) polymer and absence of ionic plutonium in both aqueous and organic phases was confirmed by UV-visible spectrophotometry using a Cary-14 spectrophotometer.

RESULTS AND DISCUSSION

Extraction of Plutonium (IV) Polymer

Table 1 lists the results of extraction of fresh and 39-day-old plutonium polymer from nitric acid by DHDECMP of different purities. OØD(IB)CMPO is included to compare a related bifunctional organophosphorus compound. TOPO is included as well. These extractions yielded easily separated phases and clean interfaces. The results show that DHDECMP and OØD(IB)CMPO extract plutonium (IV) polymer. Surprisingly, TOPO also extracts the polymer. This may be due to the presence of dioctylphosphoric acid, which probably would behave like dibutylphosphate.

The extent of extraction is the same within the error limits for the three DHDECMP purities, indicating that the impurities in the 84% and 63% pure materials are relatively unimportant to the extraction. Consequently, the 84% pure DHDECMP was used in further

TABLE 1

Extraction of Plutonium (IV) Polymer by DHDECMP and OØD(IB)CMPO (30 vol % in CCl_4)[a] and TOPO (0.1M) from 7.0M HNO_3. (Batch 1)

Extractant	D_{Pu} (Fresh Polymer)[b]	Mass Balance (%)	D_{Pu} (39 Days Old)[c]	Mass Balance (%)
DHDECMP (98% Pure)	18 ± 9	112	--	--
DHDECMP (84% Pure)	11 ± 4 (48 ± 2)[d]	96.4 (115)	270 (5.0)[d]	57.5 60.8)
DHDECMP (63% Pure)	24 ± 13	113	--	--
OØD(IB)CMPO (95% Pure)	11 ± 3	98.3	33[e] (1.0)[d,e]	27.4 (47.8)
TOPO	17 ± 1	89.0	71 ± 7[b]	13.7

a No correction applied for source purity
b Duplicate determinations
c Single determinations
d Aqueous Phase = 0.04M HNO_3
e 0.1M OØD(IB)CMPO

experiments because of better availability. The mass balances are acceptable given the tendency of plutonium (IV) polymer to sorb on all surfaces(4). The "Batch #" refers to separately prepared batches of plutonium (IV) polymer.

To determine whether some fraction of the plutonium (IV) polymer is inextractable, multiple contacts of fresh and 39-day-old polymer in 7M HNO_3 with DHDECMP were performed. Table 2 shows the results of these experiments. The distribution values of the single contacts indicate some difficulty in reproducibility in D_{Pu} between different batches of fresh polymer solution since they are much higher than the equivalent values in Table 1. In any

TABLE 2

Multiple Extractions of Plutonium (IV) Polymer in 7.0M HNO_3 with 30 vol % DHDECMP (84% Pure) in CCl_4. (Batch 2)

Procedure	Sample	[Pu], g/l	D_{Pu}
Single Contact (fresh polymer)	Organic	0.163	180
	Aqueous	8.85×10^{-4}	
	Organic	0.224	600
	Aqueous	3.75×10^{-4}	
Multiple Contacts (fresh polymer)	1st Organic	0.231	120*
	2nd Organic	5.70×10^{-4}	0.41*
	3rd Organic	6.76×10^{-4}	0.94*
	4th Organic	2.49×10^{-4}	0.52
	Final Aqueous	4.74×10^{-4}	-
Single Contact (39-day-old polymer)	Organic	0.299	270
	Aqueous	1.12×10^{-3}	
Multiple Contacts (39-day-old polymer)	1st Organic	0.402	62*
	2nd Organic	4.75×10^{-3}	2.7*
	3rd Organic	1.43×10^{-3}	4.5*
	4th Organic	2.50×10^{-4}	3.8
	Final Aqueous	6.66×10^{-5}	-

* Calculated by difference

case, the multiple extractions are successful in reducing the plutonium concentration to the 10^{-4} g/l range for 39-day-old polymer solutions. A single contact is sufficient for fresh polymer. However, the final distribution ratios after four contacts with fresh organic phase are much less than initial values, indicating the last one percent of the polymer is difficult to extract.

Stripping of Plutonium (IV) Polymer

Tables 3 and 4 show the results of using distilled water, ferrous sulfamate (0.1M), hydroxylammonium nitrate (0.05M), hydrofluoric acid (0.1M) and sodium carbonate (1.0M) to strip extracted

TABLE 3

Stripping of Fresh Plutonium (IV) Polymer from 30 vol % DHDECMP (84% Pure) in CCl_4. (Batch 3)

Stripping Agent	Sample	$[H^+]$, M	[Pu], g/l	D_{Pu}
Distilled Water	Initial AQ Contact	7.22	8.80×10^{-4}	150*
	1st Strip, AQ	1.12	7.64×10^{-3}	17*
	2nd Strip, AQ	0.17	8.50×10^{-4}	160*
	3rd Strip, AQ	0.09	3.53×10^{-4}	380*
	Final Organic		0.144	410
Ferrous Sulfamate, 0.1M	Initial AQ Contact	7.11	1.08×10^{-3}	270*
	1st Strip, AQ	1.27	3.63×10^{-3}	79*
	2nd Strip, AQ	0.21	2.29×10^{-2}	12*
	3rd Strip, AQ	0.15	2.41×10^{-3}	120*
	Final Organic		0.220	91
Hydroxylammonium Nitrate, 0.05M	Initial AQ Contact	7.11	1.03×10^{-3}	280*
	1st Strip, AQ	1.15	2.28×10^{-3}	130*
	2nd Strip, AQ	0.233	5.09×10^{-3}	56*
	3rd Strip, AQ	0.0798	1.79×10^{-3}	160*
	Final Organic		0.240	130
Hydrofluoric Acid, 0.1M	Initial AQ Contact	7.11	1.88×10^{-2}	14*
	1st Strip, AQ	1.10	1.07×10^{-2}	26*
	2nd Strip, AQ	0.196	4.30×10^{-2}	5.8*
	3rd Strip, AQ	0.00316	2.18×10^{-2}	12*
	Final Organic		0.240	11
Sodium Carbonate 1.0M	Initial AQ Contact	7.0	1.33×10^{-2}	300
	1st Strip, AQ	4.0×10^{-9}	0.379	0.015
	2nd Strip, AQ	1.0 (OH^-)	5.42×10^{-3}	0.017
	3rd Strip, AQ	1.0 (OH^-)	1.19×10^{-3}	0.062
	Final Organic		7.37×10^{-5}	--

* Calculated by difference.

TABLE 4
Stripping of 39-Day-Old Plutonium (IV) Polymer from 30 vol % DHDECMP (84% Pure) in CCl_4 by 0.1M Hydrofluoric Acid and 1.0M Sodium Carbonate. (Batch 4)

Initial $[HNO_3]$, M	Sample	$[H^+]$, M	[Pu], g/l	D_{Pu}
0.04 (0.1M HF)	Initial AQ Contact	0.10	0.105	12*
	1st Strip, AQ	0.10	0.480	1.6*
	2nd Strip, AQ	0.032	0.300	1.5*
	3rd Strip, AQ	0.020	0.200	1.3*
	Final Organic		0.0821	0.41
7.0 (0.1M HF	Initial AQ Contact	7.40	1.04×10^{-3}	690*
	1st Strip, AQ	1.46	0.120	4.9*
	2nd Strip, AQ	0.50	0.280	1.1*
	3rd Strip, AQ	0.10	0.0881	2.5*
	Final Organic		0.182	2.1
7.0 (1.0M Na_2CO_3)	Initial AQ Contact	7.30	1.61×10^{-3}	310*
	1st Wash, AQ**	1.2	2.47×10^{-3}	200*
	2nd Wash, AQ**	0.1	1.35×10^{-3}	370*
	1st Strip, AQ	1.3 (OH^-)	0.350	0.41*
	2nd Strip, AQ	1.5 (OH^-)	1.82×10^{-3}	79*
	Final Organic		3.96×10^{-4}	0.22

* Calculated by difference.
** Washed with water to remove excess acid.

polymer from 30 vol % DHDECMP in CCl_4. As might be expected, water alone is an extremely poor stripping agent for plutonium (IV) polymer since even ionic plutonium (IV) is difficult to strip from DHDECMP(15). Ferrous sulfamate and hydroxylammonium nitrate are also ineffective in stripping the plutonium (IV) polymer. Apparently, these two reducing agents are unable to reduce plutonium to the +3 oxidation state from the polymeric form.

On the other hand, fluoride ion is known to be useful in depolymerizing plutonium (IV) (12), and the results for hydrofluoric acid stripping shown in Tables 3 and 4 show HF to be more effective than the reducing agents. However, in no case did the

hydrofluoric acid strip out all the polymer. To determine whether this is due to a kinetic effect since only 1-minute contacts were used, 0.1M HF stripping with long contact times was performed. The data in Table 5 show that, after two washes with water to remove excess HNO_3, five minute contacts with 0.1M HF remove about one-third of the plutonium, but extending the contact time to 4.5 hr is no more effective. Thus stripping times between one and five minutes would be optimal.

TABLE 5

Effect of Contact Time on Stripping of Fresh Plutonium (IV) Polymer from 30 vol % DHDECMP (84% Pure) in CCl_4 by 0.1M Hydrofluoric Acid[a]. (Batch 5)

Procedure	Sample[b]		[Pu], g/l	D_{Pu}
Initial Contact	A.	AQ	1.36×10^{-2}	35[c]
(7.0M HNO_3)	B.	AQ	2.54×10^{-3}	190[c]
	C.	AQ	1.15×10^{-3}	430[c]
	D.	AQ	1.03×10^{-3}	480[c]
1st Distilled	A.	AQ	2.18×10^{-3}	220[c]
Water Wash	B.	AQ	5.06×10^{-3}	96[c]
	C.	AQ	2.14×10^{-3}	230[c]
	D.	AQ	3.19×10^{-3}	150[c]
2nd Distilled	A.	AQ	1.72×10^{-3}	280[c]
Water Wash	B.	AQ	2.42×10^{-3}	200[c]
	C.	AQ	1.28×10^{-3}	380[c]
	D.	AQ	1.47×10^{-3}	330[c]
0.1M HF Strip	A.	AQ	0.124	1.8
(5 min contact)		ORG	0.222	
	B.	AQ	0.117	2.3
		ORG	0.272	
0.1M HF Strip	C.	AQ	0.111	2.6
(4.5 hr contact)		ORG	0.292	
	D.	AQ	0.112	2.5
		ORG	0.284	

[a] Initial plutonium concentration = 0.494 g/l
[b] Four duplicate runs, designated A, B, C, and D.
[c] Determined by difference

Oddly enough, 0.1M HF appears to strip the aged polymer more easily than the fresh polymer (compare Tables 3 and 4). We cannot explain this behavior. However, the better stripping of aged polymer extracted from 0.04M HNO_3 as compared to that from 7M HNO_3 is probably caused by a higher effective concentration of fluoride ion, resulting from increased ionization of HF (pKa = 3.45) at the lower acidity.

Furthermore, Tables 3 and 4 show that 1.0M sodium carbonate is very effective in stripping polymer from DHDECMP, reducing the plutonium to the 10^{-4} g/l range for both fresh and aged polymer. Distilled water washes were used with the aged polymer to avoid the vial pressurization by carbon dioxide evolved by decomposition of carbonate by extracted nitric acid encountered with fresh polymer. The effectiveness of sodium carbonate may be due to the formation of anionic complexes between carbonate and plutonium(IV) polymer.

Mechanism of Extraction of Plutonium (IV) Polymer

Figure 1 shows the dependence of the extraction of fresh plutonium (IV) polymer from both 7.0M and 0.04M HNO_3 on the DHDECMP concentration. The curves indicate a complex behavior in which more than one extractable species exists in the organic phase. From 7.0M HNO_3, the dependence on DHDECMP concentration is approximately second power, gradually decreasing to about first power at the highest DHDECMP concentration. From 0.04M HNO_3, the dependence is about first power, decreasing to less than first power with increasing DHDECMP concentration.

In addition, Figure 1 shows the extraction changes from being essentially independent to somewhat dependent on nitric acid concentration with increasing DHDECMP concentration. The low dependence on nitric acid concentration is easy to understand

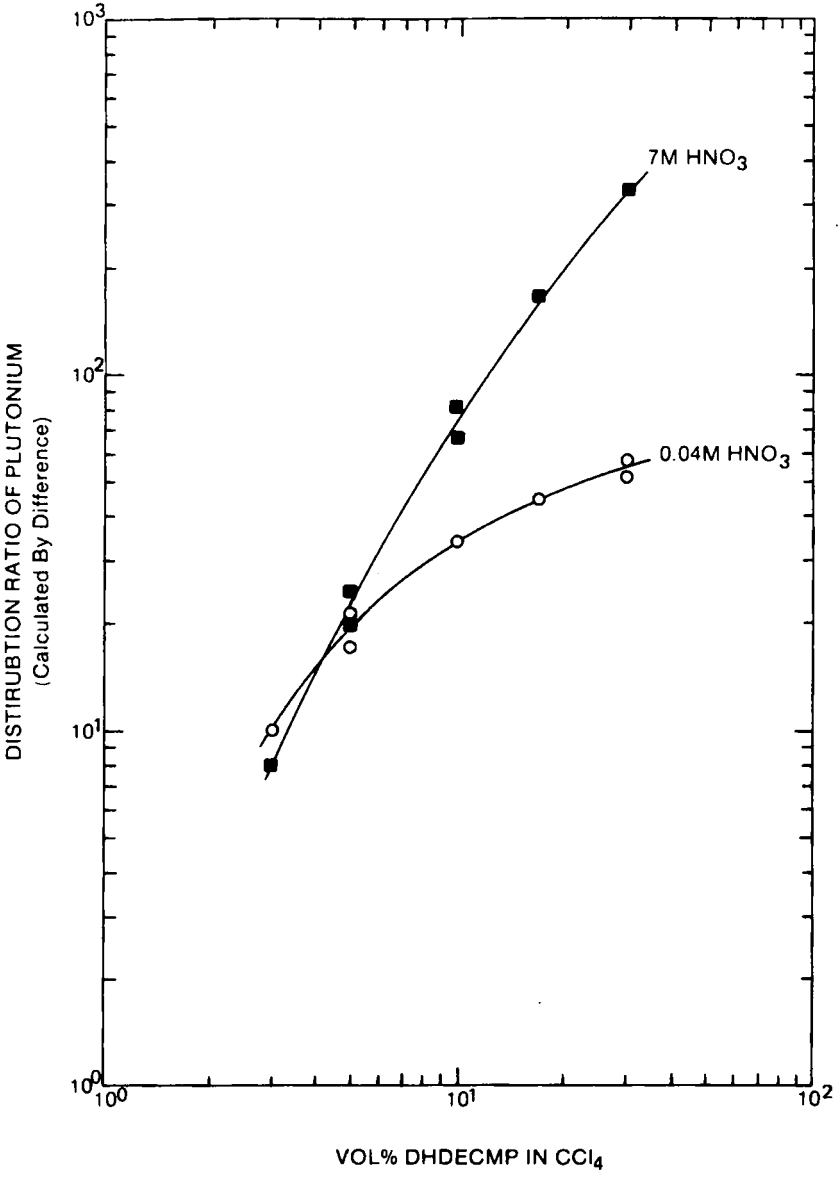

FIGURE 1. Distribution ratio of fresh plutonium (IV) polymer vs vol % DHDECMP (84% purity) in CCl_4. Aqueous phase = 0.04M or 7.0M HNO_3 as labeled. (Batch 6.)

since plutonium (IV) polymer is known the have only a small positive charge (0.15/plutonium ion)(12), so very little nitrate is needed to provide a neutral species.

The low dependence on nitric acid concentration is confirmed by the results shown in Figure 2. For extractions of fresh polymer with 30 vol % DHDECMP, D_{Pu} rises gradually with increasing nitric acid concentration. This shows that an apparent drop in D_{Pu} around 1M HNO_3 observed in stripping experiments with water (Table 3) is not significant. The extraction is very high, even from 0.04M HNO_3.

With such complex behavior it is not possible to write a detailed equation for the mechanism of extraction of fresh plutonium (IV) polymer by DHDECMP in CCl_4. For now, information about the mechanism must remain purely descriptive.

Figure 3 shows the results for similar studies of the dependence on DHDECMP concentration for the extraction of plutonium (IV) polymer aged by refluxing. The dependence on DHDECMP concentration is about first power for extraction from 7M HNO_3 and less than one-third power from 0.04M HNO_3. No mechanism can be proposed since third-phase formation and stable emulsions severely interfered with these extractions. For 0.04M HNO_3, the interfacial emulsions decreased from ~30% of the total volume of the two phases to a negligible amount of interfacial scum with increasing DHDECMP concentration. At the two highest DHDECMP concentrations, ~10% of the organic phase was a heavy, plutonium-rich second organic phase, but no second organic phase formed at lower DHDECMP concentrations. For 7M HNO_3, the interfacial emulsion increased from 10 to 60% of the total volume with increasing DHDECMP concentration, but no heavy second organic phases formed.

Spectrum of Extracted Polymer

The visible and near UV absorption spectrum of freshly prepared polymer extracted from 7.0M HNO_3 in 30 vol % DHDECMP in

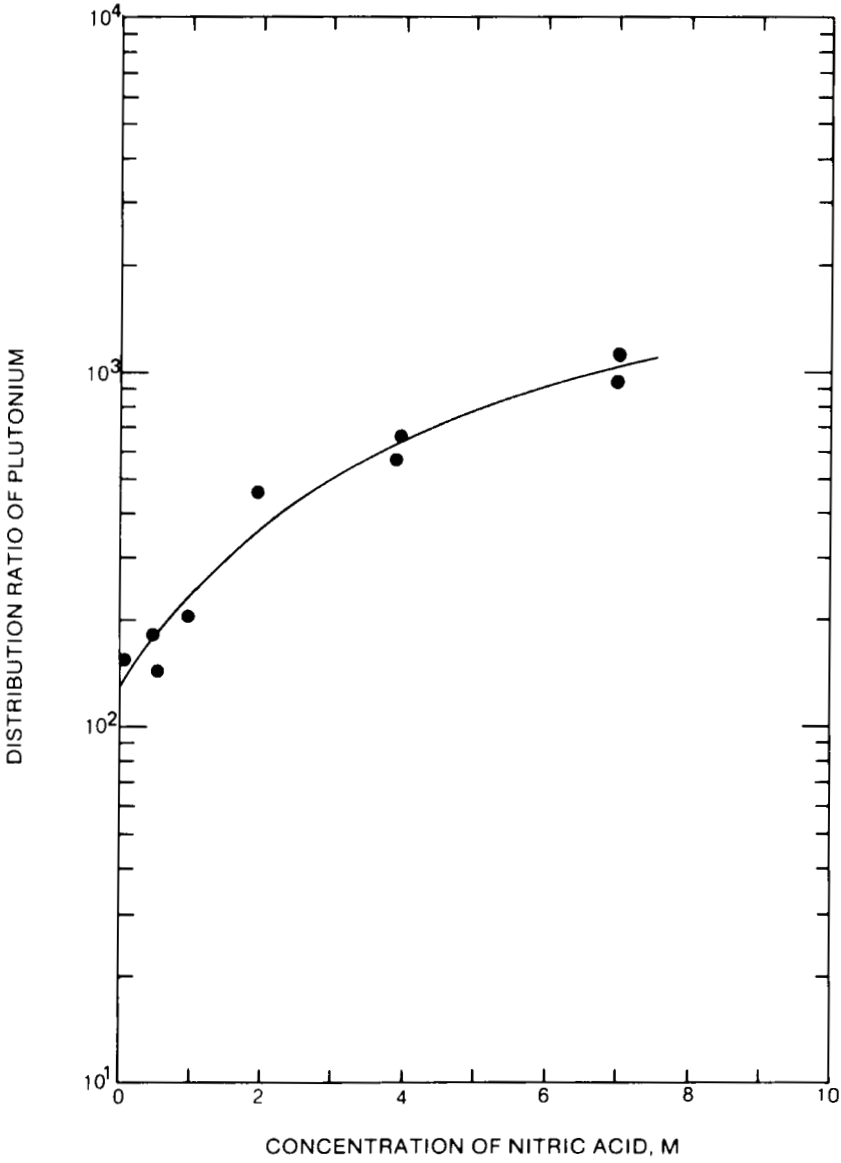

FIGURE 2. Distribution ratio of fresh plutonium (IV) polymer vs aqueous nitric acid concentration. Organic phase = 30 vol % DHDECMP (84% purity) in CCl_4. (Batch 7.)

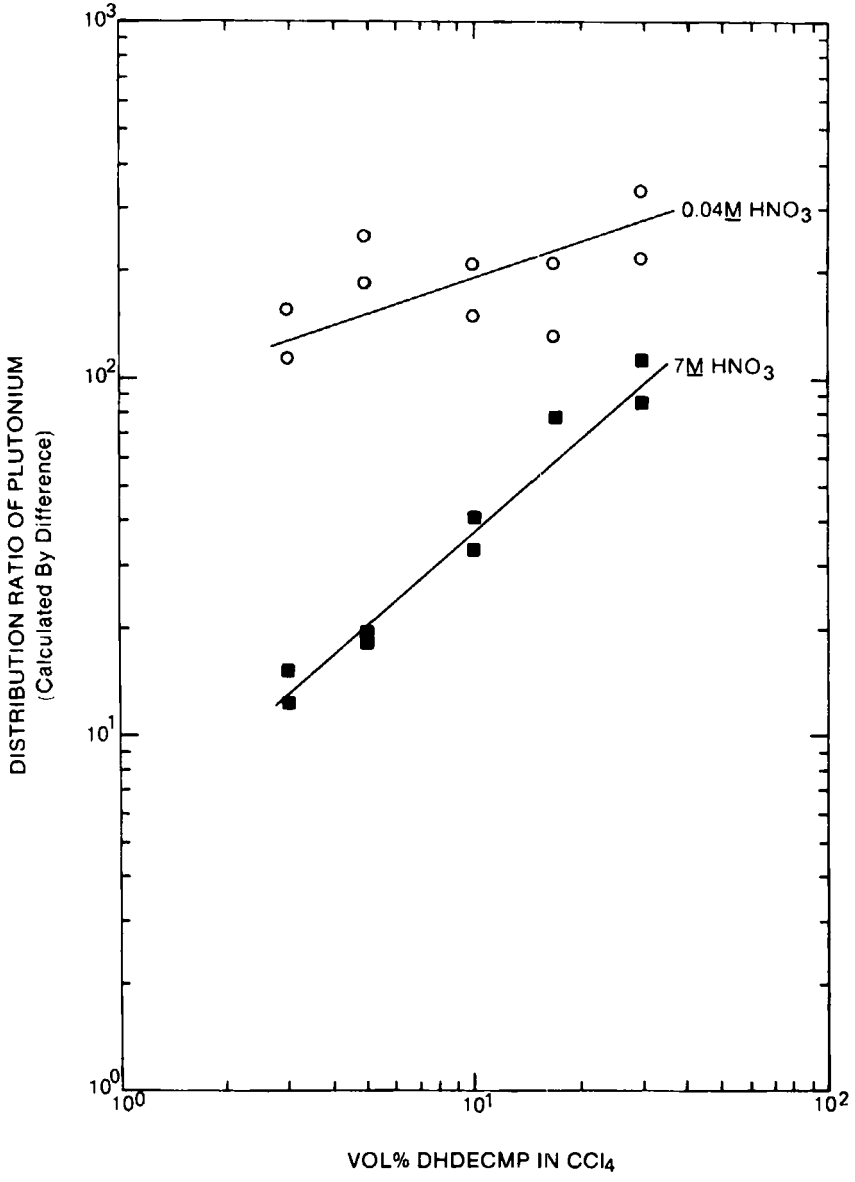

FIGURE 3. Distribution ratio of aged plutonium (IV) polymer vs vol % DHDECMP (84% purity) in CCl_4. Aqueous phase = 0.04M or 7.0M HNO_3 as labeled. (Batch 8).

CCl_4 shows that the plutonium (IV) remains in the polymeric form in the organic phase and does not revert to the ionic form. This observation is consistent with the difficulty in stripping the extracted polymer with reducing agents noted above and confirms visual observations of the distictive bright green color of plutonium (IV) polymer in the organic phases.

SUMMARY

Extractions of both fresh and aged hydrolytic plutonium (IV) polymer show that bifunctional organophosphorus extractants are effective in removing the polymer from nitric acid media. The extracted polymer is difficult to strip from DHDECMP. Only sodium carbonate is effective in stripping the polymer.

The extracted polymer complex probably contains a small amount of nitrate and one to two molecules of DHDECMP per plutonium ion, depending on the extractant concentration. The plutonium remains in a polymeric form in the organic phase.

Highly aged polymer has a very complicated behavior in these extraction systems, forming second organic phases and stable emulsions.

ACKNOWLEDGEMENTS

This work was performed under U.S. Government Contract DE-AC04-76DP03533, and the U.S. Government retains a prior nonexclusive, royalty-free license to publish, translate, reproduce, use, or dispose of the published form of the work, or allow others to do so for U.S. Government purposes.

REFERENCES

1. J. D. Navratil and G. H. Thompson, Nucl. Technol. 43, 136 (1979).

2. J. D. Navratil, L. L. Martella, and G. H. Thompson, in Actinide Separtations, (J. D. Navratil and W. W. Schulz, Eds.), American Chemical Society, Washington, D.C., 1980, p. 445.

3. W. I. Yamada, L. L. Martella, and J. D. Navratil, J. Less Common Metals 86, 211 (1982).

4. D. W. Ockenden and G. A. Welch, J. Chem. Soc. 1956, 3358.

5. R. E. Biggers and D. A. Costanzo, U.S. Atomic Energy Comm. Report, ORNL-TM-580, Oak Ridge, Tennessee, 1963.

6. Ph. Dreze and G. Duyckaerts, Euratom Report, EUR-436, Luxembourg, 1963 (Nuclear Science Abstract 18:5413).

7. N. C. Schroeder, L. D. McIsaac, and J. F. Krupa, U.S. Department of Energy Report, ENICO-1026, Idaho Falls, Idaho, 1980.

8. E. P. Horwitz, D. G. Kalina, and A. C. Muscatello, Sep. Sci. Technol. 16, 403 (1981).

9. E. P. Horwitz, D. G. Kalina, L. Kaplan, G. W. Mason, and H. Diamond, Sep. Sci. Technol. 17, 1261 (1982).

10. D. A. Costanzo, R. E. Biggers, and J. T. Bell, J. Inorg. Nucl. Chem. 35, 609 (1973).

11. D. A. Costanzo and R. E. Biggers, U.S. Atomic Energy Comm. Report, ORNL-TM-585, Oak Ridge, Tennessee, 1963.

12. J. M. Cleveland, The Chemistry of Plutonium, 2nd printing, American Nuclear Society, La Grange Park, Illinois, 1979, pp. 82-89.

13. J. D. Navratil and L. L. Martella, Sep. Sci. Technol. 16, 1147 (1981).

14. A. C. Muscatello, J. D. Navratil, and M. E. Killion, Solv. Extn. Ion Exch. 1, 127 (1983).

15. W. W. Schulz and L. D. McIsaac, U.S. Energy Research and Development Admin. Report, ARH-SA-263, Richland, Washington, 1977.