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

Degradation, Cleanup, and Reusability of Octylphenyl- *N, N'*-diisobutylcarbamoylmethyl Phosphine Oxide (CMPO) during Partitioning of Minor Actinides from High Level Waste (HLW) Solutions

J. N. Mathur; M. S. Murali; P. B. Ruikar; M. S. Nagar; A. T. Sipahimalani; A. K. Bauri; A. Banerji

To cite this Article Mathur, J. N. , Murali, M. S. , Ruikar, P. B. , Nagar, M. S. , Sipahimalani, A. T. , Bauri, A. K. and Banerji, A.(1998) 'Degradation, Cleanup, and Reusability of Octylphenyl- *N, N'*-diisobutylcarbamoylmethyl Phosphine Oxide (CMPO) during Partitioning of Minor Actinides from High Level Waste (HLW) Solutions', Separation Science and Technology, 33: 14, 2179 — 2196

To link to this Article: DOI: 10.1080/01496399808545722

URL: http://dx.doi.org/10.1080/01496399808545722

SEPARATION SCIENCE AND TECHNOLOGY, 33(14), pp. 2179–2196, 1998

Degradation, Cleanup, and Reusability of Octylphenyl-*N,N′*-diisobutylcarbamoylmethyl Phosphine Oxide (CMPO) during Partitioning of Minor Actinides from High Level Waste (HLW) Solutions

---

J. N. MATHUR,* M. S. MURALI, P. B. RUIKAR, and M. S. NAGAR
RADIOCHEMISTRY DIVISION

A. T. SIPAHIMALANI, A. K. BAURI, and A. BANERJI
BIO-ORGANIC DIVISION

BHABHA ATOMIC RESEARCH CENTRE
TROMBAY, BOMBAY-400,085, INDIA

ABSTRACT

The radiolytic degradation of the extractant mixture 0.2 M octylphenyl-*N,N′*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) + 1.2 M tributyl phosphate in *n*-dodecane [to be utilized for the partitioning of minor actinides from high level waste (HLW) solutions of PUREX origin] has been investigated in contact with 3 M HNO_3 or synthetic pressurized heavy water reactors (PHWR)-HLW solution under dynamic conditions. The distribution ratios of Am, Zr, Fe, and Ru with the irradiated extractant mixture at varying doses have been determined under various aqueous phase conditions and correlated with the formation of degradation products. Various cycles of loading the extractant mixture with Am from PHWR-HLW, irradiating at a fixed gamma dose, and then primary and secondary clean-up of the solvent has been carried out to illustrate its reusability during partitioning of minor actinides from actual HLW solutions. The degradation products of CMPO have been identified by employing GC and GC-MS techniques.

INTRODUCTION

The safe disposal of nuclear wastes, especially those containing long-lived alpha emitters, is a matter of great environmental concern. Because of these

---

*,To whom correspondence should be addressed.

www.dekker.com

nuclides, the wastes will require several tens of thousands of years for surveillance even after vitrification and storage in deep geological repositories. Since this is a global problem, laboratories all over the world are actively engaged in partitioning the long-lived minor actinides (MA) from high level waste (HLW) solutions and subsequently transmuting them into short-lived nuclides (partitioning and transmutation option). The separated MA could also be used as fuel in nuclear reactors. The various extractants widely utilized for this purpose are: dihexyl-*N,N*-diethylcarbamoylmethylphosphonate (DHDECMP) (1); one of the most promising diamides, *N,N*′-dimethyl-*N,N*-dibutyl tetradecyl malonamide (DMDBTDMA) (2–5); trialkylphosphine oxide (TRPO) (6–8); diisodecylphosphoric acid (DIDPA) (9, 10); and octylphenyl-*N,N*′-diisobutylcarbamoylmethyl phosphine oxide (CMPO) (11–20). Of these reagents, CMPO has been proposed as the best reagent for the recovery of MA from HLW solutions. During this process the extractant mixture, i.e., 0.2 M CMPO + 1.2 M TBP in *n*-dodecane, has to go through a moderately hostile environment, e.g. strong nitric acid, high temperature, and, above all, massive radiation dose. In order to assess the reusability of the extractant mixture, it is necessary to study the radiolytic degradation, to determine the nature of the products formed and their influence on the extractability of actinides, and finally to develop cleanup procedures needed to bring the extractant mixture to the reference condition. Horwitz et al. initially carried out the study of hydrolytic and radiolytic degradation of CMPO using such diluents as carbon tetrachloride and decalin (decahydronaphthalene) (21), tetrachloroethylene (TCE), or a mixture of tributylphosphate (TBP) and TCE (22). Later, the degradation of a Truex-dodecane process solvent i.e., 0.2 M CMPO + 1.2 M TBP in *n*-dodecane, was studied under unstirred condition in the presence of 5 M HNO_3 (23). The same group also studied the secondary cleanup of the gamma-irradiated Truex process solvent under the conditions of Ref. 23 using macroporous anion-exchange resins and other solid adsorbents (24). A recent publication (25) discussed the effect of alpha radiolysis on a Truex-paraffinic hydrocarbon solvent.

The present work was undertaken with the following objectives:

1. To study the gamma radiolysis of the Truex solvent in contact with 3 M HNO_3 under dynamic conditions.
2. To study the primary and secondary cleanup of such an irradiated extractant mixture and its reusability.
3. To study various effects of gamma irradiation, loading and stripping of Am on the Truex solvent from aqueous 3.0 M HNO_3, and simulated pressurized heavy water reactor (PHWR)-HLW.
4. To identify and correlate the various degradation products by employing GC and GC-MS techniques.

EXPERIMENTAL

Solvent extraction grade CMPO was synthesized and purified at this Centre (26) using a modified procedure suggested by Horwitz et al. (27). Tributyl phosphate (TBP) (Bharat Vijay Chemicals, India) was purified by contacting it with a dilute solution of sodium hydroxide, washing with water, and drying over anhydrous sodium sulfate. Dodecane (~96% C-12, specific gravity 0.751, refractive index 1.42, and aromatics <0.1%; distillation range 160–210°C) was obtained from Transware Chemia Handelsgeselschaft, Hamburg, Germany, and was used as such. All other chemicals used were of Analytical Reagent Grade.

Radioactive Tracers

The tracer ^{241}Am was prepared and purified as given elsewhere (26). The tracers ^{59}Fe, ^{95}Zr, and ^{103}Ru were obtained from the Board of Radiation and Isotope Technology, India. All tracers were assayed by using a gamma scintillation counter with a NaI(T1) detector. The synthetic PHWR-HLW was prepared from a burn-up of 6500 MWD/tonne; 800 L HLW was generated from the reprocessing of 1 tonne of the fuel. The composition of this HLW is given in Ref. 28. A ^{60}Co source was used for gamma irradiation; its dose rate was determined by Fricke's dosimetry after applying corrections as given in Refs. 29 and 30.

Experiments under Static Conditions

Three types of organic solution systems were utilized for gamma irradiation studies:

(A): 0.4 M CMPO in *n*-dodecane.
(B): 0.2 M CMPO + 1.2 M TBP in *n*-dodecane which was not preequilibrated with 3.0 M HNO_3.
(C): The extractant as in system (B) after preequilibrating with 3.0 M HNO_3 prior to irradiation.

Aliquots of the above listed organic solutions were taken out at different intervals of time corresponding to different doses. An aliquot belonging to (A) was diluted with an equal volume of 2.4 M TBP in *n*-dodecane and then divided into two portions. One portion was preequilibrated with a pH 2.0 HNO_3 solution and utilized for determination of the distribution ratio (*D*, defined as the ratio of metal ion concentration in the organic phase to that in the aqueous phase) of Am(III) at pH 2.0, and the second portion was preequilibrated with 3.0 M HNO_3 and used to determine the *D* values of

Am(III), Fe(III), Zr(IV), and Ru(III) at 3.0 M HNO_3. Similar experiments were also carried out with samples from the (B) and (C) categories.

Variation of HDBP Concentration in CMPO + TBP Solution

One milliliter of the organic phase containing 0.2 M CMPO + 1.2 M TBP in *n*-dodecane and varying concentrations of dibutyl phosphoric acid (HDBP) (0.0–0.14 M) was equilibrated with the same volume of the aqueous phase [pH 2.0, HNO_3 for Am(III) and 3.0 M HNO_3 for Fe(III) and Zr(IV)] for 30 minutes in a thermostated bath at 25 ± 0.1°C. After the solutions were settled they were centrifuged, and samples of the aqueous and organic phases were removed for radio assay.

Experiments under Dynamic Conditions

A specially fabricated electronic stirrer unit, which was placed inside the chamber provided in the gamma irradiator, was utilized for continuously stirring during irradiation of the organic (0.2 M CMPO + 1.2 M TBP in *n*-dodecane) and aqueous (3.0 M HNO_3 or synthetic-uranium-depleted PHWR-HLW) phases. The stirring speed was controlled from outside the irradiator. There was no perceptible rise in the temperature of the system due to long-term stirring friction.

The following experiments were carried out under the above conditions.

(a) Effect of Gamma Irradiation of 0.2 M CMPO + 1.2 M TBP in n*-Dodecane on the Extraction of Am(III) at pH 2.0, 0.04 M HNO_3, and 3.0 M HNO_3*

40 mL of the organic phase was stirred with an equal volume of 3.0 M HNO_3. Suitable aliquots of organic phase were taken at regular intervals. Equal volumes of the aqueous phase were also taken out and discarded to keep the phase ratio at 1:1. The organic aliquot was divided into several portions. Two portions were washed several times with a pH 2.0 solution and 0.04 M HNO_3 separately, and they were used to determine the D values of Am(III) at pH 2.0 and 0.04 M HNO_3. One portion was used in the same manner at 3.0 M HNO_3 for D_{Am}, D_{Fe}, and D_{Zr}, while another portion was washed three times with 0.25 M Na_2CO_3 at organic to aqueous phase ratios of 1:1 or 4:1, followed by distilled water. The Na_2CO_3-washed organic aliquot was used to determine D_{Am} at pH 2.0 and at 0.04 M HNO_3. One portion of the carbonate-washed organic phase was treated with 5% basic alumina (active basic alumina, for chromatography, E. Merck) successively. After the treatment with alumina, the organic phase was washed several times with water and utilized for D_{Am} at pH 2.0.

(b) Effect of Amount of Basic Alumina on the Extraction of Am(III) with Carbonate Washed, Irradiated Solution of 0.2 M CMPO + 1.2 M TBP in n-Dodecane

10 mL of the extractant mixture was irradiated with a 13 Mrad dose and washed three times with 0.25 M Na_2CO_3 solution at an organic to aqueous phase ratio of 4:1. This organic phase was divided into five portions which were treated with 1, 2, 3, 4, and 5% w/v of basic alumina, respectively. These portions were washed with water and used for D_{Am} at pH 2.0 and 3.0 M HNO_3.

(c) Reusability of the Extractant Mixture in Successive Cycles

35 mL of a synthetic PHWR-HLW solution containing ^{241}Am was contacted with an equal volume of the organic phase and irradiated with a ~10 Mrad dose. The loaded organic phase was stripped five times with an equal volume of fresh 0.04 M HNO_3. Then the lean organic phase was washed with a 0.25 M solution of sodium carbonate at an organic to aqueous phase ratio of 4:1 and the percent retention of Am was determined in the organic phase before and after the carbonate wash. Five such cycles were carried out.

(d) GC and GC-MS Studies of the Degraded Extractant Mixture

GC studies of the samples were carried out using a Shimadzu Gas Chromatograph (GC-16A, FID detector) fitted with a 2 m long, 5 mm I.D. glass column packed with 3% OV-17 on Gas Chrom Q (80–100 mesh). The carrier gas was nitrogen with a flow rate of 40 mL/min. In the case of *n*-dodecane, the initial temperature was 80°C with a hold-up time of 5 minutes, the rate of increase was 4°C/min, and the final temperature was 180°C. In the case of the TBP/CMPO/*n*-dodecane mixture, the initial temperature was 140°C, the hold-up time was 2 minutes, and the final temperature was 240°C. The temperature was increased in two steps: 2°C/min up to 180°C and 8°C/min between 180 and 240°C.

GC-MS studies were carried out in the electron-induced mode (EI, 70 eV) using a Shimadzu GC-MS (QP-1000A or QP-5000). The only difference here from the GC conditions was that the carrier gas was helium with a flow rate of 50 mL/min and that the temperature ranged between 140 and 240°C with a rate of increase of 8°C/min for the extractant mixture.

The sample preparations were done as follows: (a) The total organic phase (0.2 M CMPO + 1.2 M TBP in *n*-dodecane, control as well as irradiated sample) aliquots were directly analysed by GC, and (b) the gamma-irradiated organic phases from (a) were further fractionated into acidic and neutral parts. The acidic part was washed with Na_2CO_3 solution, acidified, and subjected to freeze-drying. Before injecting the samples to GC, they were converted into the methyl ester using diazomethane. The neutral part (still in the organic phase) was also analyzed by GC.

RESULTS AND DISCUSSION

Table 1 gives the D values of Am(III) at pH 2.0 and 3.0 M HNO_3 at varying doses under static conditions using three types of solutions, defined in Table 1 as A, B, and C. The first row gives the values with a reference solution, i.e., 0.2 M CMPO + 1.2 M TBP in *n*-dodecane preequilibrated with pH 2.0 or 3.0 M nitric acid. With an increase in the dose up to 106 Mrad, the increase in D at pH 2.0 of Am with C is much more significant than those with the A and B systems. This clearly brings out the role of extracted nitric acid by the extractant mixture in its degradation and the possible formation of acid degradation products which, in conjunction with CMPO, leads to the synergistic extraction of Am. The extent of increase in D values at pH 2.0 with A is small, thereby indicating that the relative stability of CMPO under radiation conditions is quite high. The D values with B are a composite effect of the

TABLE 1

Distribution Ratios of Am(III) at pH 2.0 and 3.0 M HNO_3 with 0.2 M CMPO + 1.2 M TBP in *n*-Dodecane under Three Different Conditions at Varying Gamma Doses under Static Conditions (without stirring)[a]

	D_{Am} at pH 2.0			D_{Am} at 3.0 M HNO_3		
Dose (Mrad)	A	B	C	A	B	C
Reference solution[b]	0.016	0.016	0.016	25.5	25.5	25.5
15.23	0.10	0.12	1.5	22.7	23.8	22.3
30.58	0.17	0.19	7.1	24.8	21.6	21.5
76.1	0.23	0.81	—	23.7	22.3	15.9
106.2	1.08	2.5	247.3	21.5	21.7	13.9

[a] Typical conditions. A: 0.4 M CMPO irradiated and subsequently diluted to give 0.2 M CMPO + 1.2 M TBP in *n*-dodecane. B: 0.2 M CMPO + 1.2 M TBP in *n*-dodecane irradiated without preequilibration. C: 0.2 M CMPO + 1.2 M TBP in *n*-dodecane preequilibrated with 3.0 M nitric acid before irradiation.

[b] Reference solution: Unirradiated solution of 0.2 M CMPO + 1.2 M TBP in *n*-dodecane preequilibrated with the respective aqueous solutions. All the aliquots after irradiation were preequilibrated with the respective aqueous solutions.

TABLE 2
Distribution Ratios of Zr(IV), Fe(III), and Ru(III) at 3.0 M HNO_3 with A, B, and C (defined in Table 1) at Various Gamma Doses under Static Conditions

	$D_{Zr(IV)}$			$D_{Fe(III)}$			$D_{Ru(III)}$		
Dose (Mrad)	A	B	C	A	B	C	A	B	C
Reference solution	2.81	2.81	2.81	0.09	0.09	0.09	0.22	0.22	0.22
15.23	2.96	3.10	3.19	0.19	0.22	0.21	0.27	0.20	0.26
30.58	4.50	6.60	98.50	0.63	1.20	9.40	0.22	0.21	0.32
76.10	8.80	20.60	95.20	0.82	1.87	46.30	0.12	0.12	0.20
106.2	15.30	24.20	90.10	1.91	6.60	45.8	0.17	0.16	0.25

degradation of TBP and CMPO. At 3.0 M HNO_3, the decrease in *D* values of Am is insignificant with A and B as expected, since the degradation of CMPO alone or in the presence of TBP is not high. In the case of C the decrease in *D* values suggests that the decrease in CMPO concentration with an increase in the dose is a complex function of the effect of the extracted HNO_3 on the degradation of CMPO. It can thus be concluded that at pH 2.0, the *D* values increase because of the formation of acidic degradation products, whereas at 3.0 M it is the decrease in the concentration of CMPO that affects the *D* values.

Table 2 gives similar data for Fe(III) (a typical corrosion product), Zr(IV), and Ru(III) (both typical fission products), all of which are present in HLW. It can be seen that for Ru the *D* values are almost constant with all three systems, whereas for Zr and Fe there is a drastic increase in *D* values after a dose of 15.2 Mrad. Also, it can be seen that the order of *D* values for these two metal ions is system C > B > A, which is similar to that observed in the case of Am at pH 2.0 (Table 1) and could be explained in the same way.

Since one of the important degradation products of TBP is HDBP under gamma irradiation conditions, it was decided to study the effect of HDBP concentration (0.0 to 0.14 M) on the extraction of a few metal ions. HDBP was added to the mixture of 0.2 M CMPO + 1.2 M TBP, and the *D* values of Am(III) at pH 2.0 and of Fe(III) and Zr(IV) at 3.0 M HNO_3 were determined. It can be seen from Table 3 that the *D* value for Am(III) at pH 2.0 at the highest concentration of HDBP used (0.14 M) is ~13. This value is a little lower than 16.4, the *D* value of Am(III) at pH 2.0 when the 0.2 M CMPO + 1.2 M TBP in *n*-dodecane mixture was irradiated with a dose of 21.1 Mrad (Table 4). This suggests that if HDBP is the only degradation product at such dose levels, then its formation will affect the backextraction of Am(III) with 0.04

TABLE 3
Variation of HDBP Concentration at 0.2 M CMPO + 1.2 M TBP in *n*-Dodecane. Aqueous phase 3.0 M HNO_3 for Fe(III) and Zr(IV) and pH 2.0 HNO_3 for Am(III).

	Distribution ratio (*D*)		
[DBP] (M)	Am	Fe	Zr
0.000	0.016	0.090	2.81
0.005	0.057	0.088	2.95
0.010	0.067	0.114	3.44
0.015	0.083	0.148	3.92
0.020	0.167	0.214	11.85
0.040	0.601	0.446	18.47
0.060	1.430	0.586	33.50
0.080	2.841	0.917	37.94
0.100	5.202	1.179	48.70
0.120	8.841	1.625	55.37
0.140	12.985	2.136	69.10

TABLE 4
Distribution Ratios of Am(III) at pH 2.0 and 0.04 M HNO_3 Before and After Primary and Secondary Cleanup at Varying Doses (under dynamic conditions)

	Distribution ratio (*D*)					
	Without any treatment		After primary cleanup^a (O/A = 1:1), pH 2.0	After secondary cleanup,^{b} pH 2.0	After primary cleanup^a (O/A = 4:1), pH 2.0	After secondary cleanup,^{b} pH 2.0
Dose (Mrad)	pH 2.0	0.04 M				
Reference solution	0.016	—	—	—	—	—
0.55	—	—	0.02	0.017	—	—
3.5	—	—	0.045	0.015	—	—
5.3	0.55	0.23	0.12	0.015	0.22	0.05
7.04	—	—	0.17	0.02	—	—
10.7	2.77	0.38	—	—	0.28	0.06
15.8	5.92	0.48	—	—	0.45	0.09
21.1	16.4	0.8	0.26	0.054	0.85	0.14
26.4	32.7	1.21	—	—	1.72	0.24
36.9	96.04	2.75	—	—	2.17	0.29

[a] Washed with 0.25 M Na_2CO_3 three times.
[b] 5% basic alumina (w/v) treatment.

M nitric acid since the *D* value of Am(III) under such conditions is ~0.8 (Table 4). In the case of Fe(III) and Zr(IV), the tolerable limit for HDBP concentration is 0.015 M. The *D* values increase sharply above this concentration. It is a well-known fact that tetravalent Zr ion is strongly held by HDBP and decreases its decontamination factor.

Under dynamic conditions the *D* values of Am(III) at pH 2.0 at different gamma radiation doses (Table 4), when compared with those under static conditions (system C, Table 1), show that the *D* values are much higher, which may be due to the formation of larger amounts of acidic degradation products. The experiments carried out under dynamic conditions are much closer to those of a mixer-settler or of pulsed column operations carried out for large volumes of HLW. In a study carried out by Chiarizia and Horwitz (24) for the radiolytic degradation of 0.2 M CMPO + 1.2 M TBP in *n*-dodecane with an equal volume of 5 M HNO_3 under static conditions, it was shown that D_{Am} values at pH 2.0 for unwashed solutions are 0.87 (for 7.09 Mrad), 0.91 (for 12.71 Mrad), 1.33 (for 19.58 Mrad). and 1.42 (for 28.40 Mrad), which are much lower than our values determined under dynamic conditions. Also, it can be seen from Ref. 24 that the increase in *D* values with increasing dose rates is not very high. This is contrary to the results obtained in the present study (Table 4). Also, the D_{Am} values at 0.04 M HNO_3 in Ref. 24 are more or less constant whereas those in the present study (Table 4) increase with increasing dose. At nitric acid concentration of 0.04 M, which is used to backextract Am(III), the *D* value of 0.48 at 15.8 Mrad suggests favorable backextraction of Am(III) when the extractant mixture is exposed to such high doses.

In order to recycle the extractant mixture to minimize its inventory, a primary cleanup procedure of washing the degraded extractant mixture with 0.25 M sodium carbonate was carried out at organic-to-aqueous-phase (O/A) ratios of 1:1 and 4:1. The latter O/A ratio was tried to minimize the generation of secondary aqueous waste. This was followed by a secondary cleanup which treated the mixture with basic alumina to restore it to the reference condition. By treatment with 0.25 M Na_2CO_3 solution at an O/A ratio of 1:1, the D_{Am} at pH 2.0 is drastically reduced but does not fall to the reference value. However, when treatment is with basic alumina, the *D* values come very close to the reference value. When the Na_2CO_3 wash was made at an O/A ratio of 4:1, the D_{Am} values at pH 2.0 are definitely higher than those obtained when the phase ratios were 1:1. After one contact with basic alumina, the *D* values are drastically reduced (Table 4, last column), but they have still not reached the reference value. It is possible that with an additional one or two contacts with basic alumina will result in values very close to the reference value. This information will be useful for deciding on the cleanup

TABLE 5
Distribution Ratio of Am(III), Fe(III), and Zr(IV) at 3.0 M HNO_3 with Degraded Mixture at Different Doses (dynamic conditions)

	Distribution ratio (*D*)		
Dose (Mrad)	Am(III)	Fe(III)	Zr(IV)
Reference solution	25.5	0.09	2.9
0.55	26.3	0.09	3.1
3.5	20.6	0.14	3.5
5.3	23.6	0.15	3.4
7.04	23.6	0.14	2.86
10.6	21.1	0.16	2.98
15.8	21.5	0.21	3.01

operations to be used during handling of very large volumes of the extractant mixture.

Table 5 gives the *D* values of Am(III), Fe(III), and Zr(IV) in 3.0 M HNO_3 at different gamma irradiation doses under the dynamic conditions. The *D* values of all these metal ions remain more or less constant under such experimental conditions.

The effect of the amount of basic alumina on the *D* values of Am(III) at pH 2.0 and 3.0 M HNO_3 is given in Table 6. It can be seen that 4 to 5% is required for a mixture irradiated to 14.3 Mrad and treated with carbonate solution at an O/A ratio of 4:1 to get a constant value. Hence, 5% alumina was used in subsequent experiments.

TABLE 6
Secondary Cleanup of Extractant Mixture; Effect of Varying Amount of Alumina on Distribution Ratio of Am(III) at pH 2.0 and 3.0 M HNO_3 at a Dose of 14.3 Mrad. Primary Cleanup with 0.25 M Sodium Carbonate at O/A Ratio of 4:1

% Al_2O_3	D_{Am} at pH 2.0	D_{Am} at 3.0 M HNO_3
Reference	0.016	25.5
1	0.43	22.2
2	0.24	22.5
3	0.15	22.5
4	0.10	22.0
5	0.11	21.8

TABLE 7
Reusability of Solvent Mixture Using Synthetic PHWR-HLW Irradiated to 10 Mrad and Subjected to Primary and Secondary Cleanup Procedures: *D* of Am at different conditions

Cycle	Distribution ratio of Am(III)					
	Without any treatment, pH = 2.0	Primary cleanup (O/A = 4:1), pH = 2.0	Primary cleanup (O/A = 4:1), 0.04 M HNO_3	Number of secondary cleanup contacts, pH = 2.0		
				1	2	3
Reference	0.016	—	—	—	—	—
1	2.7	0.28	0.22	0.026	0.022	0.017
2	2.6	0.49	0.24	0.049	0.032	0.018
3	2.9	0.63	0.21	0.064	0.038	0.017

Table 7 gives the effect of a number of contacts of 5% basic alumina on the restoration of the extractant mixture used in different cycles. In each cycle the extractant mixture was irradiated to 10 Mrad and subjected to the primary cleanup, followed by the secondary cleanup. Although it takes more than one contact with basic alumina to bring the extractant mixture back to the reference condition, this is not an essential step while using the extractant mixture under actual process conditions. The reason is that even though the mixture is not restored to the reference condition after one contact with alumina, the

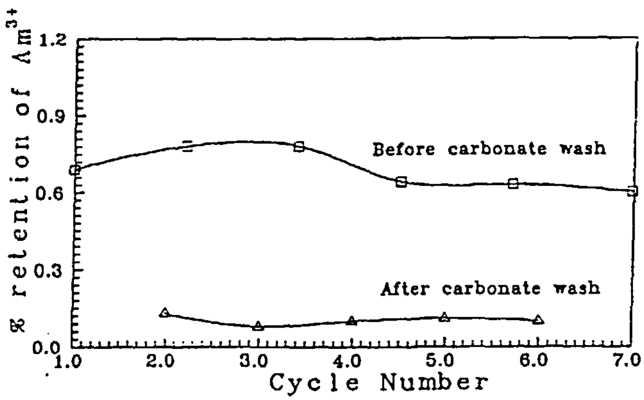

FIG. 1 Retention of Am in the organic phase in different cycles.

backextraction of Am(III) is still almost quantitative. The retention of Am(III) in the organic phase is shown in Fig. 1. The maximum retention is around 0.8% for the irradiated organic phase without subjecting it to sodium carbonate wash, whereas it reduces to about 0.1% when washed with Na_2CO_3 solution.

Figure 2 gives the capillary GC-MS profile of the degradation products of *n*-dodecane. Figure 2(A) gives the GC profile of *n*-dodecane after gamma irradiation (30 Mrad dose) under dynamic conditions in contact with 3 M HNO_3. Apart from *n*-dodecane, the major component, the appearance of minor amounts of degraded products can be seen in the retention time range of 8–16 minutes. The MS of the more prominent products arising in the 8–10 minute region are given in Figs. 2(B), 2(C), 2(D), and 2(E); Based on a library search, these were found to be similar to 2-methyl-5-undecanone, 4-undecanone, 3-undecanone, and 3-dodecanol as given in Figs. 2(B′), 2(C′), 2(D′), and 2(E′), respectively. The trace peaks observed in the time scale of 10–16 minutes were found to be comparable to amino products: 2-undecylamine, 1-methyltridodecylamine, etc. In a recent review (31) on the decomposition of nuclear reprocessing solvents, the likely principal degradation products originating from the diluents were identified as aliphatic nitro compounds, aliphatic carboxylic acids, aliphatic nitroso compounds, ketones, aldehydes, hydroxamic acid, nitronic acid, etc. The conditions reported for the formation of these compounds vary. Under our experimental conditions, only the above-mentioned products were detected.

Figure 3 gives the GC of the extractant mixture (0.2 M CMPO + 1.2 M TBP in *n*-dodecane) in contact with 3 M HNO_3 under dynamic conditions. Figure 3(a) is the control extractant mixture and Fig. 3(b) is after irradiating at a gamma dose of 30 Mrad. The peaks in Fig. 3(b) with a retention time between 10 and 13 minutes are due to the TBP degradation products, whereas those in the 24 to 32 minute region are due to various radiolytic degradation products of CMPO. Further GC-MS studies were concentrated in the 24 to 32 minute region, and the four products identified were octylphenyl phosphinic acid (**1**), methylphenyl-*N*,*N*-diisobutylcarbamoylmethyl phosphinic acid (**2**), octylphenylmethylphosphine oxide (**3**), and phenyldiisobutylcarbamoyl nitromethyl phosphine oxide (**4**). In earlier studies (24) on the degradation of CMPO, the products identified were (**1**) and (**3**) as reported above and also octylphenylphosphinyl acetic acid (**5**) and octylphenyl-*N*-monoisobutylcarbamoylphosphine oxide (**6**). However, under our experimental conditions we could not detect the formation of products **5** and **6**. The detection of **2** and **4** is reported here for the first time, and their identification is based on the MS profiles shown in Figs. 4 and 5. The pathways for the formation of the degradation products in the present study are given in Fig. 6.

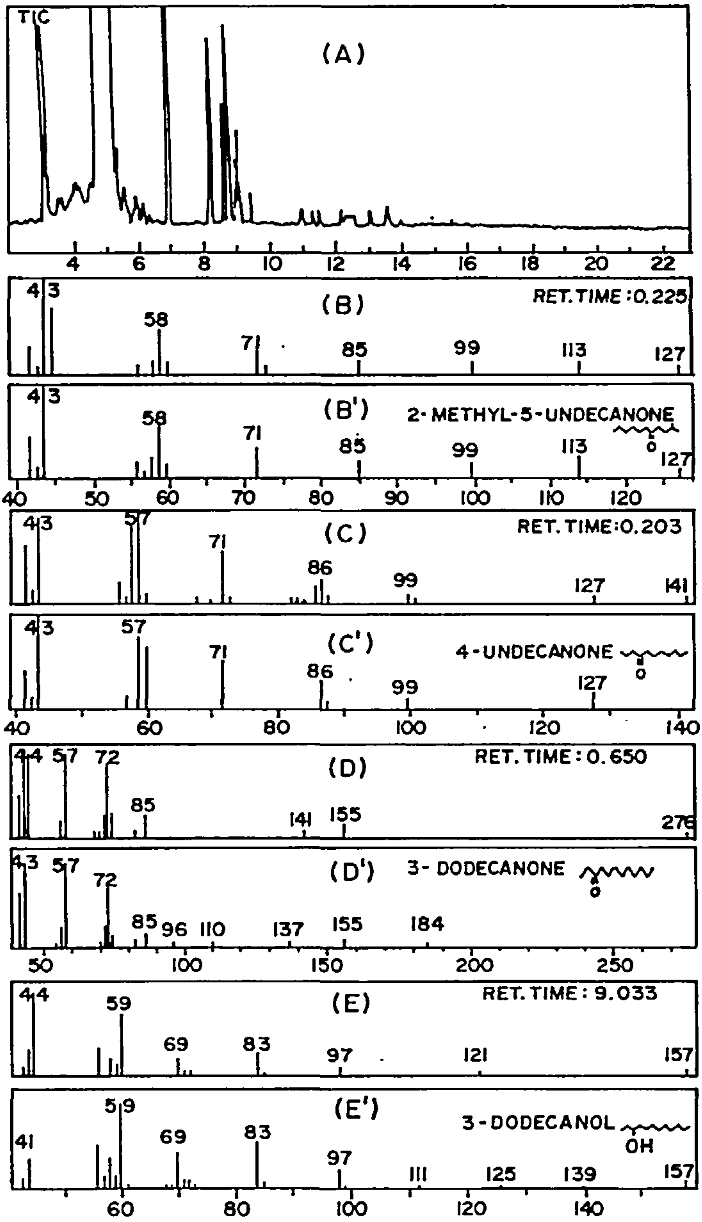

FIG. 2 GC and GC-MS profile of *n*-dodecane.

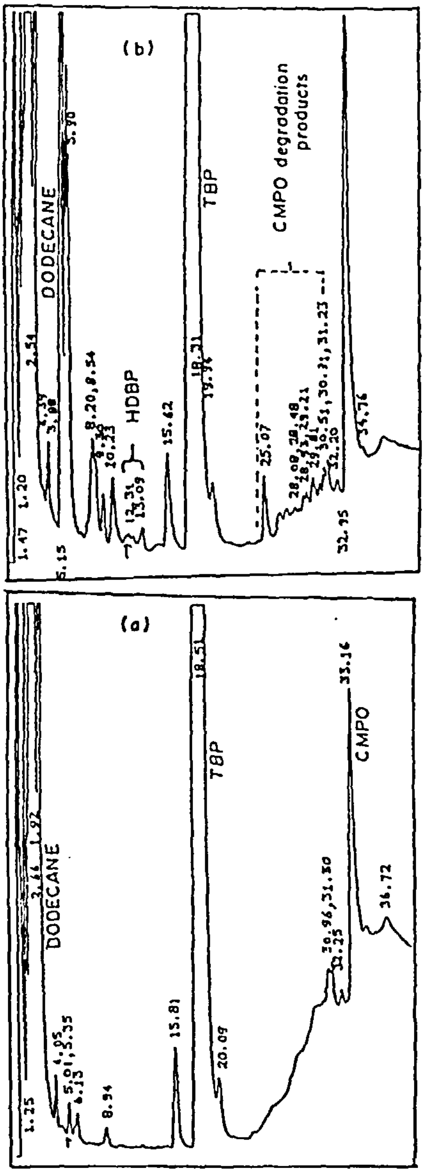

FIG. 3 GC profile of (a) unirradiated mixture of 0.2 M CMPO + 1.2 M TBP in *n*-dodecane, and (b) irradiated mixture of 0.2 M CMPO + 1.2 M TBP in *n*-dodecane under dynamic conditions in contact with 3 M HNO_3 at 30 Mrad gamma dose.

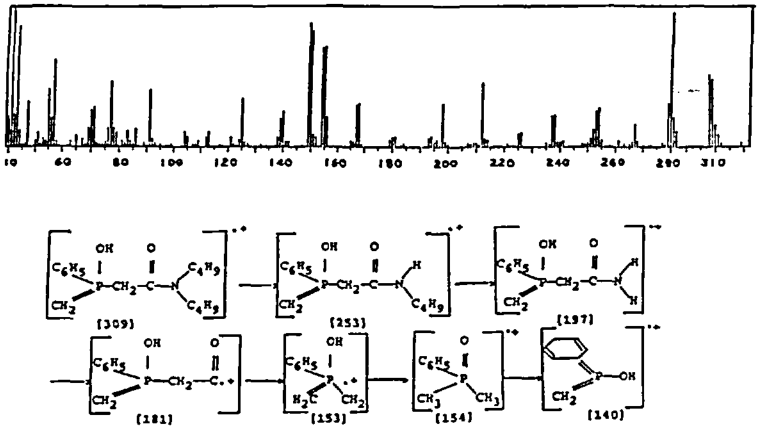

FIG. 4 MS and the fragmentation profile of methylphenyl-*N,N*-diisobutylcarbamoylmethyl phosphinic acid.

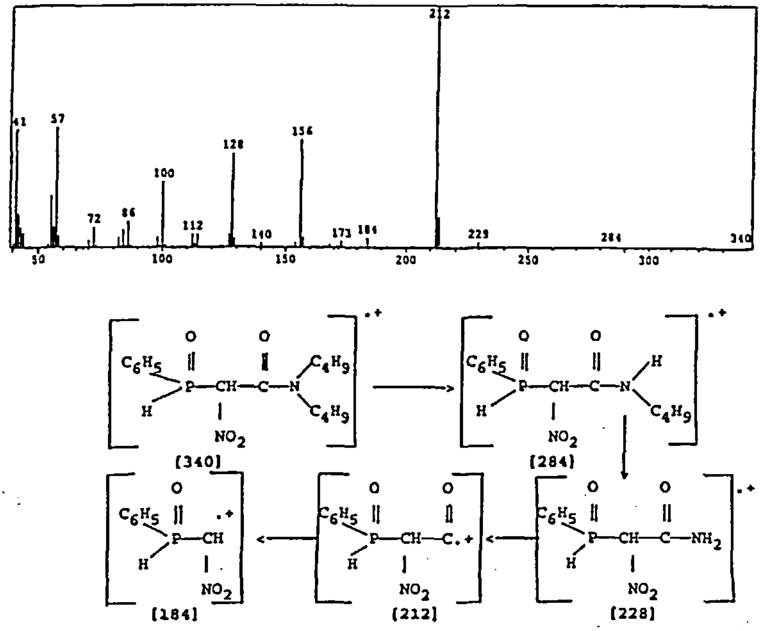

FIG. 5 MS and the fragmentation profile of phenyldiisobutylcarbamoyl nitromethyl phosphine oxide.

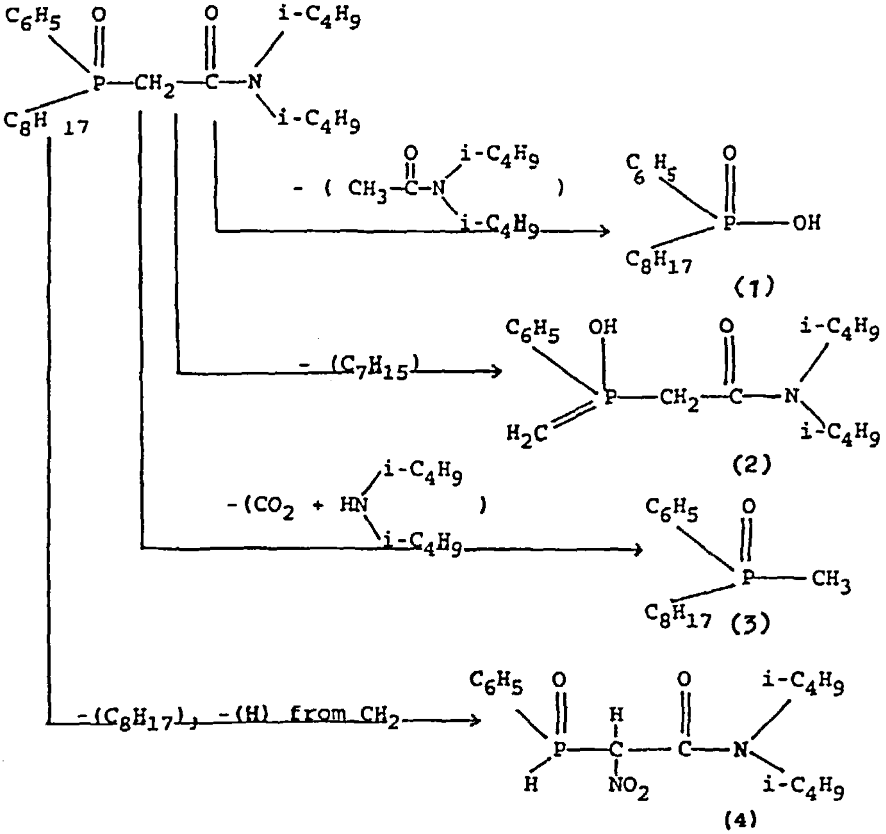

FIG. 6 Pathway for the formation of different degradation products of CMPO.

CONCLUSIONS

Radiolytic degradation studies of the extractant mixture 0.2 M CMPO + 1.2 M TBP in dodecane, to be used for the partitioning of minor actinides from HLW solutions of PUREX origin under dynamic conditions, have shown an increase in the *D* values of Am at pH 2.0 and 0.04 M HNO_3 with increasing gamma doses. At 0.04 M HNO_3 which is used for stripping Am from the loaded CMPO phase, the *D* value with the extractant mixture exposed to about 16 Mrad is reasonably low and gives nearly complete recovery of Am. The *D* value of Am at 3.0 M HNO_3 with an irradiated CMPO mixture up to about 16 Mrad remains more or less constant. The higher *D* values of Am(III) under dynamic conditions as compared to those under static conditions can be attributed to the formation of higher amounts of acidic degradation products such as **1** and **2**. In various cycles of extraction of Am from synthetic PHWR-HLW at a dose of 10 Mrad, stripping with 0.04M HNO_3, primary cleanup with Na_2CO_3 at an O/A ratio of 4:1, and secondary cleanup with 5% basic alumina, it has been observed that the extractant mixture could finally be brought to the reference condition. Very low retention of Am (0.1%) in the irradiated organic phase was observed when the cleanup was only with Na_2CO_3. GC-MS studies have identified the formation of four radiolytic degradation products of CMPO.

REFERENCES

1. B. M. Rapko and G. J. Lumetta, *Solv. Extr. Ion Exch.*, *12*, 967 (1994).
2. C. Cuillerdier, C. Musicas, and P. Hoel, in *New Separation Techniques for Radioactive Wastes and Other Specific Applications* (L. Cecille, M. Casarci, and L. Pietrelli, Eds.), Elsevier Applied Science, 1991, p. 41.
3. C. Musicas, *International Symposium on Radiochemistry and Radiation Chemistry*, BARC, Bombay, 1991.
4. C. Musicas, *Nuclear and Radiochemistry Symposium*, IGCAR, Kalpakkam, 1995.
5. G. Baudin, J. Lefevre, C. Prunier, and M. Salvatores, *Proceedings of Technical Committee on "Safety and Environmental Aspects and Partitioning and Transmutation of Actinides and Fission Products,"* Vienna, 1993; IAEA-TECDOC-783, 1995, p. 37.
6. Y. Zhu, R. Jiao, S. Wang, S. Fan, B. Liu, H. Zheng, S. Zhou, and S. Chel., *Proceedings of the International Solvent Extraction Conference, ISEC'83*, American Institute of Chemical Engineers, New York, NY, 1983, p. 9.
7. C. Apostolidis, R. De Meester, L. Koch, R. Molinet, J. Liang, and Y. Zhu, *Conference on New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications*, May 13–18, 1990, Rome, Italy.
8. Y. Zhu and C. Song, in *Transuranium Elements: A Half Century* (L. R. Morss and J. Jager, Eds.), American Chemical Society, Washington, DC, 1992, p. 318.
9. Y. Morita and M. Kubota, *Solv. Extr. Ion Exch.*, *6*, 233 (1988).
10. Y. Morita, I. Yamaguchi, Y. Kondo, K. Shirahashi, I. Yamagishi, T. Fujiwara, and M. Kubota, *Proceedings of Technical Committee* on "Safety and Environmental Aspects of Partitioning and Transmutation of Actinides and Fission Products," Vienna, 1993; IAEA-TECDOC-783, 1995, p. 93.
11. E. P. Horwitz, D. G. Kalina, H. Diamond, W. W. Schultz, and G. P. Vandergrift, *Solv. Extr. Ion. Exch.*, *3*, 75 (1985).
12. W. W. Schultz and E. P. Horwitz, *Institute of Chemical Engineers Symposium Series 103, Extraction 87, EFCE Publication Series 56*, 1987, p. 245.
13. W. W. Schultz and E. P. Horwitz, *Sep. Sci. Technol.*, *23*, 1191 (1988).
14. M. Ozawa, S. Nemoto, A. Togaski, T. Kawata, and K. Onisi, *Solv. Extr. Ion. Exch.*, *10*, 829 (1992).
15. J. N. Mathur, M. S. Murali, M. V. Balarama Krishna, R. H. Iyer, R. R. Chitnis, P. K. Wattal, T. K. Theyyunni, A. Ramanujam, P. S. Dhami, and V. Gopalakrishnan, *Sep. Sci. Technol.*, *31*, 2045 (1996).

16. J. N. Mathur, M. S. Murali, P. R. Natarajan, L. P. Badheka, A. Banerji, A. Ramanujam, P. S. Dhami, V. Gopal Krishnan, R. K. Dhumwad, and M. K. Rao, *Waste Manag.*, *13*, 317 (1993).
17. V. Gopal Krishnan, P. S. Dhami, A. Ramanujam, M. V. Balarama Krishna, M. S. Murali, J. N. Mathur, R. H. Iyer, A. K. Bauri, and A. Banerji, *J. Radioanal. Nucl. Chem. Articles*, *191*, 279 (1995).
18. J. N. Mathur, M. S. Murali, R. H. Iyer, A. Ramanujam, P. S. Dhami, V. Gopal Krishnan, M. K. Rao, L. P. Badheka, and A. Banerji, *Nucl. Technol.*, *109*, 216 (1995).
19. D. S. Deshingkar, R. R. Chitnis, P. K. Wattal, T. K. Theyyunni, A. Ramanujam, P. S. Dhami, V. Gopal Krishnan, M. K. Rao, J. N. Mathur, M. S. Murali, R. H. Iyer, L. P. Badheka, and A. Banerji, *Report*, *BARC-028* (1993).
20. D. S. Deshingkar, R. R. Chitnis, P. K. Wattal, T. K. Theyyunni, M. K. T. Nair, A. Ramanujam, P. S. Dhami, V. Gopal Krishnan, M. K. Rao, J. N. Mathur, M. S. Murali, R. H. Iyer, L. P. Badheka, and A. Banerji, *Report*, *BARC-014* (1994).
21. R. Chiarizia and E. P. Horwitz, *Solv Extr. Ion Exch.*, *4*, 677 (1986).
22. K. L. Nash, R. C. Gatrone, G. A. Clark, P. G. Rickert, and E. P. Horwitz, *Sep. Sci Technol.*, *23*, 1355 (1988).
23. K. L. Nash, P. G. Rickert, and E. P. Horwitz, *Solv. Extr. Ion Exch.*, *7*, 644 (1989).
24. R. Chiarizia and E. P. Horwitz, *Ibid.*, *8*, 907 (1990).
25. B. A. Buchholz, L. Nunez, and G. F. Vandergrift, *Sep. Sci. Technol.*, *31*, 2231 (1996).
26. J. N. Mathur, M. S. Murali, P. R. Natarajan, L. P. Badheka, and A. Banerji, *Talanta*, *39*, 493 (1992).
27. R. C. Gatrone, L. Kaplan, and E. P. Horwitz, *Solv. Extr. Ion Exch.*, *5*, 1075 (1987).
28. J. N. Mathur, M. S. Murali, M. V. Balarama Krishna, R. H. Iyer, R. R. Chitnis, P. K. Wattal, T. K. Theyyunni, A. Ramanujam, P. S. Dhami, and V. Gopal Krishnan, *Sep. Sci. Technol.*, *31*, 2045 (1996).
29. J. W. T. Spinks and R. J. Woods, *An Introduction to Radiation Chemistry*, Wiley, New York, NY, 1964, p. 94.
30. H. J. Arnikar, *Essentials of Nuclear Chemistry*, 2nd ed., Wiley Eastern Ltd., New Delhi, 1987, pp. 308, 309.
31. A. Tahraoui and J. H. Morris, *Sep. Sci. Technol.*, *30*, 2603 (1995).

Received by editor May 9, 1997
Revision received October 27, 1997