



**PARTITIONING OF ACTINIDE FROM SIMULATED
HIGH LEVEL WASTES ARISING FROM
REPROCESSING OF PHWR FUELS :
COUNTER CURRENT EXTRACTION STUDIES USING CMPO**

by

**D. S. Deshingkar, R. R. Chitnis, P. K. Wattal
T. K. Theyyuni and M. K. T. Nair**

Process Engineering and Systems Development Division

and

A. Ramanujam, P. S. Dhani, V. Gopalakrishnan and M. K. Rao
Fuel Reprocessing Group

and

J. N. Mathur, M. S. Murali and R. H. Iyer
Radiochemistry Division

and

L. P. Badheka and A. Banerji
Bio-Organic Division

1994

GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

**PARTITIONING OF ACTINIDES FROM SIMULATED
HIGH LEVEL WASTES ARISING FROM
REPROCESSING OF PHWR FUELS :
COUNTER CURRENT EXTRACTION STUDIES USING CMPO**

by

D.S. Deshingkar, R.R. Chitnis, P.K. Watal

T.K. Theyyuni and M.K.T. Nair

Process Engineering & Systems Development Division

A. Ramanujam, P.S. Dhani, V. Gopalakrishnan and M.K. Rao

Fuel Reprocessing Group

J.N. Mathur, M.S. Murali and R.H. Iyer

Radiochemistry Division

and

L.P. Badheka and A. Banerji

Bio-organic Division

BHABHA ATOMIC RESEARCH CENTRE
BOMBAY, INDIA

1994

BIBLIOGRAPHY DESCRIPTION SHEET FOR TECHNICAL REPORT
(as per IS : 9400 - 1980)

01	Security classification :	Unclassified
02	Distribution :	External
03	Report status :	New
04	Series :	BARC External
05	Report type :	Technical Report
06	Report No. :	BARC/1994/E/014
07	Part No. or Volume No. :	
08	Contract No. :	
10	Title and subtitle :	Partitioning of actinides from simulated high level wastes arising from reprocessing of PHWR fuels : counter current extraction studies using CMPO
11	Collation :	43 p., 2 tabs., 12 figs.
13	Project No. :	
20	Personal author (s) :	1) D.S. Deshingkar; R.R. Chitnis; P.K. Wattal; T.K. Theyyuni, M.K.T. Nair; (2) A. Ramanujam; P.S. Dhami; V. Gopalakrishnan; M.K. Rao; (3) J.N. Mathur; M.S. Murali; R.H. Iyer; (4) L.P. Badheka; A. Banerji
21	Affiliation of author (s) :	1) Process Engineering and Systems Development Division, BARC, Bombay (2) Fuel Reprocessing Group, BARC, Bombay; (3) Radiochemistry Division, BARC, Bombay and (4) Bio-Organic Division, BARC, Bombay
22	Corporate author(s) :	Bhabha Atomic Research Centre, Bombay-400 085
23	Originating unit :	Process Engineering and Systems Development Division, Bhabha Atomic Research Centre, Bombay
24	Sponsor(s) Name :	Department of Atomic Energy
	Type :	Government
30	Date of submission :	May 1994
31	Publication/Issue date	June 1994

contd... (ii)

(ii)

40 Publisher/Distributor : Head, Library and Information Division,
Bhabha Atomic Research Centre, Bombay

42 Form of distribution : Hard Copy

50 Language of text : English

51 Language of summary : English

52 No. of references : 13 refs.

53 Gives data on :

60 Abstract :High level wastes (HLW) arising from reprocessing of pressurised heavy water reactor (PHWR) fuels contain actinides like neptunium, americium and curium which are not extracted in the Purex process. They also contain small quantities of uranium and plutonium in addition to fission products. Removal of these actinides prior to vitrification of HLW can effectively reduce the active surveillance period of final waste form. Counter current studies using indigenously synthesised octyl (phenyl)-N, N-diisobutylcarbamoylmethylphosphine oxide (CMPO) were taken up as a follow up of successful runs with simulated sulphate bearing low acid HLW solutions. The simulated HLW arising from reprocessing of PHWR fuel was prepared based on presumed burnup of 6500 MWd/Te of uranium, 3 years cooling period and 800 litres of waste generation per tonne of fuel reprocessed. The alpha activity of the HLW raffinate after extraction with the CMPO - TBP mixture could be brought down to near background level.

70 Keywords/Descriptors : PHWR TYPE REACTORS; HIGH-LEVEL RADIOACTIVE WASTES; TBP; CMPO; DODECANE; URANIUM; PLUTONIUM; AMERICIUM; RUTHENIUM; PUREX PROCESS; MIXER-SETTLERS; ZIRCONIUM 95; IRON 59; EUROPIUM 152; EUROPIUM 154; NIOBIUM 95; CERIUM 144; TRACER TECHNIQUES; DISTRIBUTION FUNCTIONS; OXALIC ACID; SODIUM CARBONATES; NITRIC ACID; FLOWSHEETS; FISSION PRODUCTS; PARTITION; CESIUM; SOLVENT EXTRACTION; COUNTER CURRENT

71 Class No. : INIS Subject Category : E510J; B1620

99 Supplementary elements :

PARTITIONING OF ACTINIDES FROM
SIMULATED HIGH LEVEL WASTES ARISING FROM
REPROCESSING OF PHWR FUELS :
COUNTER CURRENT EXTRACTION STUDIES USING CMPO

ABSTRACT

High level wastes (HLW) arising from reprocessing of pressurised heavy water reactor (PHWR) fuels contain actinides like neptunium, americium and curium which are not extracted in the Purex process. They also contain small quantities of uranium and plutonium in addition to fission products. Removal of these actinides prior to vitrification of HLW can effectively reduce the active surveillance period of final waste form. Counter current studies using indigenously synthesised octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) were taken up as a follow up of successful runs with simulated sulphate bearing low acid HLW solutions. The simulated HLW arising from reprocessing of PHWR fuel was prepared based on presumed burn-up of 6500 MWd/Te of uranium, 3 years cooling period and 800 litres of waste generation per tonne of fuel reprocessed. An extraction step using 30 % TBP at aqueous to organic phase ratio of 2 : 1 reduced the uranium content from 18.3 to 0.044 g/litre. 98 % of plutonium was also removed in this step. A mixture of 0.2 M CMPO and 1.2 M TBP was used to study the extraction and stripping behaviour of uranium, plutonium and americium from simulated uranium lean PHWR - HLW solutions. The alpha activity of the HLW raffinate after extraction with the CMPO - TBP mixture could be brought down to near background level. Along with plutonium and americium, CMPO - TBP phase extracted 99.4 % of cerium, 99.7 % of europium, 100 % of zirconium and 31 % ruthenium. Extraction of cesium and strontium was negligible.

Americium, plutonium and uranium could be selectively stripped by 0.04 M HNO_3 , 0.05 M $\text{H}_2\text{C}_2\text{O}_4$ and 0.25 M Na_2CO_3 respectively from loaded CMPO - TBP phase. Cerium and europium followed americium during stripping runs. 28 % of the extracted (100 %) zirconium was stripped by 0.04 M HNO_3 , 67 % by 0.05 M $\text{H}_2\text{C}_2\text{O}_4$ and the remaining 5 % by Na_2CO_3 . Out of extracted (31 %) ruthenium, about 6 % was stripped by 0.04 M HNO_3 and 9 % by 0.05 M $\text{H}_2\text{C}_2\text{O}_4$ and the rest 15 % by 0.25 M Na_2CO_3 . These experiments proved the process feasibility for removal of actinides from HLW solutions to near background level.

TABLE OF CONTENTS

1.	INTRODUCTION	1
2.	PROCESS DESCRIPTION	3
3.	EXPERIMENTAL	6
	3.1 Preparation of Simulated PHWR_HLW Solution	6
	3.2 Estimation of Actinides and Fission Products	7
	3.3 Details of The Mixer Settler Unit	8
	3.4 Uranium and Plutonium Removal Step using 30 % TBP	9
	3.5 Extraction of Actinides by a Mixture of CMPO and TBP	10
	3.6 Selective Stripping of Americium from Loaded 0.2 M CMPO - 1.2 M TBP	11
	3.7 Stripping of Uranium , Plutonium and Residual Fission Products	12
4.	RESULTS AND DISCUSSION	13
5.	CONCLUSIONS	19
6.	ACKNOWLEDGMENT	19
7.	REFERENCES	20
	Tables	23
	Figures	26

PARTITIONING OF ACTINIDES FROM
SIMULATED HIGH LEVEL WASTES ARISING FROM
REPROCESSING OF PHWR FUELS :
COUNTER CURRENT EXTRACTION STUDIES USING CMPO

1.0 INTRODUCTION

Reprocessing of spent fuels from power reactors by Purex process is mainly aimed at recovery of uranium and plutonium(1). The high level waste (HLW) solution generated in this process contains fission products and small amounts of uranium and plutonium. The principal activation and decay products of uranium and plutonium, namely neptunium, and americium which are not extracted by tri-n-butyl phosphate (TBP) in the Purex process also end up in the HLW solutions. The HLW solutions are vitrified into a glass matrix for disposal in deep geological repositories. The current practice of direct vitrification of HLW results in an alpha bearing matrix that requires surveillance for thousands of years(2).

Solvent extraction techniques are being developed (3,4) to recover almost 100 % of these actinides from the HLW solutions. Octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) is presently the most accepted (5,6) extractant because of its capability to extract trivalent actinides, uranium and plutonium without any feed adjustment of HLW solutions. Neptunium can also be extracted (7) by CMPO by suitable valency adjustment.

Indigenously synthesised CMPO has been successfully tested (6) for the extraction of actinides and fission products from nitric acid solutions and also from actual HAW and HLW solutions of PUREX origin (8,9). Studies have also been carried out for the batch recovery of minor actinides from simulated sulphate bearing, low acid high salt containing HLW solutions and have subsequently been extended to the counter-current extraction runs using mixer-settlers(10). The present work deals with the counter current studies on simulated HLW arising from reprocessing of pressurised heavy water reactor (PHWR) fuels (PHWR-HLW) where the acidity encountered is about 3 M HNO₃. Based on the experience gained, modifications were incorporated in the process flow sheet after batch experiments (11). Scope of the work was limited to standardisation of the flowsheet for experiments with actual HLW solutions. The report discusses the findings of these experiments.

2.0 PROCESS DESCRIPTION

High concentrations of uranium cause third phase formation when mixture of 0.2 M CMPO and 1.2 M TBP in n-dodecane is used as the extractant (10,11). Therefore the process involves uranium removal as the first step for the HLW solutions containing significant quantities of uranium. This removal was achieved by a 4 stage mixer-settler unit using 30 % TBP in n-dodecane. Uranium lean HLW raffinate was contacted with CMPO-TBP mixture for actinide partitioning. The loaded organic phase is selectively stripped by dilute nitric acid and oxalic acid for americium and plutonium respectively. This is followed by a solvent wash step to remove residual actinides and fission products.

In the earlier experiments with simulated sulphate bearing, low acid, high salt containing HLW solution, this flow sheet was followed (10) at aqueous to organic phase ratio of 1:1. For actinide partitioning from simulated PHWR_HLW solutions using CMPO-TBP, the following process modifications were incorporated based on batch experimental studies (11) :

(i) If the waste solution contains about 20 g/l uranium, the extraction mixture of 0.2 M CMPO - 1.2 M TBP gives third phase

formation, which could not be avoided even by increasing TBP content to 1.4 M and aqueous to organic phase ratio to 1 : 2. Hence, a step to deplete the uranium content in the PHWR-HLW solutions was a prerequisite before proceeding to the CMPO-TBP extraction step. 30 % TBP extraction step at an aqueous to organic phase ratio of 2 : 1 was used to achieve higher loading of uranium. 30 % TBP also extracted plutonium from HLW solutions. No scrub was provided at this step.

(ii) As simulated PHWR-HLW solutions contain 3 M HNO_3 , the acidity of the loaded organic phase was expected to be high. Hence CMPO-TBP mixture was not preequilibrated with acid before use in the extraction step.

Extraction of corrosion product iron present in HLW was found to be high in the experiments conducted with simulated sulphate bearing HLW (10). The distribution ratios for iron and americium in 0.2 M CMPO - 1.2 M TBP mixture are known to decrease with decrease in acidity of aqueous phase. Hence low acid scrub was incorporated to strip iron from loaded CMPO-TBP phase. To avoid stripping of americium along with iron in the scrub stages, as this would have lead to only partial recovery of actinides in extraction step, the acidity of organic phase was lowered to a limited extent. Based on batch studies, 0.1 M HNO_3 was selected as scrub acid (11).

(iii) As 30 % TBP extracts most of the plutonium, the CMPO-TBP phase contains americium as the major alpha activity. The acidity of bulk loaded CMPO-TBP phase was still quite high. This had led to reflux of americium during stripping in experiments with simulated sulphate bearing low acid HLW solutions (10). Hence two separate strippings of loaded CMPO-TBP phase with 0.04 M HNO₃ were carried out. The first stripping involving 2 stages reduced the acidity of loaded organic phase and also partly stripped americium and rare earths. The second stripping with 0.04 M HNO₃ using 4 stages removed residual americium and rare earths from the organic phase. This helped in almost complete stripping of americium.

(iv) The americium lean CMPO-TBP phase contained plutonium, zirconium and ruthenium as principal activities. As zirconium forms oxalate complexes which are soluble in excess of oxalic acid, it was decided to use 0.05 M oxalic acid instead of 0.01 M used in earlier experiments(10). The zirconium present in organic phase is about 0.01 M. Oxalic acid could strip both plutonium and zirconium. The alpha lean CMPO-TBP solvent contained only uranium and the residual zirconium and ruthenium activities. As in earlier runs, 0.25 M sodium carbonate wash was given to make CMPO - TBP solvent suitable for recycle.

The revised flow sheet used in these sets of experiments is shown in Fig. 1.

3.0 EXPERIMENTAL

3.1 Preparation of Simulated PHWR-HLW Solutions

PHWR's use natural uranium in the form of UO_2 as fuel. An average burn-up of 6500 MWD/Te of uranium and 3 year cooling period for the fuels was assumed to arrive at the fission product concentrations. HLW generation rate of 800 liters/Te of fuel reprocessed was also assumed. The sodium and corrosion product contents were added based on experience with PHWR-HLW solutions. Uranium content was maintained at 18.3 g/l to be on the conservative side in order to gain experience in dealing with such wastes. For rare fission products, equimolar quantities of chemically similar elements were added. Use of chlorides, sulphates and oxalates was avoided by converting them into nitrates before mixing using appropriate chemical methods. Concentrated solutions of hygroscopic substances were analysed by volumetric (mainly complexometric) methods to find the actual concentrations. It was found that the simulated PHWR_HLW solution thus prepared gave small quantities of precipitates. Hence it was filtered through Whatman No. 1 paper before use.

3.5 liters of this solution was spiked with 0.5 ml of high active waste concentrate (HAW CON) from the reprocessing plant to

follow the fission product profiles during extraction and stripping. ^{95}Zr - ^{95}Nb , $^{152,154}\text{Eu}$, ^{59}Fe , plutonium and americium tracers were added in the nitrate form. The composition of the simulated PHWR HLW is given in Table 1.

3.2 Estimation of Actinides and Fission Products

For the estimation of uranium from the aqueous samples, it was first extracted by tri-n-octyl phosphine oxide (TOPO) in benzene to avoid the interference due to the presence of other metal ions; especially iron. The organic phase was analysed by 2-(5-Bromo-2 pyridylazo)-5 diethyl-aminophenol (Bromo-PADAP) method (12). At higher concentrations, it was analysed by thiocyanate method (13) after appropriate dilution. Organic samples were analysed for uranium content by the same method without any pretreatment. The gross alpha activities in the samples were estimated by direct planchetting on a 25 mm dia. SS planchette and counting in an alpha proportional counter. Plutonium alpha activities were determined by extracting plutonium in 0.5 M thenoyltrifluoro acetone (TTA) in xylene and subjecting an aliquot of the extract to alpha radiometry. The difference between gross alpha and that due to plutonium is reported as americium activity. The gross beta activities were determined by counting a dried aliquot in a beta proportional counter and the gross gamma activities on a scintillation counter

using NaI(Tl) detector. Individual fission products were determined by gamma spectrometry with a HPGe detector connected to a 4K multichannel analyser. The behaviour of iron, a corrosion product, was studied by using ^{59}Fe radiotracer.

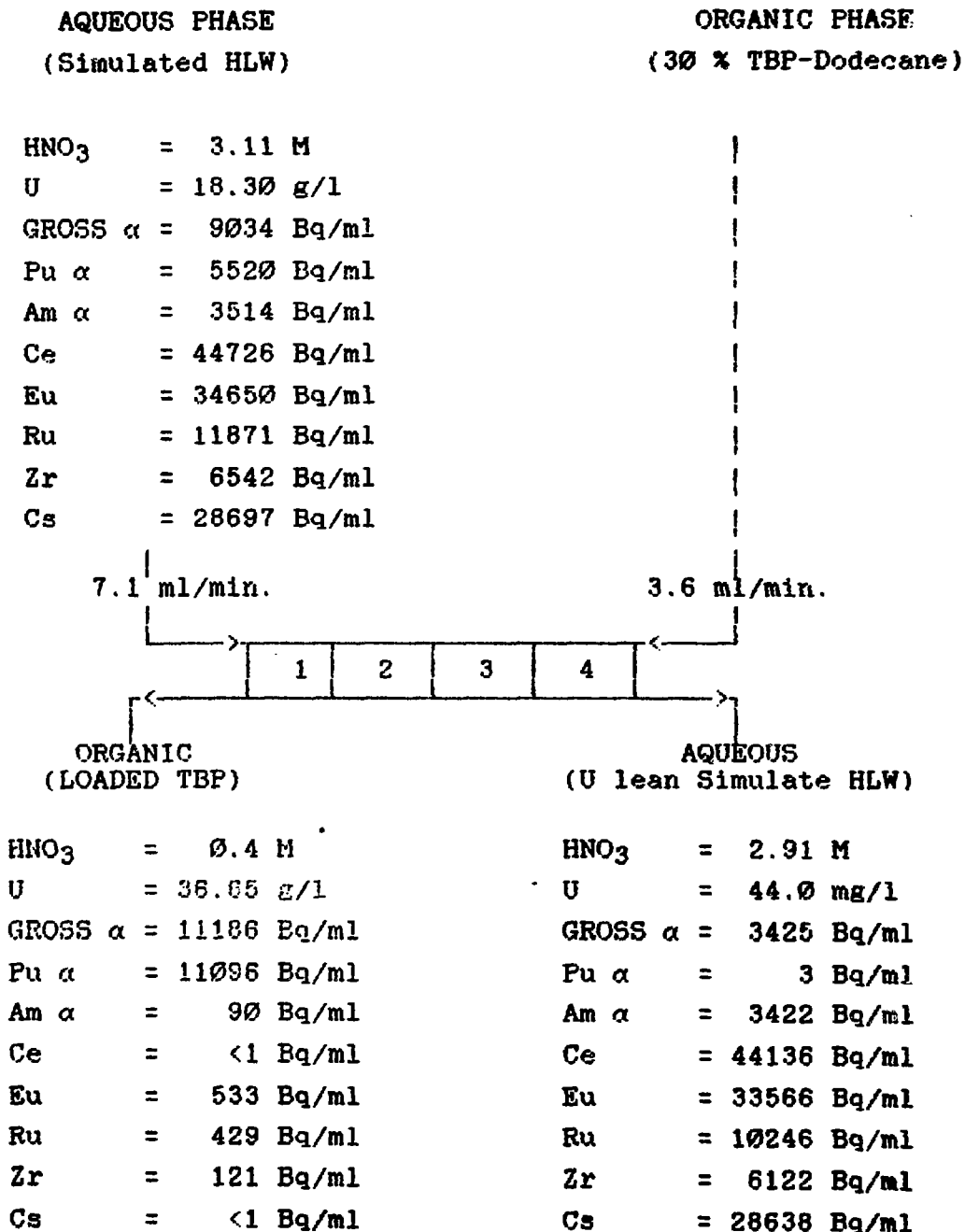
3.3 Details of Mixer-Settler Unit

The mixer-settler had mixer capacity of 30 ml. The mixer to settler volume ratio was 1:4.3. The mixing chamber had bottom inlets for organic and aqueous feeds. The contents of the mixing chamber were continuously stirred by a 12 Volt D.C. motor. The stirrer also provided suction for both the feed solutions. The overflow from mixer to settler was through a trap to minimise the disturbances at the interphase. Mixer settler units having different number of stages were assembled to meet the required operational scheme of each run. To start with, the mixer-settler was filled with equal volumes of both the phases. Feed solutions were introduced to the mixer-settler at the predetermined rates using peristaltic pumps kept outside the fume hood.

During extraction as well as stripping runs, exit spot samples were collected from both the aqueous and organic phases at different time intervals to check the attainment of equilibrium. Stage samples were collected at the end of the run. The bulk exit phases collected during mixer-settler operation were analysed and used as feed for the next run.

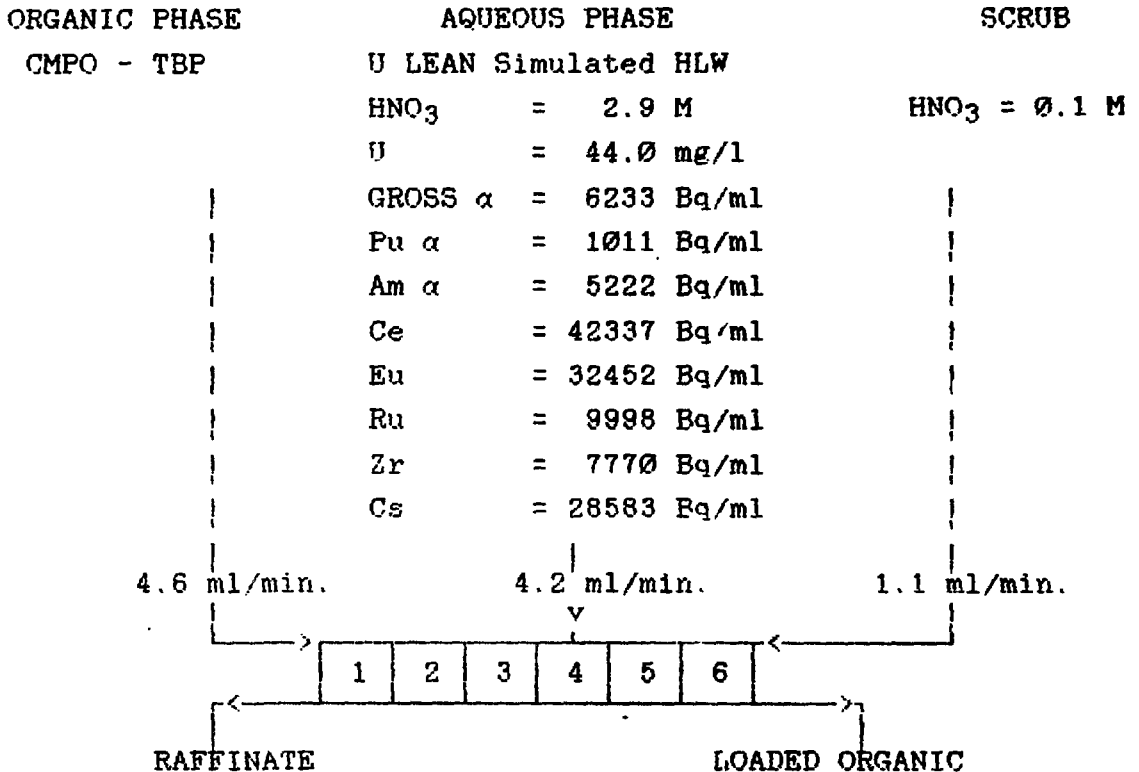
3.4 Uranium and Plutonium Removal Step using 30 % TBP

The scheme used for this process step along with the actinide and fission product activities in the feed and exit spot samples is indicated below :



3.5 Actinide Extraction using a Mixture of CMPO and TBP

To the bulk raffinate from TBP run, plutonium, americium, ^{95}Zr - ^{95}Nb and ^{59}Fe were added to increase the respective activity levels to achieve accuracy in activity balance. Two scrub and 4 extraction stages were used. The following scheme was employed :



(Alpha free Simulated HLW)

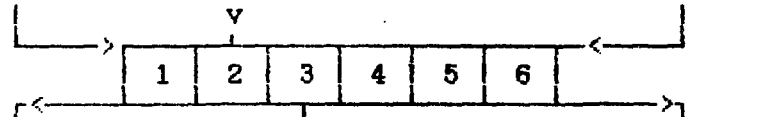
HNO_3 = 1.88 M	HNO_3 = 0.36 M
U = <0.1 mg/l	U = 44 mg/l
GROSS α = <1 Bq/ml	GROSS α = 6031 Bq/ml
Pu α = <1 Bq/ml	Pu α = 918 Bq/ml
Am α = <1 Bq/ml	Am α = 5113 Bq/ml
Ce = 259 Bq/ml	Ce = 41082 Bq/ml
Eu = 93 Bq/ml	Eu = 31248 Bq/ml
Ru = 6623 Bq/ml	Ru = 3275 Bq/ml
Zr = <1 Bq/ml	Zr = 7219 Bq/ml
Cs = 28538 Bq/ml	Cs = <1 Bq/ml

3.6 Selective Stripping of Americium from Loaded CMPO-TBP Phase

Two steps of strippings of loaded CMPO-TBP by 0.04 M HNO₃ were carried out simultaneously. The aqueous phases of these strippings were separately collected.

The following scheme was used:

	ORGANIC LOADED CMPO+TBP	STRIP 1 0.04 M HNO ₃	STRIP 2 0.04 M HNO ₃
HNO ₃	= 0.35 M		
U	= 44 mg/l		
GROSS α	= 4836 Bq/ml		
Pu α	= 965 Bq/ml		
Am α	= 3871 Bq/ml		
Ce	= 40543 Bq/ml		
Eu	= 30993 Bq/ml		
Ru	= 3257 Bq/ml		
Zr	= 7585 Bq/ml		
	4.6 ml/min.	4.6 ml/min.	4.6 ml/min.



		PRODUCT AQ. 1	PRODUCT AQ. 2	Am LEAN ORGANIC
HNO ₃	(M)	0.38	0.08	0.07
U	(mg/l)	0.0	0.0	44
GROSS α	(Bq/ml)	1491	2047	959
Pu α	(Bq/ml)	<1	5	959
Am α	(Bq/ml)	1491	2042	<1
Ce	(Bq/ml)	16567	23893	<1
Eu	(Bq/ml)	15916	15695	<1
Ru	(Bq/ml)	<1	615	2778
Zr	(Bq/ml)	736	1369	5180

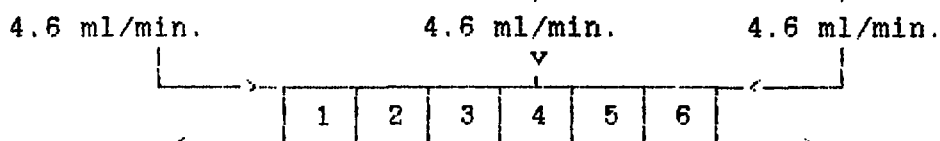
3.7 Stripping of Uranium, Plutonium and Residual Fission Products:

The americium lean organic phase contained only zirconium and ruthenium as major fission product activities. It was decided to carry out oxalic acid stripping and sodium carbonate wash steps simultaneously.

Following scheme was used:

AMERICIUM	H ₂ C ₂ O ₄	Ø.25 M
LEAN	Ø.Ø5 M	Na ₂ CO ₃
CMPO-TBP	STRIP	STRIP

HNO ₃	= Ø.Ø7 M		
U	= 44 mg/l		
GROSS α	= 959 Bq/ml		
Pu α	= 959 Bq/ml		
Ru	= 2698 Bq/ml		
Zr	= 4749 Bq/ml		



	H ₂ C ₂ O ₄		Na ₂ CO ₃		ORGANIC
U	(mg/l) Ø.Ø		44		ØØ
GROSS α	(Bq/ml) 95Ø		3		8
Pu α	(Bq/ml) 95Ø		3		8
Ru	(Bq/ml) 92Ø		1523		16Ø
Zr	(Bq/ml) 3525		1ØØ4		76

Stagewise profiles of activities obtained during these runs are indicated in Figs. 2 to 12.

4.0 RESULTS AND DISCUSSIONS

The distribution of activities to different secondary streams generated by using the scheme given in Fig. 1 for simulated PHWR-HLW (composition given in Table 1) is presented in Table 2.

Fig. 2 shows the uptake of activities by 30 % TBP-dodecane. It can be seen that only a small fraction of beta and gamma activities are extracted by 30 % TBP. The gross alpha activity in the aqueous phase stabilises after 2 stages due to the extraction of most of plutonium.

Fig. 3 shows the extraction of uranium, plutonium and americium by 30 % TBP. About 99.7 % of uranium, 98 % of plutonium and about 1 % of americium were extracted by 30 % TBP.

From Fig. 4 it can be seen that the extraction of europium, ruthenium and zirconium was about 3, 1 and 2 percent respectively. The cerium was extracted by fresh 30 % TBP in the stages where uranium loading was less and was stripped back when uranium loading increased.

The uranium lean simulated HLW solution had an acidity of 2.9 M as against 3.1 M of the simulated waste solution indicating small acid uptake by 30 % TBP.

The loaded TBP contained about 36.65 g of uranium per litre and small amounts of plutonium, americium and fission products. It will be advantageous if a solvent extraction step is introduced for removal of uranium and plutonium from HAW CON solution before the same is transferred to Waste Tank Farm Facility for storage.

For removal of actinides from uranium lean simulated HLW, 4 extraction stages and 2 low acid scrub stages were employed. The aqueous to organic phase ratios of about 1 : 1.2 in extraction stages and 1 : 4 in scrub stages were maintained. From Figs. 5 and 6 it can be seen that all plutonium and americium alpha activities were removed from the uranium lean simulated HLW solution in 3 stages of extraction. As the distribution ratio of plutonium in CMPO-TBP phase is high, it was not detected in aqueous scrub streams. Decrease in distribution ratio for americium with acidity resulted in its partial stripping in scrub stages. However, this did not lead to release of americium in the HLW raffinate. Alpha activity of the raffinate was near background level.

It may be noted that actual HLW solutions may contain neptunium in addition to uranium, plutonium and americium. Neptunium can be extracted by CMPO after reducing it to Np(IV) state (7). Hence minor modification of this extraction step can effectively remove all actinides from HLW solutions.

From Fig. 5, it is further seen that along with alpha activities, fission product β and τ activities are extracted by CMPO-TBP phase in significant quantities. From Fig. 7 it can be seen that about 99.4 % of cerium, 99.6 % of europium and 100 % of zirconium get extracted during the process. Because of scrubbing effect, cerium and europium get extracted to lesser extent compared to americium as observed from Fig. 7. The extraction of ruthenium was about 31 % and that of cesium negligible. Strontium extraction is expected to be similar to that of cesium.

The acidity of organic phase in the extraction stages was about 0.74 M and could be brought down to 0.35 M by incorporating 2 scrub stages with 0.1 M HNO₃ (Fig. 6). Iron uptake was noticed in the extraction stages but due to stripping in the scrub stages only 1 % was found in the loaded CMPO-TBP phase. This is much lower than that observed in experiments with simulated sulphate bearing wastes (16 %) (10).

It was decided to carry out 2 step stripping process for the loaded CMPO-TBP phase using 0.04 M HNO₃ as proposed in the scheme (Fig. 1). The aqueous to organic phase ratio was maintained at 1 : 1 in both the strippings so as to ensure complete recovery of americium. The first two stages were mainly to reduce the acidity of the loaded CMPO-TBP phase to facilitate stripping of americium in the rest of 4 stages. The aqueous phase containing americium from the last 4 stages was collected separately. This prevented reextraction of americium in the organic phase.

As seen in Fig. 8, during stripping with 0.04 M HNO₃, the gross alpha activity of loaded CMPO-TBP phase initially decreased and then stabilised. This was due to complete removal of americium from organic phase. Major amount of plutonium remained with the organic phase as seen in Fig. 9. Stripping of americium was about 38.5 % in first step and all the rest in the 2 stages of second step.

From Fig. 8 and 10, it can be seen that large fractions of fission products were also stripped along with americium. The cerium and europium follow similar stripping pattern as that of americium (Fig. 9). In the first 0.04 M HNO₃ stripping step,

40.9 % of cerium, 51.4 % of europium, 9.7 % of zirconium were stripped from loaded CMPO-TBP phase. In the second step of 4 stages, all the rest of cerium and europium and 18.4 % of zirconium were stripped. Out of 31 % of ruthenium extracted in the CMPO-TBP phase, only 6 % was stripped in 4 stages of second step. All of the iron extracted in CMPO-TBP phase (1 %) was completely stripped by first 0.04 M HNO₃ stripping.

Even though the volume of secondary streams had increased by 2 step stripping, it ensured the complete and selective recovery of americium. The product nitric acid streams had low dissolved solids and were almost identical in chemical composition. Hence they can be mixed and evaporated to a much smaller volume.

Plutonium was the only significant alpha activity left in nitric acid stripped CMPO-TBP phase. 0.05 M oxalic acid was employed for stripping of plutonium using 4 stages. After oxalic acid stripping, trace quantities of only uranium, zirconium and ruthenium remain in CMPO-TBP phase. A two stage stripping step using 0.25 M sodium carbonate solution was necessary to make organic phase free from residual activity before recycling.

From Fig. 11, it can be seen that almost all plutonium was stripped by 0.05 M oxalic acid in 4 stages. The uranium stripping was negligible. The traces of uranium and plutonium left in CMPO-TBP phase were stripped by 0.25 M carbonate.

From Fig. 12 it can be seen that zirconium and ruthenium were stripped by $H_2C_2O_4$ partially. The residual ruthenium and zirconium were stripped by 0.25 M Na_2CO_3 . Out of 72 % of zirconium present in americium lean CMPO-TBP, 67 % was stripped by oxalic acid and 5 % by sodium carbonate. Out of 25 % of ruthenium present in americium lean CMPO-TBP, 8.9 % was stripped by oxalic acid and 14.5 % by sodium carbonate. Small quantity of crud was observed in the first 2 stages of oxalic acid stripping step. The exit aqueous phases were clear. The exit organic phase had turbid appearance due to emulsion formation. A contact with acid was found to be sufficient to get the organic phase clear. The exit organic phase is suitable for recycle. 0.05 M $H_2C_2O_4$ stripped substantial ruthenium.

As seen from Table 2, the overall activity balance was satisfactory and was within ± 2 %. Ruthenium and zirconium were distributed in almost all stripping solutions unlike the observations made in earlier experiments with sulphate bearing HLW (10).

5.0 CONCLUSIONS

The alpha activity of PHWR-HLW solution could be brought down to near background level by using a mixture of 0.2 M CMPO and 1.2 M TBP in dodecane as extractant. In case the uranium content of these wastes is high, extraction with 30 % TBP is a prerequisite before CMPO extraction step to avoid third phase formation. Low acid scrub was successfully used to decrease the iron content of the loaded organic phase. Two step stripping process with 0.04 M HNO₃ was found to be useful for selective and complete stripping of americium. Use of 0.05 M H₂C₂O₄ and 0.25 M Na₂CO₃ as strip solutions removed plutonium and residual uranium respectively. The CMPO used in these experiments was the one already used for experiments with simulated sulphate bearing HLW solutions.

6.0 ACKNOWLEDGMENTS

The authors thank Mr. A. N. Prasad, Director, Bhabha Atomic Research Centre for his interest, encouragement and guidance during the course of this work.

7.0 REFERENCES

1. S. Glasstone and A. Sesonske, " Nuclear Reactor Engineering" Chapter 8 Van Nostrand Reinhold Company New York (1967).
2. J. L. Desvaux, D. Jean and L. Baillif " Industrial HLW Immobilization in Glass in France . Vitrified Waste Characterization and Quality Control Programme" Proceedings of Symposium on Geological disposal of Spent Fuel and High Level and Alpha Bearing Wastes held at Antwerp Germany 19-23 October 1992 IAEA-SM-326/42 pp201 -208 (1992).
3. E. P. Horwitz, H. Diamond, D. G. Kalina, L. Kaplan and G. W. Mason "Octyl(phenyl) - N, N'-diisobutylcarbamoylmethylphosphine Oxide as an Extractant for Actinides from Nitric Acid Waste". International Solvent Extraction Conference. Denver, U.S.A. August 21-September 2, (1983).
4. M. Ozawa, S. Nemoto, A. Togashi, T. Kawata and K. Onishi. "Partitioning of Actinides and Fission Products in Highly Active Raffinate from Purex Process by Mixer Settlers", Sol. Ex. and Ion Exch. 10 (5), 829-846 (1992).

5. E. P. Horwitz and W. W. Shultz. "The TRUEX Process : A Vital Tool for Disposal of U.S. Defence Nuclear wastes", Proceedings of Symposium on New Separation Chemistry for Radioactive wastes and Other specific Applications, held at Rome May 16-18 (1990).

6. J. N. Mathur, M. S. Murali, P. R. Natarajan, L. P. Badheka and A. Banerji. "Extraction of Actinides and Fission Products by Octyl(phenyl)- N,N-diisobutylcarbamoylmethylphosphine Oxide from Nitric Acid Media", Talanta 39 (5), 493-496 (1992).

7. D. S. Wisnubroto, S. Nagasaki, Y. Enokida and A. Suzuki "Solvent Extraction of Neptunium by "Octyl(phenyl) - N, N' - diisobutylcarbamoylmethylphosphine Oxide from Nitric Acid Solution Containing Hydrogen Peroxide" Solvent Extr. and Ion Exch. 11 (4) 569-83 (1993).

8. J. N. Mathur, M. S. Murali, P. R. Natarajan, L. P. Badheka, A. Banerji, A. Ramanujam, P. S. Dhami, V. Gopalakrishnan, R. K. Dhumwad and M. K. Rao " Partitioning of Actinides from High Level Waste Streams of Purex Process using Mixtures of CMPO and TBP in Dodecane" Waste Management 13 317-325 (1993).

9. J. N. Mathur, M. S. Murali, P. R. Natarajan, L. P. Badheka, A. Banerji, A. Ramanujam, P. S. Dhami, V. Gopalakrishnan, R. K. Dhumwad and M. K. Rao. "Extraction of Actinides from High Level Waste Streams of PUREX Process Using Mixtures of CMPO and TBP in Dodecane", BARC Report BARC/1992/E/009 (1992).

10. D. S. Deshingkar, R. R. Chitnis P. K. Wattal, T. K. Theyyuni, A. Ramanujam, P. S.Dhami, V. Gopalakrishnan, M. K. Rao, J. N. Mathur, M. S. Murali and R. H. Iyer, L. P. Badheka and A. Banerji " Counter Current Studies on Actinide Partitioning from Sulphate Bearing Simulated High Level Waste using CMPO" BARC Report BARC/1993/E/028 (1993)

11. D. S. Deshingkar, R. R. Chitnis P. K. Wattal. T. K. Theyyuni, A. Ramanujam, P. S.Dhami, V. Gopalakrishnan, M. K. Rao, J. N. Mathur, M. S. Murali and R. H. Iyer, L. P. Badheka and A. Banerji " Partitioning of Actinides from High Level Waste Solutions Using CMPO-Counter Current Studies" National Symposium on Organic Reagents- Synthesis and Use in Extraction Metallurgy (ORSUEM-94) Held at Bombay February 9-11, 1994 (1994).

12. S. K. Das, S. G. Rege, A. Mukherjee, A. Ramanujam and R. K. Dhumwad. " Direct Spectrometer Method for the Determination of Microgram Quantities of Uranium with Bromo-PADAP in Aqueous and Organic Waste Streams of Purex and Thorex Processes", BARC Report, BARC-1539 (1991).

13. C. D. Crouthamel and C. E. Johnson. " Spectrophotometric Determination of Uranium by Thiocyanate Method in Acetone Medium", Anal. Chem., vol. 24 1780-83 (1952).

LIST OF TABLES

- Table 1 Composition of Simulated High Level Wastes Arising
 from Reprocessing of Pressurised Power Reactor Fuel
- Table 2 Distribution of Activities to Different Secondary
 Streams During Actinide Partitioning from Simulated
 HLW Arising from Reprocessing of PHWR Fuel

Table 1

COMPOSITION OF SIMULATED HIGH LEVEL WASTES
ARISING FROM REPROCESSING OF PHWR FUELS

Element	Concn. (g/Te of UO ₂)	concn. g/l in HLW	Salt used	Activity added (Bq/ml)
Se	11.13	0.0123	Se metal	
Br	4.460	0.0049	KBr	
Rb	67.6	0.0745	CsNO ₃	
Sr	168.9	0.1836	Sr(NO ₃) ₂	
Y	89.84	0.0990	La(NO ₃) ₃ .6H ₂ O	
Zr	700.1	0.7714	Zr(NO ₃) ₄	6542
Mo	663.2	0.7307	Na ₂ MoO ₄	
Tc	164.8	0.1836	Na ₂ MoO ₄	
Ru	421.3	0.4652	Ru(NO ₃) ₃	11871
Rh	115.7	0.1275	Co(NO ₃) ₂ .6H ₂ O	
Pd	242.5	0.2672	Ni(NO ₃) ₂ .6H ₂ O	
Ag	16.92	0.0186	AgNO ₃	
Cd	14.38	0.0159	Cd(NO ₃) ₂ .4H ₂ O	
Sn	13.75	0.0152	Sn metal	
Te	93.29	0.1028	TeO ₂	
I	46.85	0.0520	KI	
Cs	493.4	0.5437	CsNO ₃	28697
Ba	280.3	0.3089	Ba(NO ₃) ₂	
La	239.8	0.2643	La(NO ₃) ₃ .6H ₂ O	
Ce	483.1	0.5323	Co(NO ₃) ₃ .6H ₂ O	44726
Pr	221.3	0.2436	La(NO ₃) ₃ .6H ₂ O	
Nd	782.7	0.8624	Nd(NO ₃) ₃ .6H ₂ O	
Pm	25.65	0.0283	La(NO ₃) ₃ .6H ₂ O	
Sm	148.8	0.1640	Sm ₂ O ₃	
Eu	20.52	0.0227	Eu ₂ O ₃	34650
Gd	15.0	0.0165	Gd(NO ₃) ₃ .6H ₂ O	
Inert Ingredients :				
Na		3.0	NaNO ₃	
Fe		0.5	Fe(NO ₃) ₃ .9H ₂ O	1671
Cr		0.1	CrO ₃	
Ni		0.1	Ni(NO ₃) ₂ .6H ₂ O	
actinides :				
U	9.815x10 ⁵	0.9030	UO ₂ (NO ₃) ₂ .6H ₂ O	18.325*
Pu			Pu(NO ₃) ₄	5520
Am			Am(NO ₃) ₃	3514

* g/liter

Table 2

DISTRIBUTION OF ACTIVITIES TO DIFFERENT STREAMS DURING
ACTINIDE PARTITIONING FROM SIMULATED
HLW ARISING FROM REPROCESSING OF PHWR FUEL

Sr. No.	Activity	30 % TRP	Percent Activity Distributed to Secondary stream Generated				
			CMPO raffinate	HNO ₃ Strip1	Strip 2	H ₂ C ₂ O ₄ stripping	Na ₂ CO ₃ stripping
1	U	99.7	< 0.01	< 0.01	< 0.01	< 0.01	0.3
2	Pu	98.0	<< 0.01	<< 0.01	< 0.01	2.00	<< 0.01
3	Am	1.2	<< 0.01	38.5	63.8	< 0.01	<< 0.01
4	Ce	< 0.1	0.6	40.9	59.0	< 0.01	<< 0.01
5	Eu	0.8	0.3	51.4	50.6	< 0.01	<< 0.01
6	Ru	1.5	65.1	0.0	6.1	8.9	14.7
7	Zr	0.9	<< 0.01	9.7	18.4	67.4	5.8
8	Cs	0.0	100.0	0.0	0.0	0.0	0.0
9	Fe	0.0	99.0	1.0	0.0	0.0	0.0

LIST OF FIGURES

- Fig. 1 Actinide Partitioning Scheme for Simulated PHWR High Level Wastes using TBP and CMPO
- Fig. 2 Extraction of Gross Activities from Simulated PHWR - HLW Solution by 30 % TBP
- Fig. 3 Extraction of Actinides from Simulated PHWR-HLW Solution by 30 % TBP
- Fig. 4 Behaviour of Fission Products during Extraction of Actinides from Simulated PHWR - HLW Solution by 30 % TBP
- Fig. 5 Extraction of Gross Activities from Uranium Lean Simulated HLW by CMPO + TBP
- Fig. 6 Extraction of Actinides from Uranium Lean Simulated HLW by CMPO - TBP and Acidity of Organic and Aqueous Phases
- Fig. 7 Behaviour of Fission Products during Extraction of Actinides from Uranium Lean Simulated HLW by CMPO - TBP
- Fig. 8 Stripping of Gross Activities by 0.04 M HNO₃ from Loaded CMPO - TBP
- Fig. 9 Stripping of Actinides by 0.04 M HNO₃ from Loaded CMPO - TBP and Acidity of Organic and Aqueous Phases
- Fig. 10 Behaviour of Fission Products during Stripping of Actinides by 0.04 M HNO₃ from Loaded CMPO - TBP
- Fig. 11 Stripping of Gross Activities by 0.05 M H₂C₂O₄ and 0.25 M Na₂CO₃ from Americium Lean CMPO - TBP
- Fig. 12 Behaviour of Fission Products During Stripping of Actinides by 0.05 M H₂C₂O₄ and 0.25 M Na₂CO₃ from Americium Lean CMPO - TBP

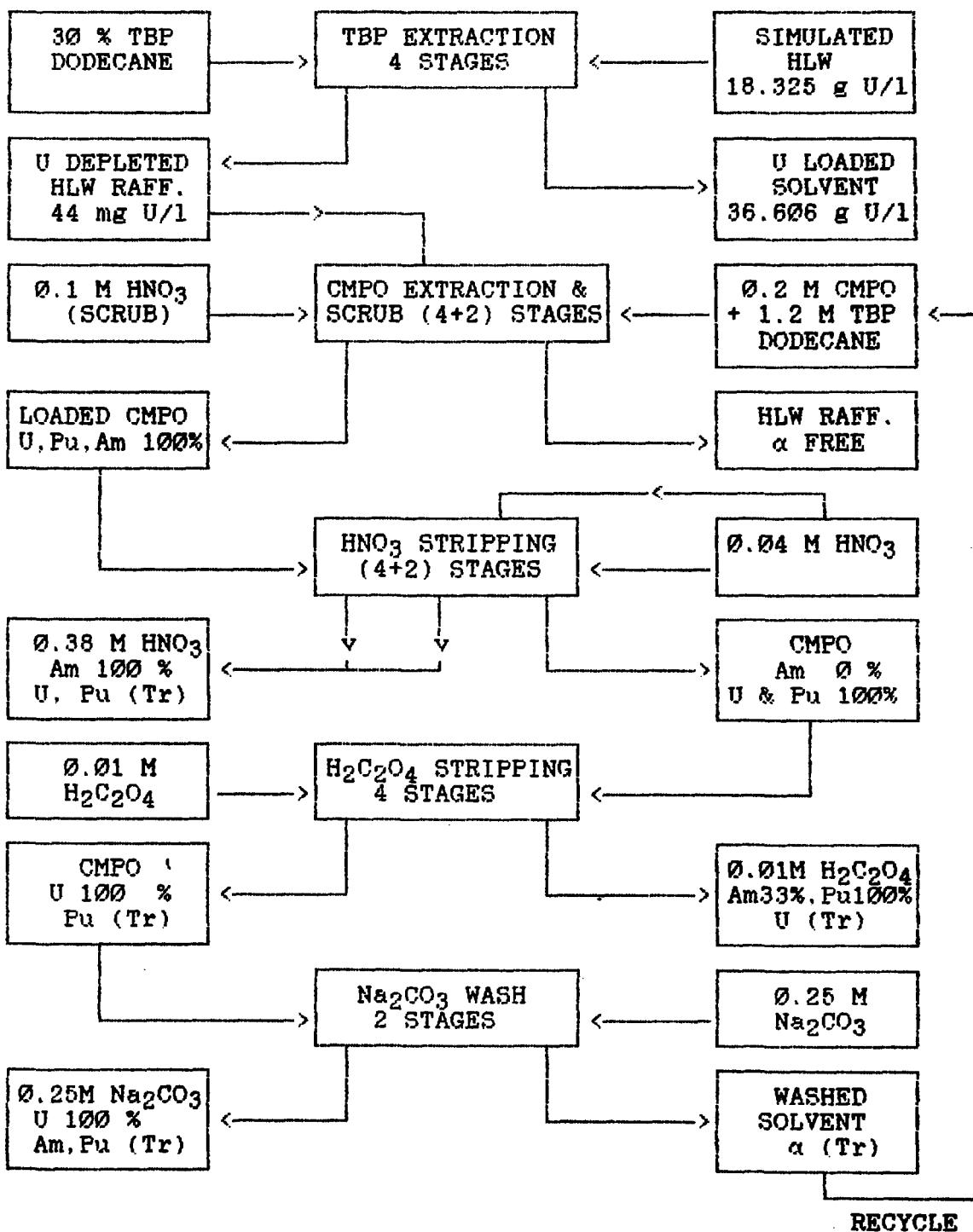


FIG. 1 ACTINIDE PARTITIONING SCHEME FOR SIMULATED PHWR HIGH LEVEL WASTES USING TBP AND CMPO

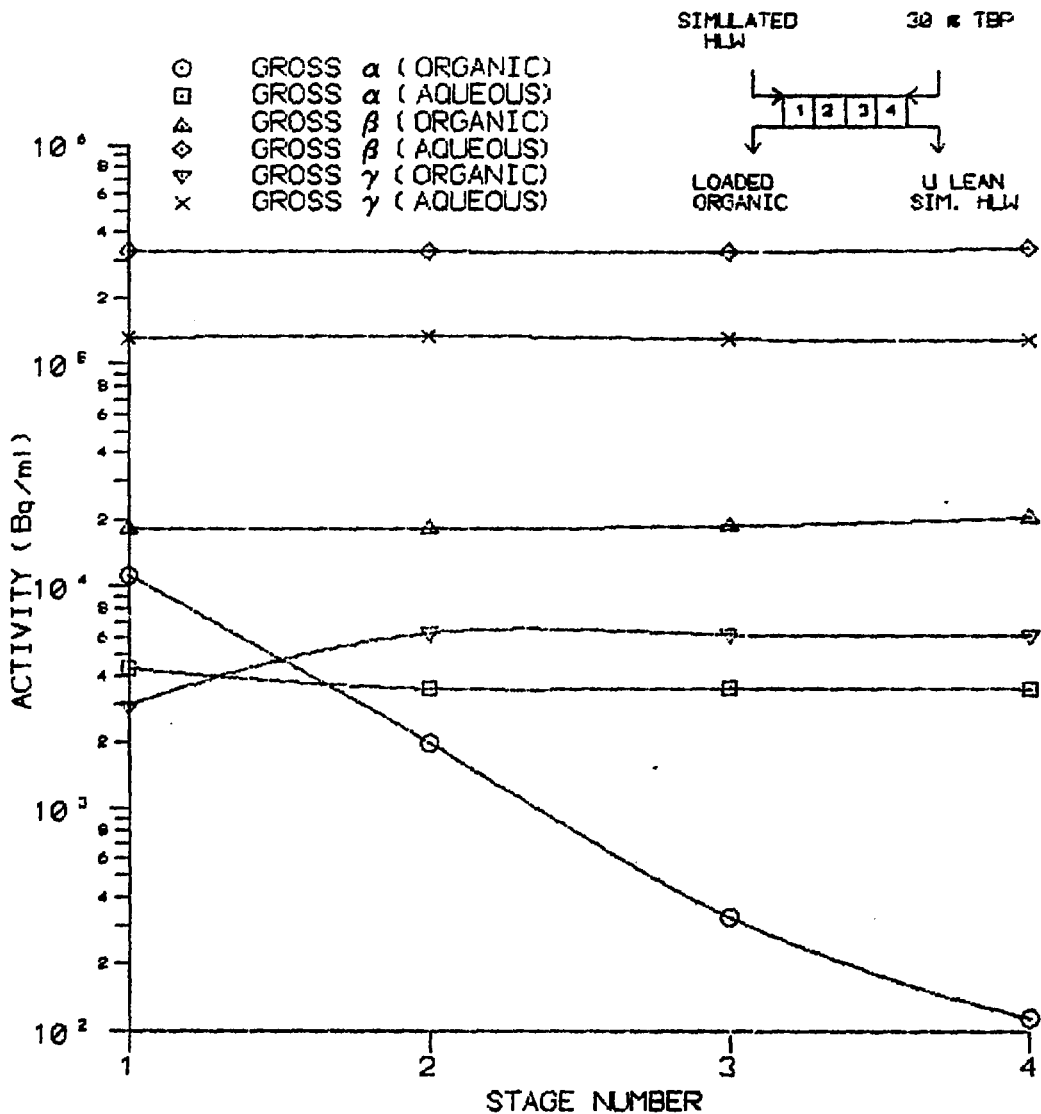


FIG. 2 EXTRACTION OF GROSS ACTIVITIES FROM SIMULATED PHWR - HLW SOLUTION BY 30% TBP

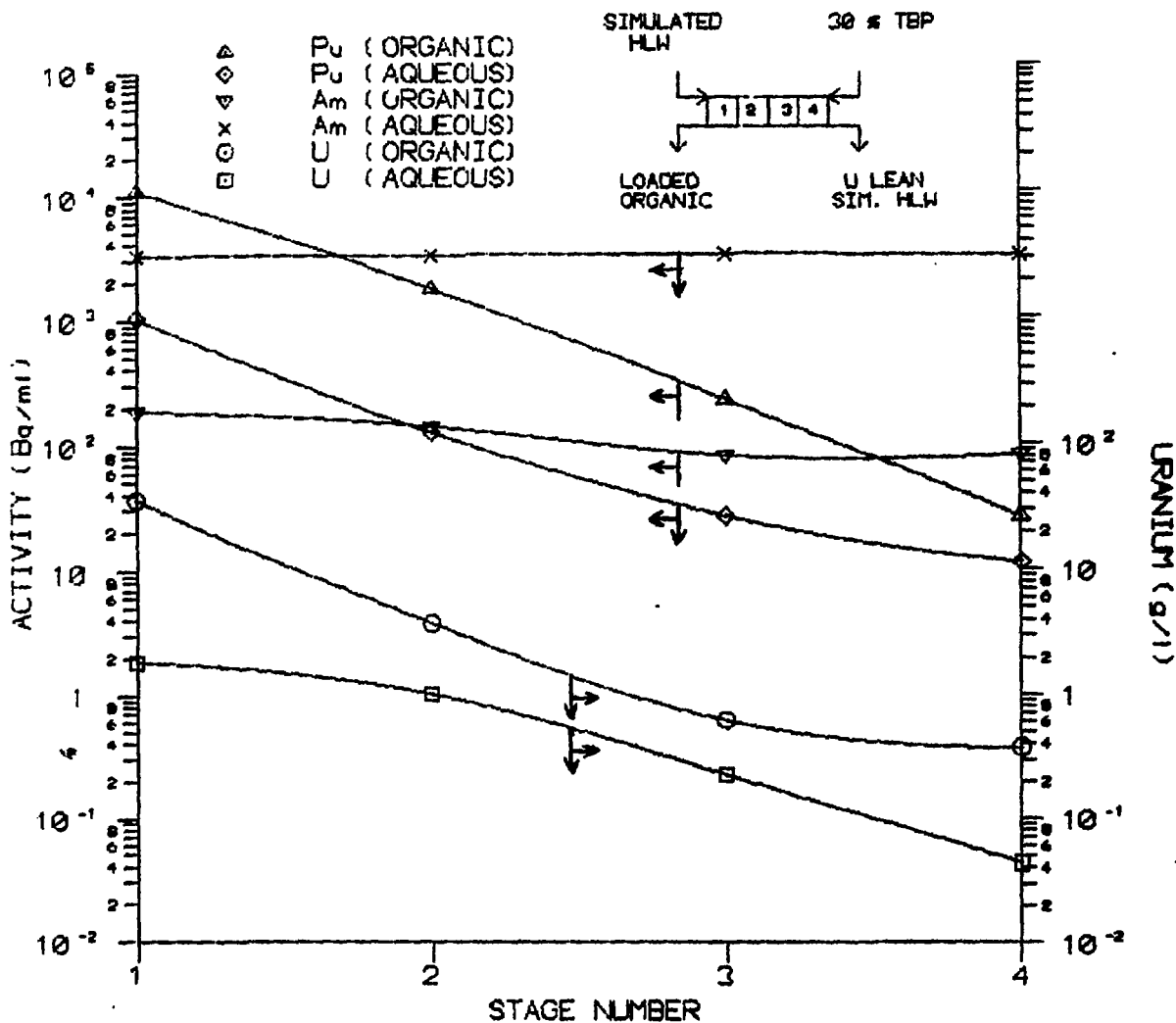


FIG. 3 EXTRACTION OF ACTINIDES FROM SIMULATED PHWR-HLW SOLUTION BY 30% TBP

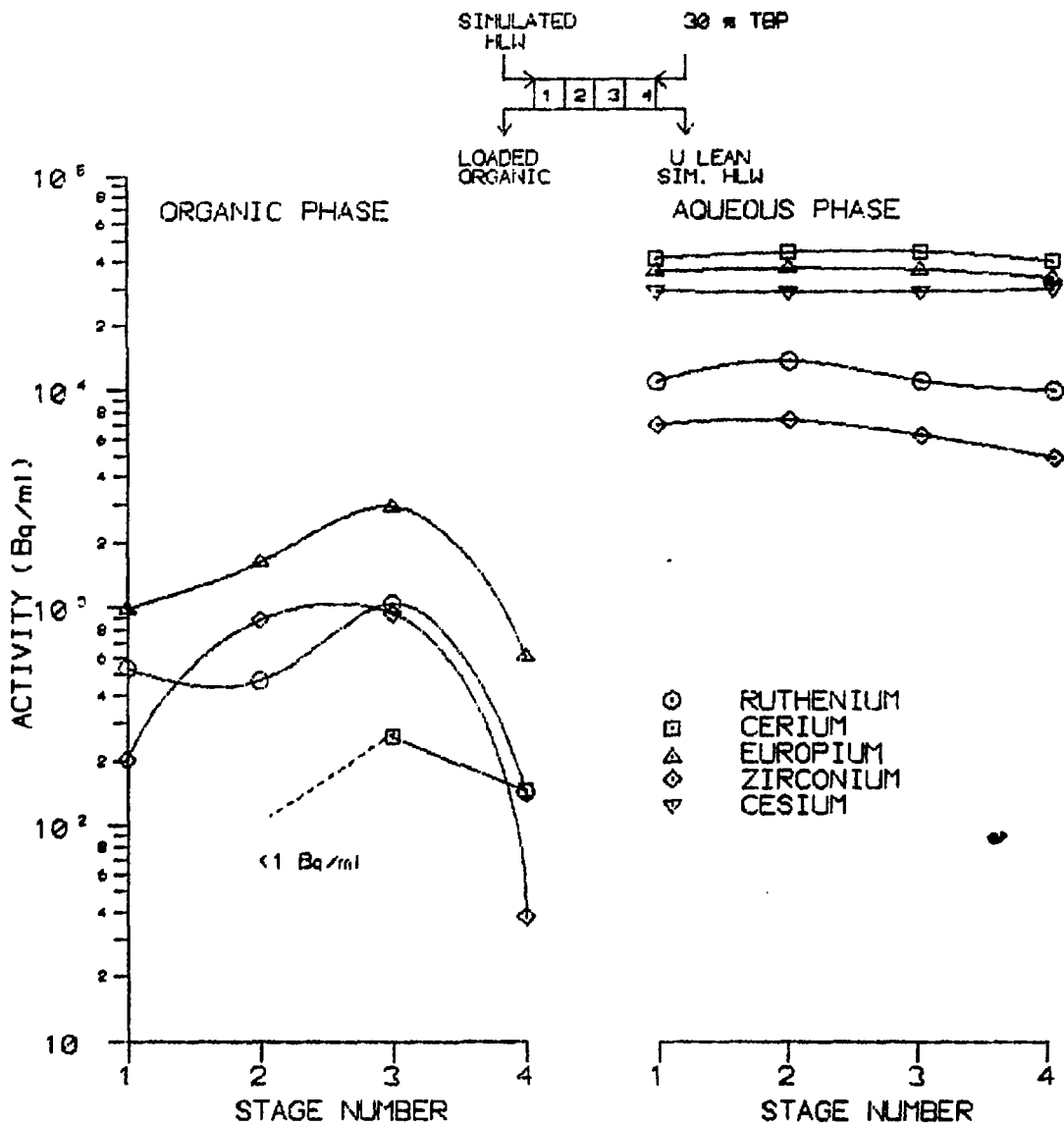


FIG. 4 BEHAVIOUR OF FISSION PRODUCTS DURING EXTRACTION OF ACTINIDES FROM SIMULATED PHWR - HLW SOLUTION BY 30% TBP

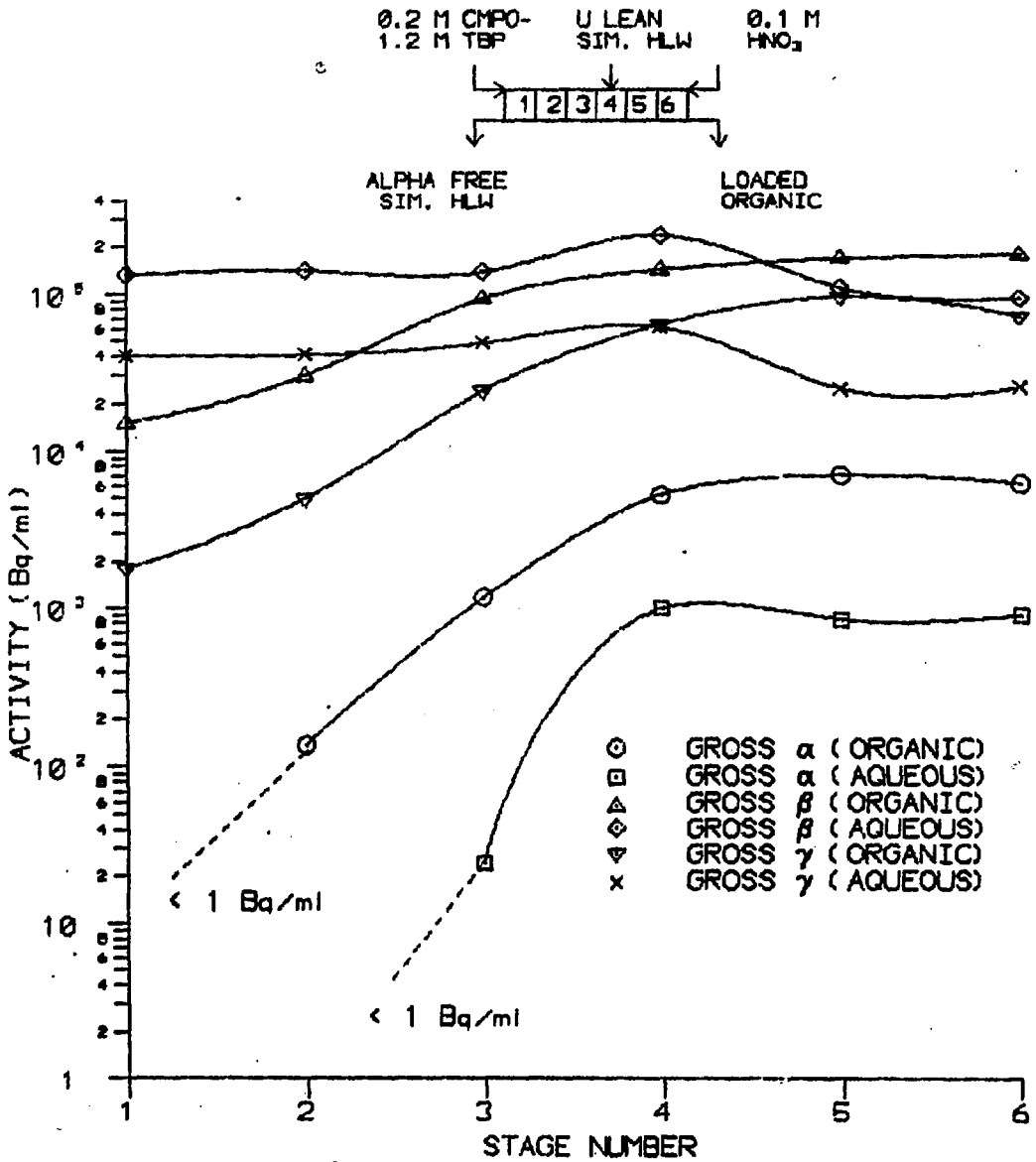


FIG. 5 EXTRACTION OF GROSS ACTIVITIES FROM U LEAN SIMULATED HLW BY CMPO - TBP

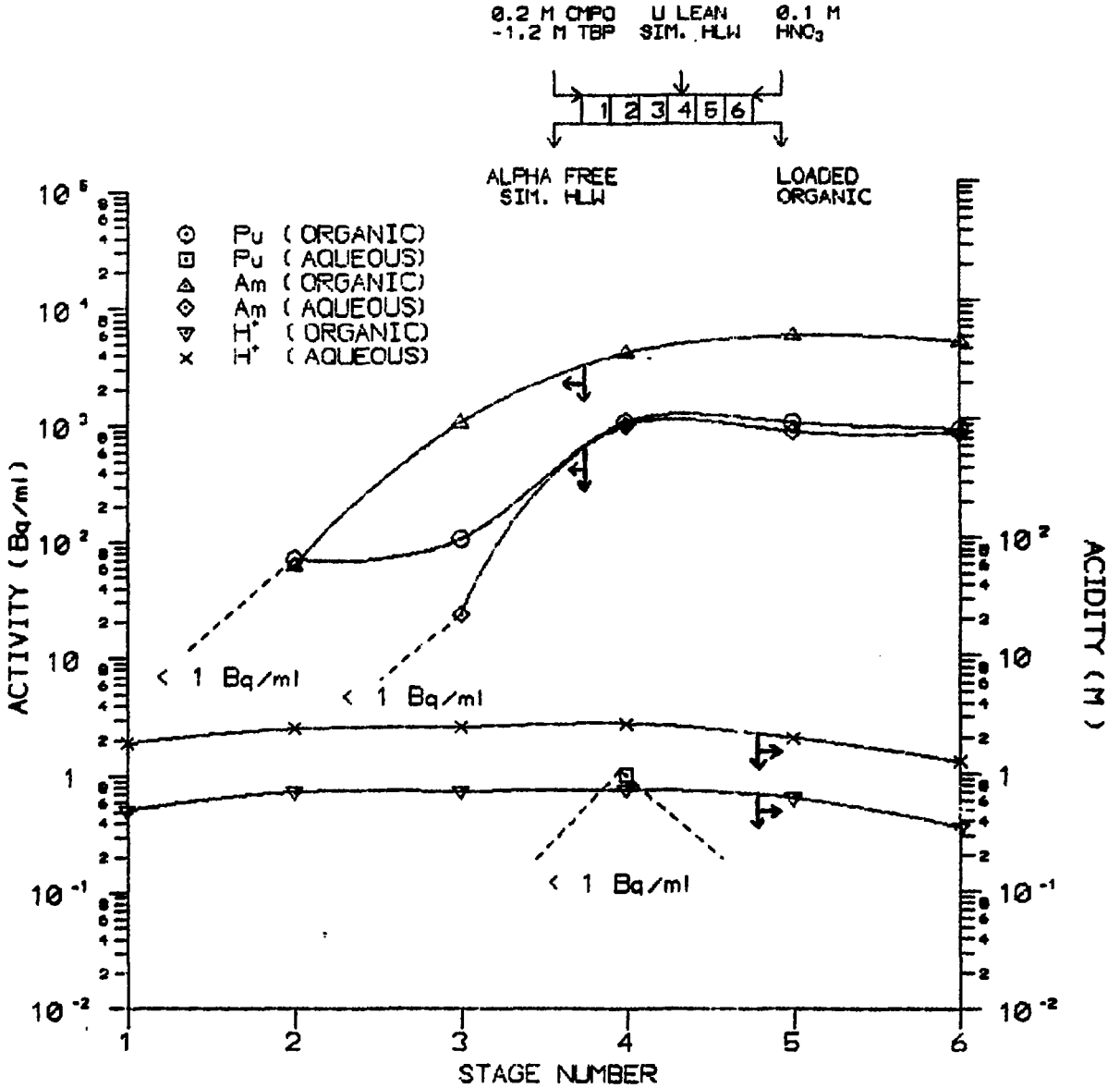


FIG.6 EXTRACTION OF ACTINIDES FROM URANIUM LEAN SIMULATED HLW BY CMPO - TBP AND ACIDITY OF ORGANIC AND AQUEOUS PHASES

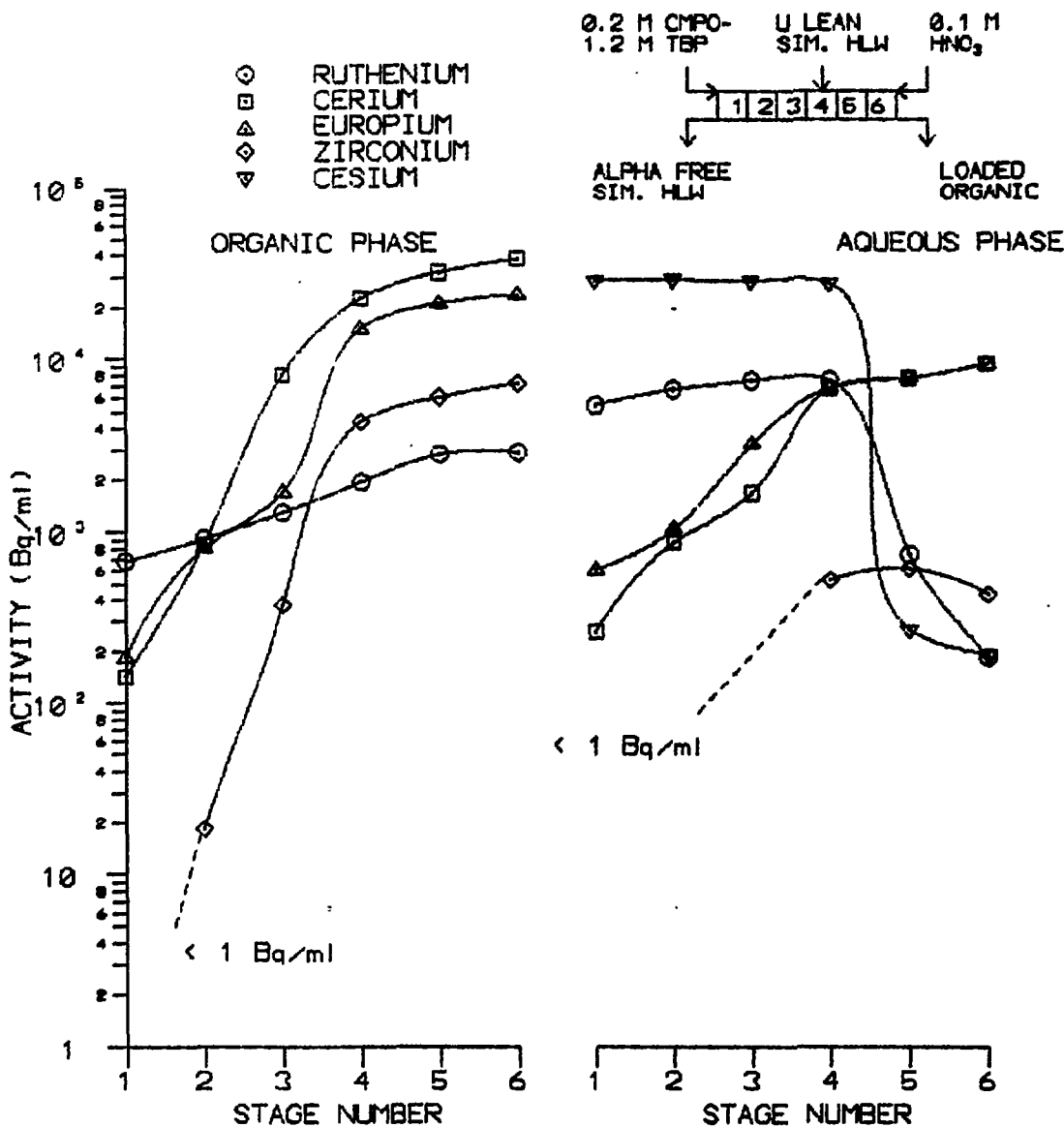


FIG. 7. BEHAVIOUR OF FISSION PRODUCTS DURING EXTRACTION OF ACTINIDES FROM URANIUM LEAN SIMULATED HLW BY CMPO - TBP

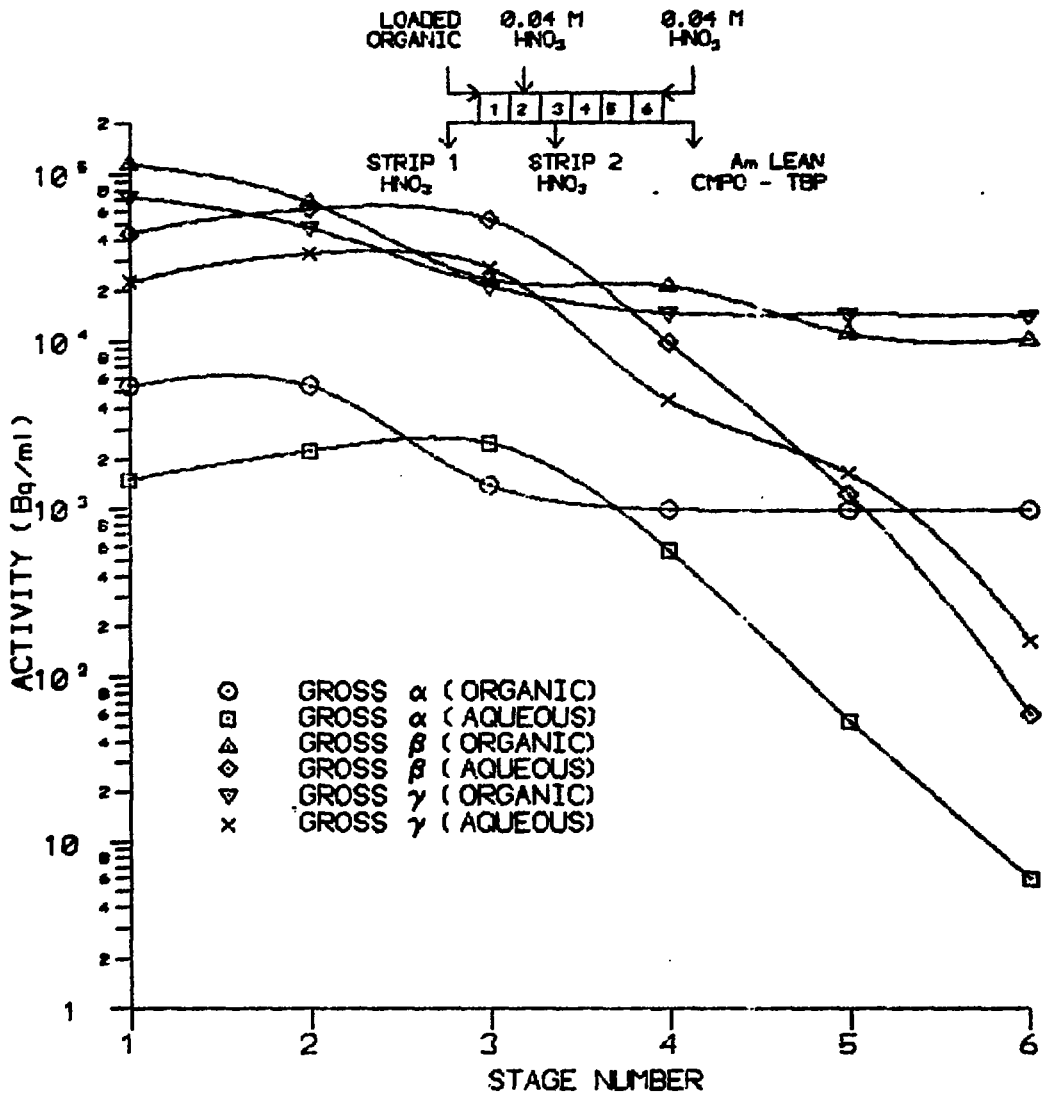


FIG. 8 STRIPPING OF GROSS ACTIVITIES BY 0.04 M NITRIC ACID FROM LOADED CMPO - TBP

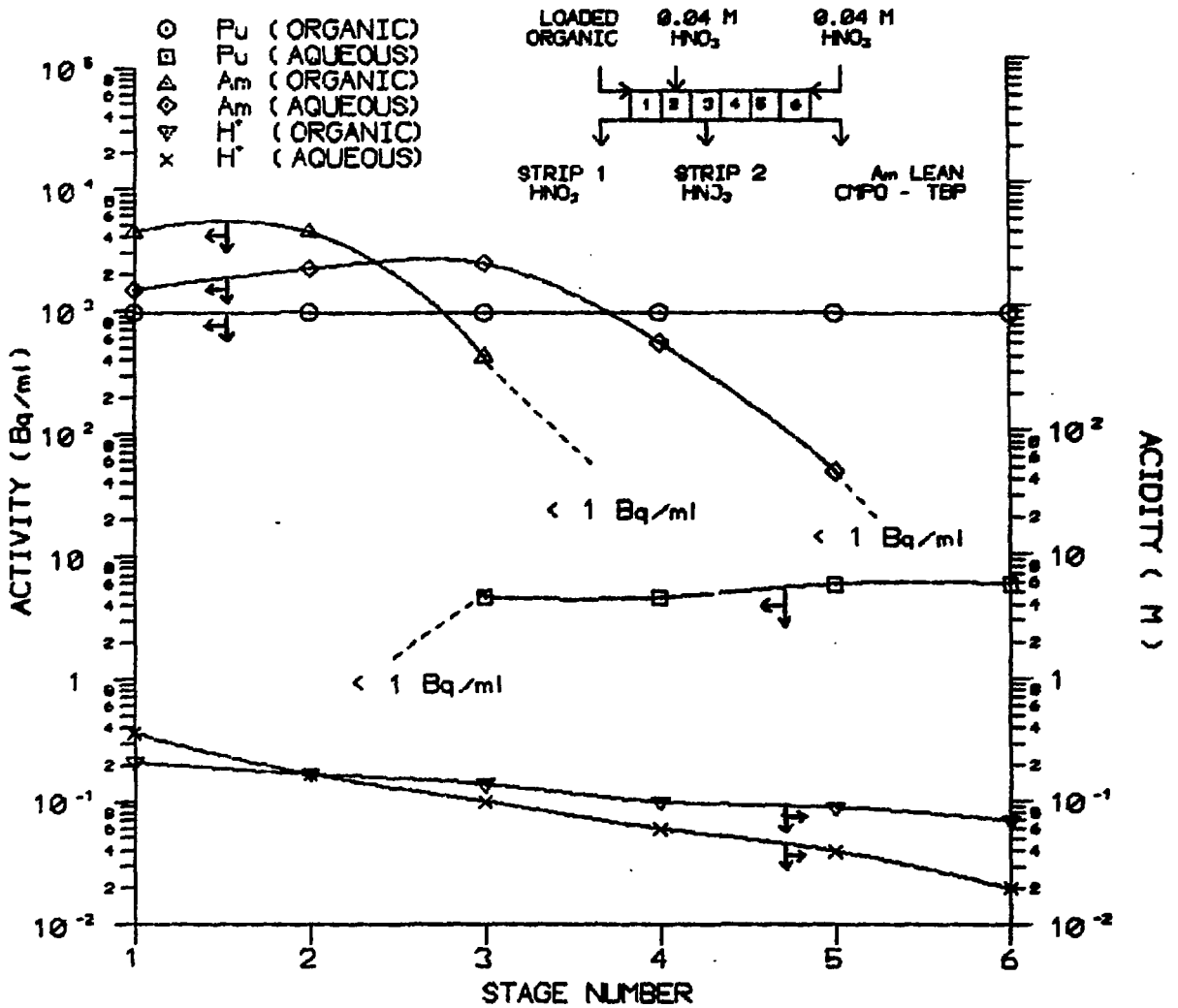


FIG. 9. STRIPPING OF ACTINIDES BY 0.04 M HNO_3 FROM LOADED CMPO - TBP AND ACIDITY OF ORGANIC AND AQUEOUS PHASES

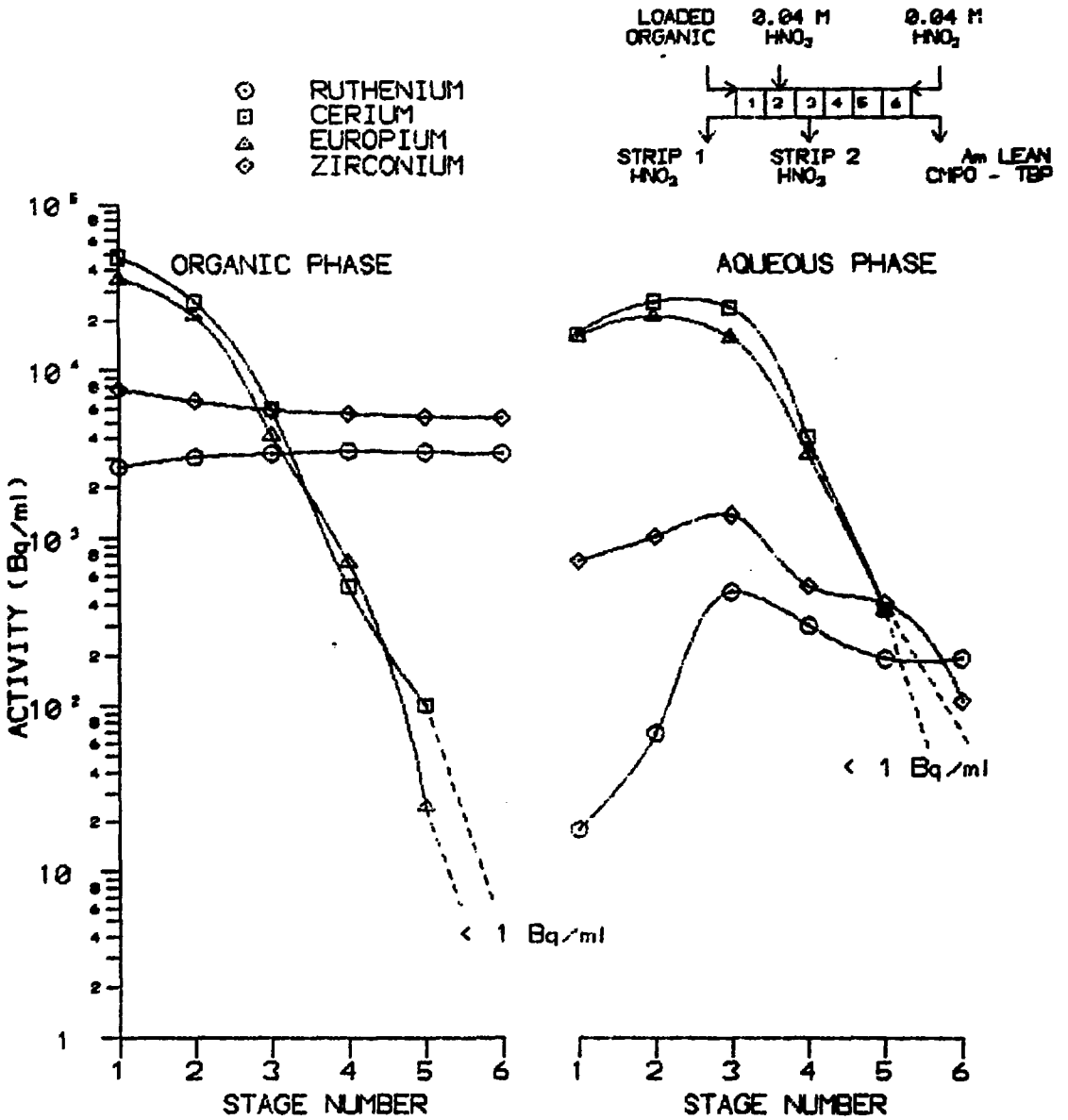


FIG. 10 BEHAVIOUR OF FISSION PRODUCTS DURING STRIPPING OF ACTINIDES BY 0.04 M NITRIC ACID FROM LOADED CMPO - TBP

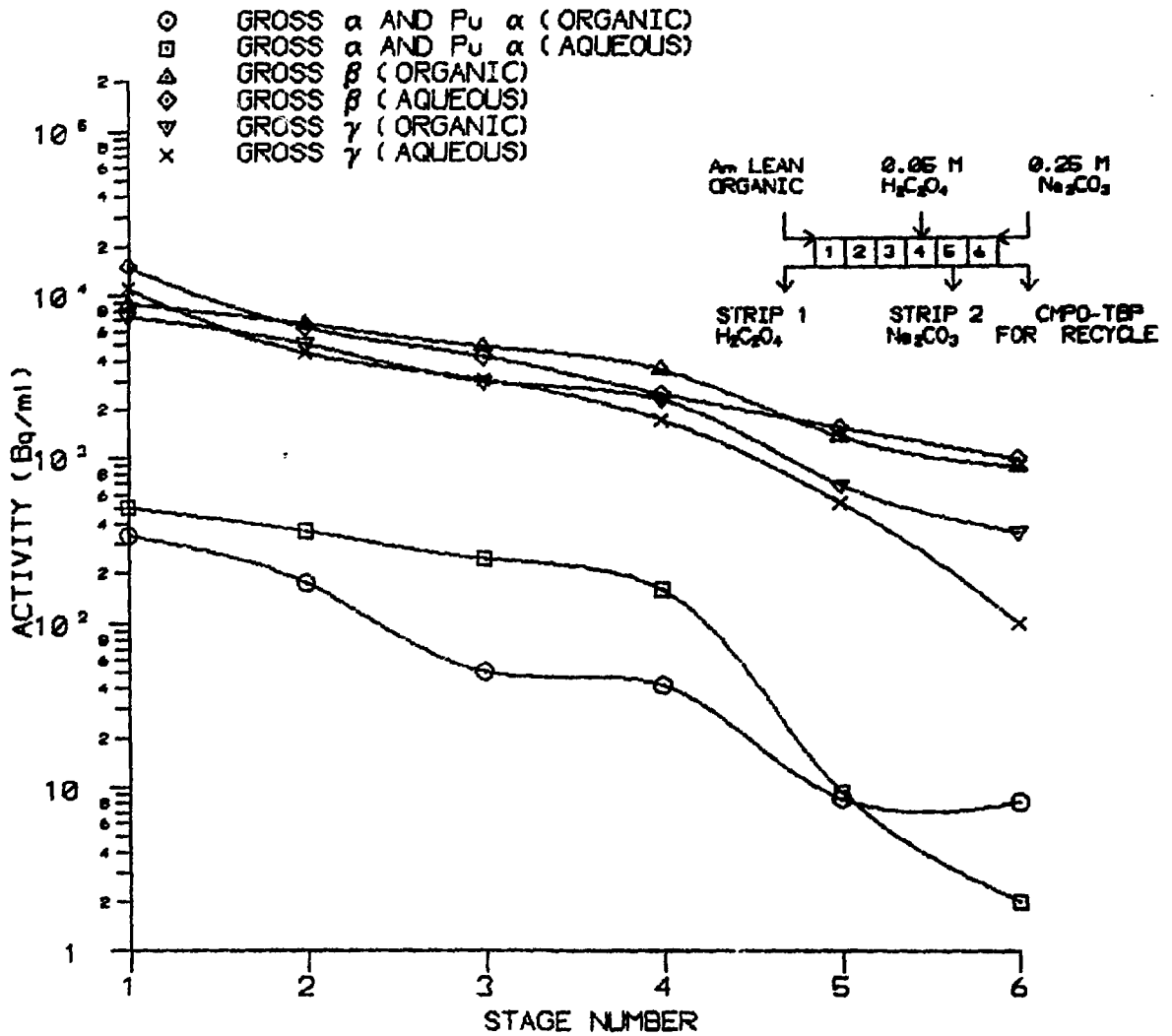


FIG. 11 STRIPPING OF GROSS ACTIVITIES BY 0.05 M OXALIC ACID AND 0.25 M SODIUM CARBONATE FROM AMERICIUM LEAN CMPO - TBP

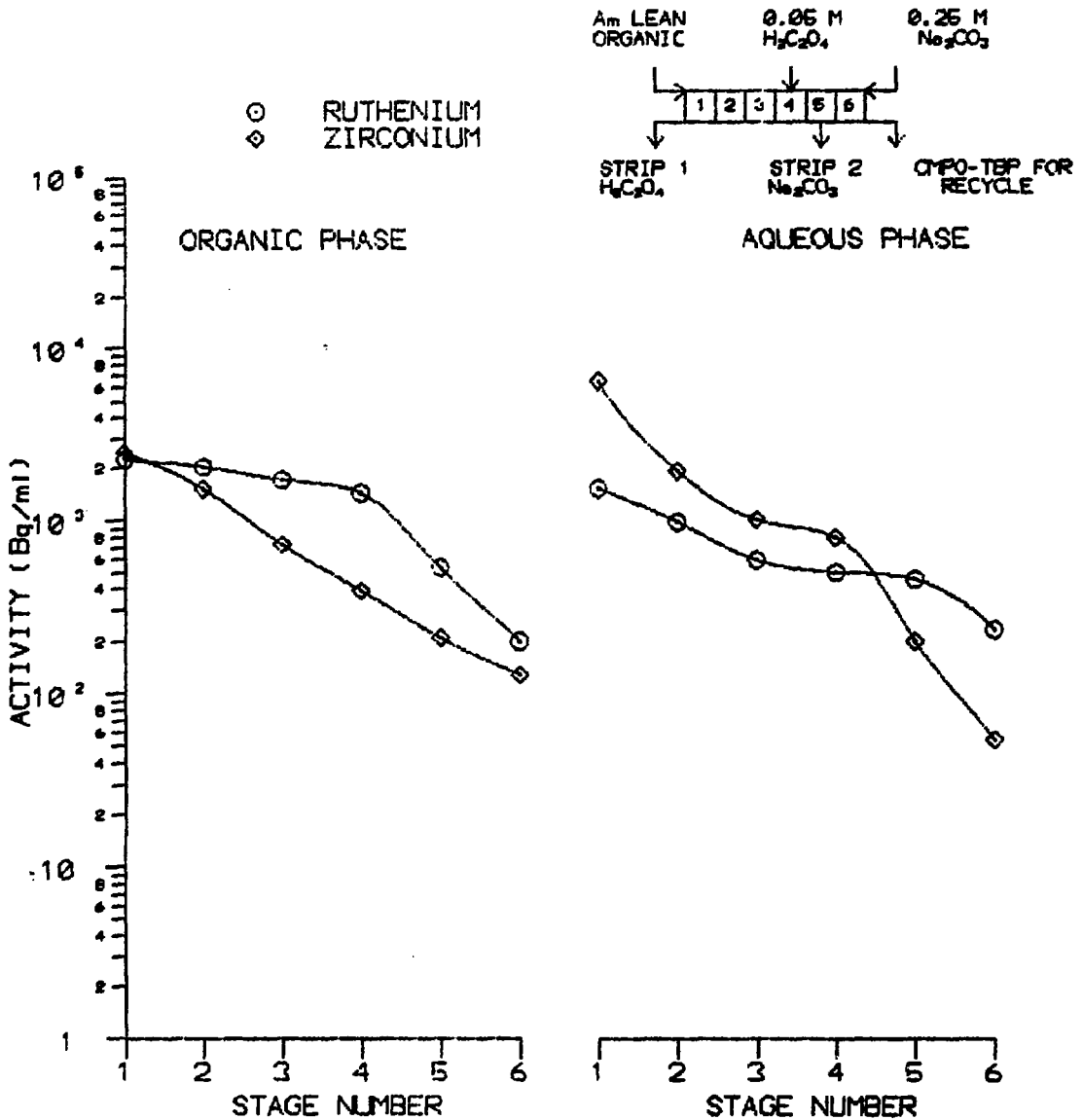


FIG. 12 BEHAVIOUR OF FISSION PRODUCTS DURING STRIPPING OF ACTINIDES BY 0.05 M H₂C₂O₄ AND 0.25 M Na₂CO₃ FROM Am LEAN CMPO-TBP

