



PARTITIONING AND RECOVERY OF NEPTUNIUM FROM HIGH LEVEL WASTE
STREAMS OF PUREX ORIGIN USING 30% TBP

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60 Abstract : ²³⁷Np is one of the longest-lived nuclides among the actinides present in the high level waste solutions of reprocessing origin. Its separation, recovery and transmutation can reduce the problem of long term storage of the vitrified waste to a great extent. With this objective, the present work was initiated to study the extraction of neptunium into TBP under the conditions relevant to high level waste, along with uranium and plutonium by oxidising it to hexavalent state using potassium dichromate and subsequently recovering it by selective stripping. Three types of simulated HLW solutions namely sulphate bearing (SB), with an acidity of ~ 0.3 M and non-sulphate wastes originating from the reprocessing of fuels from pressurised heavy water reactor (PHWR) and fast breeder reactor (FBR) with acidities of 3.0 M HNO₃ were employed in these studies. The extraction of U(VI), Np(VI) and Pu(VI) was very high for PHWR- and FBR-HLW solutions, whereas for the SB-HLW solution, these values were less but reasonably high. Quantitative recovery of neptunium and plutonium was achieved using a stripping solution containing 0.1 M H₂O₂ and 0.01 M ascorbic acid at an acidity of 2.0 M . Since, cerium present in the waste solutions is expected to undergo oxidation in presence of K₂Cr₂O₇, its extraction behaviour was also studied under similar conditions. Based on the results, a scheme was formulated for the recovery of neptunium along with plutonium and was successfully applied to actual high level waste solution originating from the reprocessing of research reactor fuels.

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**PARTITIONING AND RECOVERY OF NEPTUNIUM FROM HIGH LEVEL
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1. INTRODUCTION

The alpha emitting long-lived nuclides present in the high level waste (HLW) solutions originating from the reprocessing of spent nuclear fuels are of great environmental concern due to their long half-lives, requiring millions of years for their complete decay. In the last ten years, considerable amount of work has been carried out all over the world on partitioning of actinides from acidic waste solutions using various extracting agents (1-7). Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) has been adjudged as the best reagent for this purpose because of its ability to extract trivalent actinides without any feed adjustment (1-5). Neptunium which normally exists in the inextractable pentavalent state has very low distribution ratio (D) even with CMPO. Since, ^{237}Np is one of the longest-lived nuclides among the actinides present in the HLW solutions, its separation, recovery and transmutation can reduce the problem of long term storage of the vitrified waste to a great extent. Kolarik and Horwitz (8) and Mincher (9) have studied the extraction of neptunium in the valency states of IV, V and VI from nitric acid solutions using a mixture of CMPO and TBP and its subsequent stripping from the loaded organic phase using various reagents.

In our earlier scheme on the partitioning of minor actinides from HLW solutions using either solvent extraction (1) or extraction chromatographic technique (2) employing CMPO, a uranium depletion step was incorporated using 30 % TBP in dodecane. The present study deals with the removal of neptunium along with plutonium during the uranium depletion step from three types of simulated HLW solutions originating from

reprocessing of nuclear fuels: (1) stored HLW containing considerable amounts of SO_4^{2-} (sulphate bearing, SB), (2) pressurised heavy water reactors (PHWR) and (3) fast breeder reactors (FBR). In SB-HLW, the sulphate ions arise from ferrous sulphamate used for the reduction of Pu(IV) to Pu(III) in the partitioning stage of PUREX processing. The sulphate bearing waste is characterised by high salt content and has an acidity of only 0.3 M. PHWR-HLW and FBR-HLW are non-sulphate wastes having low salt content and an acidity of ~ 3.0 M. Studies were extended to actual HLW solution originated from the reprocessing of fuels from research reactors of this Centre.

The separation of neptunium is achieved by oxidising it to extractable hexavalent state using potassium dichromate and subsequently extracting it into 30 % TBP. The extraction behaviour of UO_2^{2+} and PuO_2^{2+} was also studied under similar experimental conditions. The stripping of neptunium from the loaded organic phase was carried out using various reagents with the aim of either recovering uranium, neptunium and plutonium together or neptunium and plutonium in one fraction and uranium separately.

2. EXPERIMENTAL

2.1. Materials:

TBP was procured from M/s. Bharat Vijay Chemicals, India and purified by contacting with a dilute solution of sodium hydroxide and subsequent washing with water. Dodecane (~ 93 % C-12), procured from M/s. Transware Chemia Handelsgesellschaft, Hamburg, Germany was used as diluent in these studies (10). All the other chemicals used were of Analytical Reagent grade. The radioactive tracers ^{233}U , ^{239}Pu and ^{141}Ce were prepared and purified by standard procedures (11-13). The radioactive tracer ^{238}Np was prepared by irradiating ^{237}Np at Apsara research reactor of this centre and dissolving the target in 6 M HCl. The acidity was adjusted to 1 M and Fe^{2+} solution was added to make

it 0.02 M with respect to iron (8). Neptunium in the tetravalent state was extracted with 0.5 M thenoyl trifluoroacetone (TTA)/xylene leaving most of the fission product activities in the aqueous phase. Neptunium was then stripped with a small volume of 8 M HNO_3 . This process of extraction and stripping of neptunium was repeated twice and finally the purity of the tracer was checked by gamma spectrometry (Fig. 1). In all the neptunium extraction studies, Np(V) was used for initial spiking. For conversion of Np(IV) to Np(V), Np(IV) solution in 1.0 M HNO_3 was heated on a water bath for about four hours at 60°C. The fraction of neptunium not converted to Np(V) was removed by repetitive extraction with a mixture containing 0.2 M CMPO and 1.2 M TBP in dodecane (9), till the distribution ratio (D) for neptunium remained constant at ~ 0.05 . Four CMPO extractions were necessary to get a reproducible low D for neptunium.

In the experiments with simulated waste solutions, uranium and plutonium were assayed by liquid scintillation counting. While assaying plutonium in presence of large amounts of uranium, corrections were also applied for the alphas due to uranium present in both the aqueous and organic phases. ^{238}Np and ^{141}Ce were assayed with a well type gamma scintillation counter using a NaI(Tl) detector.

In the case of actual HLW solution, plutonium in aqueous phase was assayed by extracting it into 0.5 M TTA/xylene and directly planchetting the TTA phase. The assay of plutonium in organic phase was carried out by direct planchetting. For the estimation of neptunium in aqueous phase, it was necessary to separate neptunium from fission product activities to avoid the interference. Neptunium was extracted in 0.5 M TTA/xylene after reducing it to tetravalent state by 0.1 M Fe^{2+} . Neptunium in TTA phase was analysed by gamma spectrometry with a 4k multichannel analyser using HPGe detector. However, analysis of neptunium in the organic phase was carried out directly. Uranium was analysed

spectrophotometrically using 2-(5-Bromo-2 pyridylazo)-5 diethyl-aminophenol (Bromo-PADAP) method for aqueous phase (14) and thiocyanate method (15) for organic phase. The material balance in each system was better than 95 %. The error limit in the estimation of activities was generally less < 2 %. The compositions of the three simulated waste solutions are given in Table 1.

2.2. Extraction Procedures:

For the extraction studies, feed solutions were spiked with the necessary radiotracers (^{233}U , ^{238}Np or ^{239}Pu) after addition of either $\text{K}_2\text{Cr}_2\text{O}_7$ with concentration varying between 0.0 to 0.01 M or NaNO_2 with concentration varying between 0.0 to 0.05 M. The solutions were equilibrated with equal volumes of 30 % TBP/dodecane by slow rotation for 30 minutes in a thermostated bath at $25 \pm 0.1^\circ\text{C}$. After the equilibration, the solutions were centrifuged, phases separated and pipetted for radioassay.

The extraction of cerium in presence of 0.01 M $\text{K}_2\text{Cr}_2\text{O}_7$ by 30 % TBP was studied in nitric acid medium (with concentration varied from 0.3 to 3.0 M) containing Ce either in a tracer level or in the millimolar range as well as from the simulated waste solutions. The volume of the TBP phase taken was same as that of the aqueous phase. The equilibration and analysis was carried out as discussed above.

2.3. Stripping procedures:

Stripping of neptunium, plutonium and uranium from the loaded TBP phases was carried out under various conditions of acidity and organic to aqueous phase ratios. Various stripping agents used include hydrogen peroxide, hydroxylamine hydrochloride and hydrazine sulphate. Ascorbic acid was also used as one of the constituents in stripping solutions. In the cases where repetitive contacts of fresh strippants were given, the

organic phase was transferred to a fresh equilibration tube after each contact and the aqueous phase containing the stripping agents was added to that tube. The assay of the activities in the separated organic and aqueous phases was done as discussed earlier.

3. RESULTS AND DISCUSSION

Studies were carried out with three types of simulated HLW solutions (compositions given in Table 1) namely sulphate bearing SB-HLW with an acidity of about 0.3 M and non-sulphate wastes PHWR- and FBR- HLW with an acidity of 3.0 M as well as the actual HLW originated from the reprocessing of research reactor fuels. Extraction of uranium, neptunium and plutonium in presence of 0.01 M $K_2Cr_2O_7$ by 30 % TBP/dodecane showed the order of extraction as $U > Np > Pu$ (Table 2). This is the order of their effective cationic charge i.e. 3.2, 3.0 and 2.9, respectively for the actinyl MO_2^{2+} ions (16). The distribution ratios are in general higher for the extraction from PHWR- or FBR-HLW solutions as compared to those from SB-HLW, which is logical, since later contains large amount of sulphate ions and has a low acidity of only 0.3 M. Except in the case of extraction of plutonium from SB-HLW (where D was about 1.3), in all other systems reasonably high D values have been obtained. This shows that it is possible to remove quantitatively uranium, neptunium and plutonium from HLW solutions by oxidising the later two metal ions to hexavalent state using 0.01 M $K_2Cr_2O_7$ and extracting into 30 % TBP/dodecane. Optimisation of concentration of $K_2Cr_2O_7$ was carried out by studying the extraction of neptunium from simulated PHWR-HLW solution using 30 % TBP at varied concentrations of $K_2Cr_2O_7$. From the results presented in Table 3, it can be inferred that even 0.005 M $K_2Cr_2O_7$ is sufficient to oxidize neptunium to extractable hexavalent state. However, in further studies, its concentration was always maintained at 0.01 M.

Sodium nitrite was another reagent, tested for its effectiveness as an oxidising agent for converting neptunium from waste solutions to hexavalent state. When NaNO_2 was added to a solution containing Np(V) in 3.0 M HNO_3 , D value increased from 0.004 to 0.4 (Table 4). Similar increase in D values has been reported by Kolarik and Horwitz (8) while extracting Np(V) in presence of NaNO_2 by a mixture containing 0.2 M CMPO and 1.2 M TBP in dodecane. In a recent publication, Tochiyama et al (17) also suggest a catalysed oxidation of neptunium in nitric acid - TBP system in presence of nitrous acid.

Studies with all the three simulated wastes showed that D value for Np decreased as the concentration of NaNO_2 increased (Table 4). In absence of NaNO_2 , D values of Np in PHWR- and FBR-HLW solutions were much higher (> 100 times) compared to D value in pure 3.0 M HNO_3 solution containing no other metal ions. D value for Np in SB-HLW was much lower than those in PHWR- or FBR-HLW. It suggests that neptunium though expected to be in inextractable pentavalent state under HLW conditions, actually disproportionates in presence of the different metal ions in the simulated waste solutions leading to a higher D value. With the addition NaNO_2 to the waste solutions, however, D value for Np decreased with increasing NaNO_2 concentration. Although this contradictory behaviour of neptunium in presence of NaNO_2 in nitric acid solution compared to those in the HLW solutions is not clear, it appears that the addition of NaNO_2 under the waste conditions reduces Np(VI) to Np(V) resulting in lower D values.

Among the other oxidising agents, potassium permanganate was not tried, since it reacts with CMPO (8) which will be used for the separation of remaining actinides (Am, Cm, etc.) from the TBP raffinate. Potassium bromate may not be preferred for plant scale operations due to the hazardous reaction products.

Smith and Moore (18) have reported the separation of radiocerium by oxidising it to tetravalent state with $\text{K}_2\text{Cr}_2\text{O}_7$

and extracting it into TTA/xylene phase. If cerium is oxidised to Ce(IV), it will be extracted into 30 % TBP along with U, Np and Pu. To assess this, the extraction of Ce was carried out at tracer and millimolar levels in different nitric acid concentrations as well as with the three simulated waste solutions. As can be seen from Table 1, the concentration of Ce is in tracer level in SB-HLW, whereas it is in millimolar range in other two wastes. Table 5 shows that at both the concentration levels, D of Ce in presence of 0.01 M $K_2Cr_2O_7$ in 30 % TBP increases with increasing concentration of HNO_3 . D values of Ce in millimolar concentrations are lower than those at tracer level concentrations at least by an order of magnitude. In the case of simulated PHWR- and FBR-HLW, D values for Ce are ~ 0.03, suggesting that under these conditions Ce will be taken up by the TBP phase only to a negligible extent. However, in the case of SB-HLW solution, D of nearly 1 suggests a significant amount of Ce being taken up in the TBP phase. These results agree with the findings of Smith and Moore, indicating high extraction of Ce at tracer level concentrations. However, at millimolar level, extent of extraction is negligible.

The reduction of Np(VI) to inextractable Np(V) by H_2O_2 in dilute nitric acid is immediate and that of Np(V) to Np(IV) is very slow (19). This fact suggests that H_2O_2 can be used for stripping Np from TBP phase. Stripping of Np from loaded TBP phase was studied using 0.1 M H_2O_2 with nitric acid concentrations varying from 0.1 M to 2.0 M. It can be seen from Table 6 that with only 2 contacts of 0.1 M H_2O_2 as strippant, more than 97 % of Np could be stripped from TBP phase. These studies were followed by stripping of Np at various organic to aqueous phase ratios using 0.1 M H_2O_2 in 2.0 M HNO_3 as a strippant. Table 7 shows that the total Np stripped after 4 contacts decreases with increasing organic to aqueous phase ratios. However, even at a ratio of 6 : 1, a major portion of Np

(~ 87 %) was stripped from organic phase.

It was observed in the extraction studies of Ce from the simulated waste solutions in presence of $K_2Cr_2O_7$ by 30 % TBP that only in the case of SB-HLW, D for Ce was as high as ~ 1. As such, it was necessary to study the behaviour of Ce during the stripping of Np. Stripping of Ce from the loaded TBP phase was carried out with 0.1 M H_2O_2 in 0.5, 1.0 and 2.0 M HNO_3 . H_2O_2 reduces tetravalent cerium to inextractable trivalent cerium. Table 8 shows that Ce is almost quantitatively stripped in 3 contacts with 0.1 M H_2O_2 . Thus, under the conditions where Ce is extracted into organic phase, it will be stripped along with Np and Pu.

Since, it is known (19) that the reduction of Pu(VI) to Pu(IV) in the presence of H_2O_2 in nitric acid is fast even at room temperature, it is expected that Pu would be held up in the TBP phase. On the contrary, a large amount of Pu was found to be stripped into the aqueous phase along with Np (Table 9). The percentage of Pu stripped decreased with increasing HNO_3 concentration. As a typical example, for TBP phase containing Pu extracted from simulated PHWR-HLW solution, the total amount of Pu stripped decreased from 99.9 % to 67.9 % with the nitric acid concentration increased from 0.1 to 2.0 M. These results suggest that although Np could be stripped almost quantitatively by a mixture of H_2O_2 and HNO_3 , it will be associated with considerable amounts of Pu in the aqueous phase. To avoid the distribution of Pu in organic and aqueous phase, it was essential to reduce Pu(IV) to inextractable Pu(III) before stripping and then to strip it along with Np in the same fraction. Since ascorbic acid can reduce Pu(IV) to Pu(III) without affecting Np(V), a small amount of ascorbic acid was incorporated in the stripping mixture. Table 10 shows that solutions containing 0.1 M H_2O_2 and 0.01 M ascorbic acid with HNO_3 concentrations varying from 0.1 to 2.0 M could strip Pu completely from TBP phase.

In the next set of experiments, stripping of Pu from TBP phase was studied at various organic to aqueous phase ratios using a strippant containing 0.1 M H₂O₂, 0.01 M ascorbic acid and 2.0 M HNO₃. Even at the high organic to aqueous phase ratio of 4 : 1, complete stripping of Pu was achieved in 4 contacts (Table 11). From the same Table, it can be seen that in the absence of ascorbic acid stripping of Pu was very poor.

It is known that in PUREX process, during the stripping of Pu from the TBP phase, presence of dibutyl phosphoric acid (DBP) in organic phase leads to a formation of Pu-DBP-TBP synergistic complex. This results in incomplete removal of Pu from organic phase. To investigate the stripping behaviour of Pu under the conditions of HLW, Pu was extracted from PHWR-HLW solution by 30 % TBP containing 2 g/l of DBP and subsequently stripped with a mixture containing 0.1 M H₂O₂ and 0.01 M ascorbic acid at nitric acid concentrations of 0.1 and 2.0 M with an organic to aqueous phase ratio of 4 : 1. Almost complete stripping of Pu from loaded organic phase suggests that presence of DBP in the organic phase will not pose any serious problems (Table 12). Np is expected to behave in a similar manner.

The effect of other reducing agents such as hydroxylamine hydrochloride and hydrazine sulphate on the stripping of Pu from TBP phase at the organic to aqueous phase ratio of 4 : 1 was also studied and compared with H₂O₂ in 2.0 M HNO₃ (in the absence as well as in the presence of 0.01 M ascorbic acid). It can be seen from Table 13 that although in absence of ascorbic acid, the stripping of Pu from the TBP phase follows the order hydroxylamine > hydrazine > hydrogen peroxide, the order is completely reversed in presence of ascorbic acid. Complete stripping of Pu was possible using a stripping reagent containing 0.1 M H₂O₂ and 0.1 M ascorbic acid in 2.0 M HNO₃. As expected, ascorbic acid did not have any adverse effect on the stripping of Np (Table 14). This shows that a quantitative recovery of Np and Pu is possible using a mixture of H₂O₂ and

ascorbic acid as a strippant.

Also, the stripping of uranium from loaded TBP phase was carried out using a mixture of 0.1 M H_2O_2 and 0.01 M ascorbic acid in 0.1 and 2.0 M HNO_3 at various organic to aqueous phase ratios. At high organic to aqueous phase ratios, a major fraction of uranium was expected to remain in the organic phase while using 2.0 M HNO_3 . Only about 7 % of uranium was released from the TBP phase after 4 contacts at an organic to aqueous phase ratio of 4 : 1, as per the expectations (Table 15). On the other hand, at an acidity of 0.1 M where major portion of uranium is expected to be stripped, only ~ 31 % was released after 4 contacts while keeping organic to aqueous phase ratio of 4 : 1. This shows an incomplete removal of uranium from the loaded TBP phase even at lower acidities. Additional wash of the TBP phase with 0.01 M nitric acid is essential for the removal of remaining uranium.

In the next experiment, uranium, neptunium and plutonium were added together to the simulated PHWR-HLW solution in presence of 0.01 M $\text{K}_2\text{Cr}_2\text{O}_7$ and their extraction in 30 % TBP was carried out at an organic to aqueous phase ratio of 1 : 1. The stripping of the loaded TBP was carried out using a stripping mixture containing 0.1 M H_2O_2 and 0.01 M ascorbic acid at acidities of 0.1 M and 2.0 M, keeping organic to aqueous phase ratio of 4 : 1. During the stripping at an acidity of 0.1 M, more than 99 % of neptunium and plutonium were found to be stripped after 4 contacts (Table 16). Only 35 % of uranium was stripped along with neptunium and plutonium, leaving 65 % in the TBP phase. Further wash involving 4 contacts of 0.01 M HNO_3 was required to remove remaining uranium from the organic phase. With the stripping solution having an acidity of 2.0 M HNO_3 , nearly 99 % of neptunium and plutonium were released from the TBP phase in 4 contacts. Total uranium stripped from TBP phase amounted to < 6 %. The aqueous phase containing neptunium, plutonium and a small amount of uranium was given a scrub with

30 % TBP at an organic to aqueous phase ratio of 1 : 4. This could recover all of the uranium from the aqueous phase leaving behind a mixture of pure Np and Pu.

Based on the data generated, a scheme for the extraction and recovery of neptunium, plutonium and uranium from HLW solutions was prepared (Fig. 1) and tested with actual HLW solution generated during the reprocessing of research reactor fuels. The solution was spiked with ^{238}Np . Extraction of uranium, neptunium and plutonium was carried out in presence of 0.01 M $\text{K}_2\text{Cr}_2\text{O}_7$ at an organic to aqueous phase ratio of 1 : 1. Results of replicate experiments (Table 17) are in agreement with those obtained from previous experiments. Distribution ratios were found to be 17.7, 14.4 and 9.3 for U, Np and Pu, respectively, showing a removal of more than 90 % of these actinides in a single contact. Stripping of the metal ions from the loaded TBP phase was carried out with 2.0 M HNO_3 containing 0.1 M H_2O_2 and 0.01 M ascorbic acid at an organic to aqueous phase ratio of 4 : 1. Nearly 99 % of Np and Pu were recovered. Separation of Np from Pu can be carried out with known methods.

4. CONCLUSION

Quantitative extraction of neptunium and plutonium from simulated SB-, PHWR- and FBR-HLW solutions by 30 % TBP along with uranium could be achieved by oxidising neptunium and plutonium to hexavalent state using 0.01 M $\text{K}_2\text{Cr}_2\text{O}_7$. More than 99 % of neptunium and plutonium could be recovered from the loaded TBP phase using a mixture containing 0.1 M H_2O_2 and 0.01 M ascorbic acid in 2.0 M HNO_3 as a strippant leaving behind most of the uranium in organic phase. The proposed scheme was successfully tested with actual HLW solution.

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TABLE 1

COMPOSITIONS OF SIMULATED HIGH LEVEL WASTE SOLUTIONS

CONSTITUENT	SB-HLW	PHWR-HLW	FBR-HLW
ACIDITY (M)	0.30	3.0	3.0
FISSION PRODUCTS (g/l) :			
1. Selenium	—	0.0123	0.0020
2. Rubidium	—	0.0745	0.0546
3. Strontium	—	0.1863	0.1470
4. Yttrium*	—	0.0990	0.0738
5. Zirconium	—	0.7713	0.8221
6. Molybdenum	—	0.7313	1.0921
7. Technetium*	—	0.1813	0.2622
8. Ruthenium	0.0001	0.4638	0.8131
9. Rhodium*	—	0.1275	0.2622
10. Palladium*	—	0.2675	0.6001
11. Silver	—	0.0186	0.1089
12. Cadmium	—	0.0159	0.0381
13. Tin	—	0.0151	0.0222
14. Antimony	—	0.0047	0.0068
15. Tellurium	—	0.1028	0.1626
16. Cesium	0.0932	0.5438	1.1251
17. Barium	—	0.3088	0.4140
18. Lanthanum	—	0.2638	0.3420
19. Cerium	0.0006	0.5325	0.6841
20. Praseodymium	—	0.2438	0.3390
21. Neodymium	—	0.8625	1.1251
22. Promethium*	—	0.0283	0.0531
23. Samarium	—	0.1638	0.3060
24. Europium	—	0.0226	0.0318
25. Gadolinium	—	0.0165	0.0657
26. Terbium*	—	0.0005	0.0113
27. Dysprosium*	—	0.0002	0.0051
OTHER INGREDIENTS (g/l) :			
1. Uranium	25.315	18.325	2.637
2. Sodium	21.950	3.0	3.0
3. Iron	2.860	0.5	0.5
4. Chromium	0.510	0.1	0.1
5. Nickel	0.450	0.1	0.1
6. Aluminium	5.710	—	—
6. Calcium	1.000	—	—
7. Sulphate	14.320	—	—

* La was added for Y, Pm, Tb, Dy; Mo for Tc; Co for Rh; Ni for Pd.

TABLE 2

EXTRACTION OF URANIUM, NEPTUNIUM AND PLUTONIUM
FROM SIMULATED WASTE SOLUTIONS
IN PRESENCE OF 0.01 M $K_2Cr_2O_7$ BY 30 % TBP

ORGANIC TO AQUEOUS PHASE RATIO = 1 : 1

AQUEOUS FEED	DISTRIBUTION RATIO		
	U(VI)	Np(VI)	Pu(VI)
SB-HLW	6.99	5.09	1.28
PHWR-HLW	13.12	12.66	5.20
FBR-HLW	17.81	14.15	6.72

TABLE 3

EFFECT OF $K_2Cr_2O_7$ CONCENTRATION ON EXTRACTION OF NEPTUNIUM
FROM SIMULATED PHWR-HLW BY 30 % TBP

ORGANIC TO AQUEOUS PHASE RATIO = 1 : 1

CONCENTRATION OF $K_2Cr_2O_7$, M	D FOR Np	% EXTRACTION
0.0	5.84	85.37
0.005	11.71	92.13
0.008	12.64	92.67
0.010	12.66	92.68

TABLE 4

EFFECT OF NaNO_2 CONCENTRATION ON EXTRACTION OF NEPTUNIUM
FROM SIMULATED PHWR-HLW BY 30 % TBP

ORGANIC TO AQUEOUS PHASE RATIO = 1 : 1

AQUEOUS FEED	D FOR Np AT NaNO_2 CONCENTRATION, M		
	0.00	0.01	0.05
3.0 M HNO_3	0.004	0.418	0.392
SB-HLW	0.521	0.119	0.055
PHWR-HLW	5.84	2.53	0.965
FBR-HLW	8.79	1.68	0.816

TABLE 5

EXTRACTION OF CERIUM
FROM NITRIC ACID AND SIMULATED HLW SOLUTIONS
IN PRESENCE OF 0.01 M $\text{K}_2\text{Cr}_2\text{O}_7$ BY 30 % TBP

ORGANIC TO AQUEOUS PHASE RATIO = 1 : 1

ACIDITY	DISTRIBUTION RATIO FOR Ce				
	FROM HNO_3 SOLUTION AT CERIUM CONCENTRATION		FROM SIMULATED WASTE SOLUTIONS		
	TRACER	5.0 mM	SB-HLW	PHWR-HLW	FBR-HLW
0.3 M	0.362	0.009	0.902	—	—
1.0 M	0.879	0.025	—	—	—
2.0 M	1.029	0.036	—	—	—
3.0 M	2.229	0.050	—	0.030	0.040

TABLE 6

STRIPPING OF NEPTUNIUM FROM LOADED TBP PHASE
(ORIGINALLY EXTRACTED FROM SIMULATED HLW SOLUTIONS
IN PRESENCE OF 0.01 M $K_2Cr_2O_7$)

STRIPPING REAGENTS = 0.1 M H_2O_2 +
VARYING HNO_3 CONCENTRATIONS
ORGANIC TO AQUEOUS PHASE RATIO = 1 : 1

CONTACT	% Np STRIPPED, REAGENTS USED			
	0.1 M H_2O_2 0.1 M HNO_3	0.1 M H_2O_2 0.5 M HNO_3	0.1 M H_2O_2 1.0 M HNO_3	0.1 M H_2O_2 2.0 M HNO_3
SIMULATED SB-HLW				
I	—	97.94	97.16	92.37
II	—	1.76	2.50	5.82
Total	—	99.70	99.66	98.19
SIMULATED PHWR-HLW				
I	98.57	85.13	83.35	80.94
II	—	13.16	13.91	16.72
Total	98.57	98.29	97.26	97.66
SIMULATED FBR-HLW				
I	—	90.45	92.27	89.91
II	—	9.23	7.48	8.92
Total	—	99.68	99.75	98.83

TABLE 7

STRIPPING OF NEPTUNIUM FROM LOADED TBP PHASE
 (ORIGINALLY EXTRACTED FROM SIMULATED PHWR-HLW
 IN PRESENCE OF 0.01 M $K_2Cr_2O_7$)
 AT VARIOUS ORGANIC TO AQUEOUS PHASE RATIOS
 STRIPPING REAGENT = 0.1 M H_2O_2 + 2.0 M HNO_3

CONTACT	% Np STRIPPED			
	O:A = 1:1	O:A = 2:1	O:A = 4:1	O:A = 6:1
I	80.94	66.32	39.12	20.52
II	16.72	22.91	33.96	38.02
III	1.61	6.00	14.19	18.66
IV	0.72	1.97	6.01	9.68
Total	99.99	97.20	93.28	86.88

TABLE 8

STRIPPING OF CERIUM FROM LOADED TBP PHASE
 (ORIGINALLY EXTRACTED FROM SIMULATED SB-HLW
 IN PRESENCE OF 0.01 M $K_2Cr_2O_7$)

STRIPPING REAGENTS = 0.1 M H_2O_2 +
 VARYING HNO_3 CONCENTRATIONS
 ORGANIC TO AQUEOUS PHASE RATIO = 1 : 1

CONTACT	% Ce STRIPPED, REAGENTS USED		
	0.1 M H_2O_2 0.5 M HNO_3	0.1 M H_2O_2 1.0 M HNO_3	0.1 M H_2O_2 2.0 M HNO_3
I	95.22	93.65	93.63
II	4.24	5.83	5.41
III	0.37	0.26	0.58
Total	99.83	99.74	99.62

TABLE 9

STRIPPING OF PLUTONIUM FROM LOADED TBP PHASE
(ORIGINALLY EXTRACTED FROM SIMULATED HLW SOLUTIONS
IN PRESENCE OF 0.01 M $K_2Cr_2O_7$)

STRIPPING REAGENTS = 0.1 M H_2O_2 +
VARYING HNO_3 CONCENTRATIONS
ORGANIC TO AQUEOUS PHASE RATIO = 1 : 1

CONTACT	% Pu STRIPPED, REAGENTS USED			
	0.1 M H_2O_2 0.1 M HNO_3	0.1 M H_2O_2 0.5 M HNO_3	0.1 M H_2O_2 1.0 M HNO_3	0.1 M H_2O_2 2.0 M HNO_3
SIMULATED SB-HLW				
I	—	62.41	50.48	40.03
II	—	18.24	20.87	20.45
III	—	11.81	11.81	11.62
IV	—	—	—	—
Total	—	92.46	83.16	72.10
SIMULATED PHWR-HLW				
I	77.14	72.37	64.74	45.99
II	16.56	17.29	14.18	13.52
III	3.85	3.57	6.73	8.36
IV	2.31	1.23	—	—
Total	99.86	94.46	85.65	67.87
SIMULATED FBR-HLW				
I	—	88.47	76.70	46.69
II	—	7.22	16.49	19.46
III	—	3.24	3.32	8.47
IV	—	—	—	—
Total	—	98.93	96.51	74.62

TABLE 10

STRIPPING OF PLUTONIUM FROM LOADED TBP PHASE
(ORIGINALLY EXTRACTED FROM SIMULATED PHWR-HLW
IN PRESENCE OF 0.01 M $K_2Cr_2O_7$)

STRIPPING REAGENTS = 0.1 M H_2O_2 + 0.01 M ASCORBIC ACID +
VARYING HNO_3 CONCENTRATIONS
ORGANIC TO AQUEOUS PHASE RATIO = 1 : 1

CONTACT	% Pu STRIPPED USING REAGENTS			
	0.1 M H_2O_2 0.01 M ASCORBIC ACID 0.1 M HNO_3	0.1 M H_2O_2 0.01 M ASCORBIC ACID 0.5 M HNO_3	0.1 M H_2O_2 0.01 M ASCORBIC ACID 1.0 M HNO_3	0.1 M H_2O_2 0.01 M ASCORBIC ACID 2.0 M HNO_3
I	95.20	95.54	91.90	91.26
II	4.80	3.09	7.28	7.37
III	0.00	1.37	0.82	0.96
IV	0.00	0.00	0.00	0.41
TOTAL	100.00	100.00	100.00	100.00

TABLE 11

STRIPPING OF PLUTONIUM FROM LOADED TBP PHASE
 (ORIGINALLY EXTRACTED FROM SIMULATED PHWR-HLW
 IN PRESENCE OF 0.01 M $K_2Cr_2O_7$)
 AT VARIOUS ORGANIC TO AQUEOUS PHASE RATIOS

STRIPPING REAGENT : 1) 0.1 M H_2O_2 + 0.01 M ASCORBIC ACID
 + 2.0 M HNO_3
 2) 0.1 M H_2O_2 + 2.0 M HNO_3

STRIPPING REAGENT	CONTACT	% Pu STRIPPED		
		O:A = 1:1	O:A = 2:1	O:A = 4:1
0.1 M H_2O_2 + 0.01 M ASCORBIC ACID + 2.0 M HNO_3	I	91.26	85.32	37.40
	II	7.37	12.22	51.97
	III	0.96	2.04	8.74
	IV	0.41	0.42	1.89
TOTAL Pu STRIPPED		100.00	100.00	100.00
0.1 M H_2O_2 + 2.0 M HNO_3	I	45.99	30.98	15.20
	II	13.52	17.20	10.90
	III	8.36	8.04	5.93
	IV	—	3.71	3.21
TOTAL Pu STRIPPED		67.87	59.93	35.24

TABLE 12

STRIPPING OF PLUTONIUM FROM LOADED TBP + DBP PHASE
(ORIGINALLY EXTRACTED FROM SIMULATED PHWR-HLW SOLUTIONS
IN PRESENCE OF 0.01 M $K_2Cr_2O_7$)

ORGANIC PHASE = 30 % TBP CONTAINING 2 g/l OF DBP
IN N-DODECANE
STRIPPING REAGENTS = 0.1 M H_2O_2 + 0.01 M ASCORBIC ACID +
VARYING HNO_3 CONCENTRATIONS
ORGANIC TO AQUEOUS PHASE RATIO = 4 : 1

STRIPPING REAGENT	CONTACT	% Pu STRIPPED FROM LOADED TBP + DBP PHASE	
		HNO_3 : 0.1 M	HNO_3 : 2.0 M
0.1 M H_2O_2 + 0.01 M ASCORBIC ACID	I	53.07	35.03
	II	39.20	48.52
	III	7.51	13.16
	VI	0.22	2.91
TOTAL Pu STRIPPED		100.00	99.62

TABLE 13

STRIPPING OF PLUTONIUM FROM LOADED TBP PHASE
 (ORIGINALLY EXTRACTED FROM SIMULATED PHWR-HLW
 IN PRESENCE OF 0.01 M $K_2Cr_2O_7$)
 USING VARIOUS REAGENTS

ORGANIC TO AQUEOUS PHASE RATIO = 4 : 1

CONTACT	% Pu STRIPPED, USING REAGENTS					
	0.05 M NH ₂ OH.HCl 2.0 M HNO ₃		0.05 M NH ₂ NH ₂ .H ₂ SO ₄ 2.0 M HNO ₃		0.1 M H ₂ O ₂ 2.0 M HNO ₃	
	0.0 M ASCORBIC ACID	0.01 M ASCORBIC ACID	0.0 M ASCORBIC ACID	0.01 M ASCORBIC ACID	0.0 M ASCORBIC ACID	0.01 M ASCORBIC ACID
I	3.56	3.92	6.48	9.67	15.20	37.40
II	47.99	29.53	28.24	71.18	10.90	51.97
III	13.69	51.24	16.81	9.63	5.93	8.74
IV	10.14	7.20	9.40	4.56	3.21	1.89
TOTAL	75.38	91.89	60.93	95.04	35.24	100.00

TABLE 14

STRIPPING OF NEPTUNIUM FROM LOADED TBP PHASE
 (ORIGINALLY EXTRACTED FROM SIMULATED PHWR-HLW
 IN PRESENCE OF 0.01 M $K_2Cr_2O_7$)
 AT VARIOUS ORGANIC TO AQUEOUS PHASE RATIOS

STRIPPING REAGENTS = 0.1 M H_2O_2 + 0.01 M ASCORBIC ACID +
 VARYING HNO_3 CONCENTRATIONS

STRIPPING REAGENT	CONTACT	% Np STRIPPED		
		O:A = 1:1	O:A = 2:1	O:A = 4:1
0.1 M H_2O_2 + 0.01 M ASCORBIC ACID + 0.1 M HNO_3	I	96.30	81.62	22.73
	II	3.10	16.69	63.50
	III	0.42	1.02	12.40
	IV	0.13	0.33	0.97
TOTAL Np STRIPPED		99.95	99.66	99.60
0.1 M H_2O_2 + 0.01 M ASCORBIC ACID + 0.5 M HNO_3	I	94.11	57.46	11.07
	II	4.37	37.44	78.64
	III	0.89	3.67	7.59
	IV	0.23	0.64	1.00
TOTAL Np STRIPPED		99.60	99.21	98.30
0.1 M H_2O_2 + 0.01 M ASCORBIC ACID + 2.0 M HNO_3	I	76.93	70.47	61.33
	II	16.42	17.16	24.02
	III	3.94	7.61	8.49
	IV	1.03	2.81	4.21
TOTAL Np STRIPPED		98.32	98.05	98.05

TABLE 15

STRIPPING OF URANIUM FROM LOADED TBP PHASE
 (ORIGINALLY EXTRACTED FROM SIMULATED PHWR-HLW
 IN PRESENCE OF 0.01 M $K_2Cr_2O_7$)
 AT VARIOUS ORGANIC TO AQUEOUS PHASE RATIOS

STRIPPING REAGENTS = 0.1 M H_2O_2 + 0.01 M ASCORBIC ACID +
 VARYING HNO_3 CONCENTRATIONS

STRIPPING REAGENT	CONTACT	% U STRIPPED		
		O:A = 1:1	O:A = 2:1	O:A = 4:1
0.1 M H_2O_2 + 0.01 M ASCORBIC ACID + 0.1 M HNO_3	I	26.46	13.12	3.41
	II	31.00	18.57	6.37
	III	21.67	18.83	9.98
	IV	12.48	13.32	10.97
TOTAL U STRIPPED		91.61	63.84	30.73
0.1 M H_2O_2 + 0.01 M ASCORBIC ACID + 2.0 M HNO_3	I	9.39	5.48	2.37
	II	9.65	3.60	1.08
	III	6.51	3.22	2.04
	IV	—	2.94	1.96
TOTAL U STRIPPED		25.55	15.24	7.45

TABLE 16

STRIPPING OF URANIUM, NEPTUNIUM AND PLUTONIUM
FROM LOADED TBP PHASE
(ORIGINALLY EXTRACTED FROM SIMULATED PHWR-HLW
CONTAINING URANIUM, NEPTUNIUM AND PLUTONIUM TOGETHER
IN PRESENCE OF 0.01 M $K_2Cr_2O_7$)

ORGANIC TO AQUEOUS PHASE RATIO = 4 : 1

STRIPPING REAGENT	CONTACT	U STRIPPED (%)	Np STRIPPED (%)	Pu STRIPPED (%)
STRIPPING OF U, Np AND Pu				
0.1 M HNO_3 + 0.1 M H_2O_2 + 0.01 M ASCORBIC ACID	I	4.66	15.52	73.18
	II	8.68	82.09	17.75
	III	11.31	1.52	6.81
	IV	10.60	0.17	1.32
	TOTAL	35.25	99.30	99.06
0.01 M HNO_3	I	20.86	—	—
	II	15.18	—	—
	III	11.66	—	—
	IV	16.72	—	—
	TOTAL	64.42	—	—
TOTAL U, Np, Pu STRIPPED		99.67	99.30	99.06
SELECTIVE STRIPPING OF Np AND Pu				
2.0 M HNO_3 + 0.1 M H_2O_2 + 0.01 M ASCORBIC ACID	I	2.03	46.78	31.87
	II	1.25	32.01	54.46
	III	1.15	12.72	7.57
	IV	1.20	7.53	4.85
TOTAL U, Np, Pu STRIPPED		5.63	99.04	98.75

TABLE 17

EXTRACTION AND STRIPPING OF URANIUM, NEPTUNIUM AND PLUTONIUM
FROM ACTUAL HLW BY 30 % TBP

EXTRACTION :

ORGANIC TO AQUEOUS PHASE RATIO = 1 : 1

METAL ION	DISTRIBUTION RATIO	% EXTRACTION
U(VI)	17.91	94.71
Np(VI)	14.46	93.53
Pu(VI)	9.338	90.33

STRIPPING :

STRIPPING REAGENT = 0.1 M H₂O₂ + 0.01 M ASCORBIC ACID
+ 2.0 M HNO₃
ORGANIC TO AQUEOUS PHASE RATIO = 4 : 1

CONTACT No.	U STRIPPED (%)	Np STRIPPED (%)	Pu STRIPPED (%)
I	2.31	65.43	67.62
II	1.80	21.60	27.29
III	1.11	8.18	3.74
IV	0.53	3.55	0.81
TOTAL	5.75	98.76	99.46

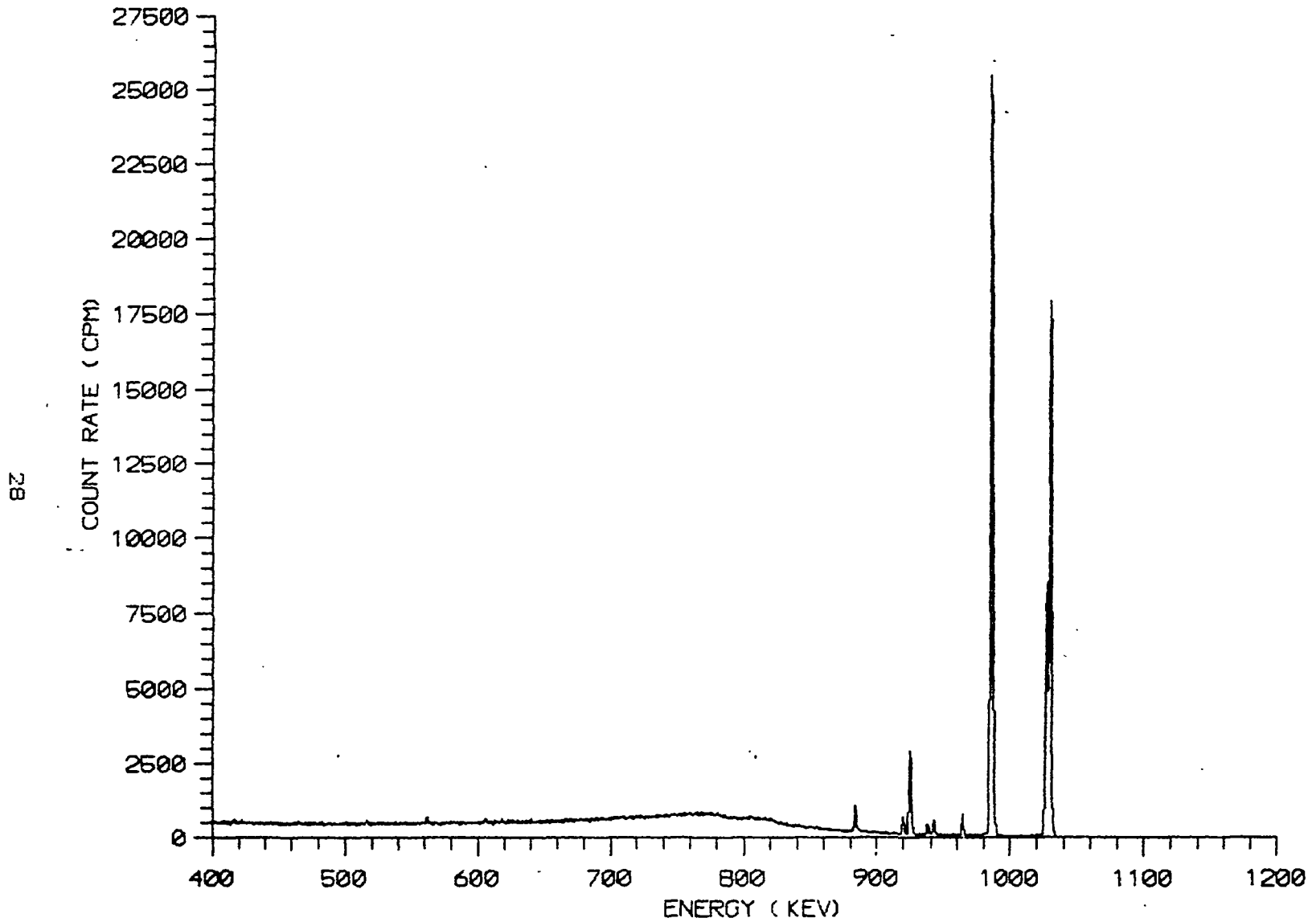


FIG. 1. GAMMA SPECTRUM OF PURIFIED ^{238}Np

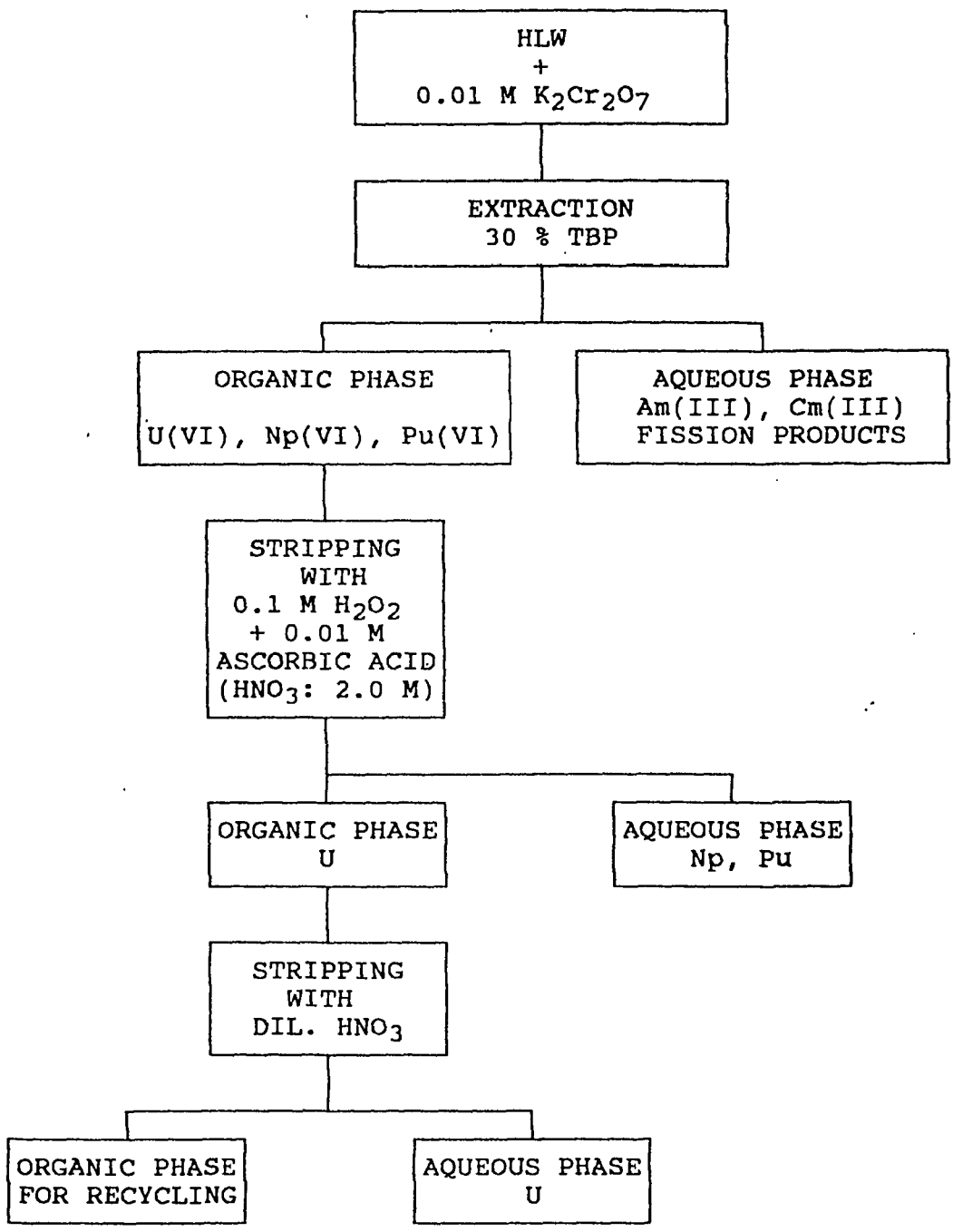


FIG. 2. FLOWSHEET FOR PARTITIONING OF NEPTUNIUM, PLUTONIUM AND URANIUM FROM HIGH LEVEL WASTE.

